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THERMAL DEGRADATION OF COPOLYMERS

N. Grassie, B. J. D. Torrance, and J. D. Fortune

University of Glasgow
Glasgow, Scotland

TECHNICAL REPORT AFML-TR-71-6

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FOREWORD

This report was prepared by the University of Glasgow, Glasgow, Scotland, on Air Force Contract No. AF 61(052)-883. The contract was initiated under Project 7342, "Fundamental Research on Macromolecular Materials and Lubrication," Task 734203, "Fundamental Principles Determining the Behavior of Macromolecules," and was administered by the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio, with Dr. Ivan J. Goldfarb (AFML/LNP) as Project Scientist.

This report covers work from 1 October 1965 to 31 January 1970.

This technical report has been reviewed and is approved.

R. L. Van Deusen

R. L. VAN DEUSEN
Acting Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

This report is principally concerned with the thermal degradation of two copolymer systems, namely methyl methacrylate/methyl acrylate and methyl methacrylate/butyl acrylate. The photo-degradation of the methyl methacrylate/methyl acrylate system was also studied insofar as it is relevant to the thermal reaction. In view of the similarity of the monomers, reliable values of reactivity ratios were not available. An accurate method, making use of nuclear magnetic resonance spectroscopy, was devised and applied to these and other acrylate/methacrylate systems.

For both systems a series of copolymers covering the whole composition range was synthesised. Degradations were carried out under vacuum either in a dynamic molecular still or using a new technique developed in these laboratories. Thermal methods of analysis, such as thermogravimetric analysis (TGA) and thermal volatilisation analysis (TVA), showed that the copolymers became more stable to thermal breakdown as the acrylate content was increased. These techniques allowed a suitable temperature range to be chosen in which to study the reactions isothermally. The gaseous degradation products, liquid products, chain fragments and residue were each examined separately, using, among other techniques, infra-red spectroscopy, gas-liquid chromatography, mass spectrometry and combined gas chromatography - mass spectrometry. The complex nature of the pyrolysis of these copolymer systems is reflected by the variety of products obtained.

The main gaseous products were found to be carbon dioxide and smaller amounts of hydrogen from the methyl acrylate copolymer and carbon dioxide and but-1-ene from the butyl acrylate copolymer. The most important liquid products are methyl methacrylate from both systems and n-butanol from the butyl acrylate copolymers with high butyl acrylate contents. Quantitative measurements enabled the build-up of these products to be followed as degradation proceeds,

and mass balance tables were drawn up for each copolymer studied. The large chain fragments were only briefly examined. Molecular weight measurements on the residue indicated that breakdown by random scission processes becomes more important relative to breakdown by depolymerization processes as the acrylate content is increased. Degradation schemes and mechanisms are postulated to account for the formation of all of the important products, although no really satisfactory route for alcohol evolution has been found.

TABLE OF CONTENTS

	FIGURES	ix
	TABLES	xvi
CHAPTER 1.	INTRODUCTION	1
CHAPTER 2.	REACTIVITY RATIOS FOR THE COPOLYMERIZATION OF ACRYLATES AND METHACRYLATES BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY	3
	INTRODUCTION	3
	EXPERIMENTAL	3
	Monomer Purification	3
	Polymerization	4
	Copolymer Analysis	4
	RESULTS AND DISCUSSION	4
CHAPTER 3.	THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND METHYL ACRYLATE. A. PRODUCTS AND GENERAL CHARACTERISTICS OF THE REACTION	11
	INTRODUCTION	11
	EXPERIMENTAL	11
	Preparation of Copolymers	11
	Degradation Techniques	12
	Molecular Weights	14
	Spectroscopic Measurements	14
	RESULTS AND DISCUSSION	14
	Thermal Volatilization Analysis	14
	Changes in Molecular Weight	17
	Volatile Products of Analysis	19
	Unsaturation in the Residual Copolymer	19
	Absence of Methanol among the Reaction Products	23
	Production of Methyl Acrylate and Chain Fragments	24
	Production of Carbon Dioxide	24
	CONCLUSIONS	25

CHAPTER 4. THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND METHYL ACRYLATE. B. CHAIN SCISSION AND THE MECHANISM OF THE REACTION 26

INTRODUCTION 26
EXPERIMENTAL 26
RESULTS AND DISCUSSION 26

Chain Scission and Carbon Dioxide Production 26
Volatilization, Chain Scission, and Zip Length 28
Chain Scission and Copolymer Composition 32
Activation Energy for Chain Scission 33
Chain Scission and the Production of Permanent Gases 33

CONCLUSIONS 41

CHAPTER 5. PHOTODEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND METHYL ACRYLATE AT ELEVATED TEMPERATURES 43

INTRODUCTION 43
EXPERIMENTAL 43

Copolymers 43
Molecular Weights 43
Photodegradation Techniques 44

RESULTS 44

Influence of Temperature on Rate of Volatilization 44
Molecular Weight Changes 47
Volatile Products of Degradation 49
Rates of Volatilization 49
Chain Scission and the Production of Carbon Dioxide 49
Chain Scission and Volatilization 51
Chain Scission and Copolymer Composition 51

DISCUSSION 54

CHAPTER 6. THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. A. EXPERIMENTAL METHODS 57

SYNTHESIS OF COPOLYMERS 57
DEGRADATION APPARATUS 58
PRODUCT ANALYSIS 60
PRESSURE MEASUREMENT 61
MOLECULAR WEIGHT MEASUREMENTS 61
THERMAL METHODS OF ANALYSIS 61
GAS-LIQUID CHROMATOGRAPHY 64
MASS SPECTROMETRY 65
SPECTROMETRIC MEASUREMENTS 65
SOL-GEL ANALYSIS 66

CHAPTER 7. THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. B. THERMAL ANALYSIS 68

INTRODUCTION 68
THERMAL VOLATILIZATION ANALYSIS 68

Collection of T.V.A. Data 68
Interpretation of T.V.A. Data 79

THERMOGRAVIMETRIC ANALYSIS 80

Determination of Kinetic Parameters from T.G.A. 80
Dynamic T.G.A. 82
Isothermal T.G.A. 84

DISCUSSION OF RESULTS 90

CHAPTER 8. THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. C. IDENTIFICATION OF THE PRODUCTS OF REACTION 92

INTRODUCTION 92
ANALYSIS OF PRODUCT GASES 92

Gas Chromatography 92
Mass Spectrometry 92
Infra-red 98

ANALYSIS OF LIQUID VOLATILES 101

Gas Liquid Chromatography 101
Combined Gas Chromatography-Mass Spectrometry 101

CHAPTER 9. THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. D. QUANTITATIVE ANALYSIS OF LIQUID AND GASEOUS PRODUCTS 115

INTRODUCTION 115
ANALYSIS OF THE GASEOUS DEGRADATION PRODUCTS 115

Analytical Techniques 115

Gas Chromatography 115
Infra-red Spectroscopy 118
Treatment of Results 118

DISCUSSION OF RESULTS 138

CALCULATION OF MASS BALANCE DATA 145

ANALYSIS OF THE LIQUID DEGRADATION PRODUCTS 145

Analytical Techniques 145
Treatment of Results 164
Discussion of Results 172

CHAPTER 10. THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. E. THE RESIDUE AND CHAIN FRAGMENTS 177

INTRODUCTION 177
INVESTIGATION OF THE RESIDUE 177

Spectroscopic Techniques 177

Infra-red 177
U.V.-Visible 180
N.M.R. 180

Elemental Analysis 183
Molecular Weight Measurements 183
Sol-Gel Analysis 185

Effect of Copolymer Composition on Gel Formation 189
Effect of Molecular Weight on Gel Formation 189
Effect of Degradation Temperature on Gel Formation 189

Degradation at a Lower Temperature 192

Carbon Dioxide Production and Chain Scission 192

Mass Spectrometry 193

INVESTIGATION OF CHAIN FRAGMENTS 193

CHAPTER 11. SURVEY OF RESULTS AND GENERAL DISCUSSION 198

INTRODUCTION 198
METHYL METHACRYLATE/METHYL ACRYLATE COPOLYMERS 198
METHYL METHACRYLATE/BUTYL ACRYLATE COPOLYMERS 202

Production of Alcohol 202
Production of But-1-ene 209
Production of Carbon Dioxide 209
Production of n-Butyl Methacrylate 210
Production of n-Butyl Acrylate 211
Other Products 211

SUMMARY 212

REFEREMCES 213

FIGURES

1. Nuclear magnetic resonance spectrum of 1-4 MMA-PrA copolymer. 5

2. Nuclear magnetic resonance spectrum of 1-5 MMA-MA copolymer. 7

3. r_1 versus r_2 plots for (a) MMA-MA; (b) MMA-EA; (c) MMA-PrA; (d) MMA-BuA; (e) MMA-EMA. 9

4. Degradation apparatus. 13

5. Thermal volatilization analysis thermograms of poly(methyl methacrylate) and methyl methacrylate -methyl acrylate copolymers. 15

6. Molecular weight changes during degradation of 26/1 methyl methacrylate-methyl acrylate copolymer. 18

7. Ultraviolet absorption spectra of 2/1 methyl methacrylate-methyl acrylate copolymer in chloroform solution: (A) undegraded; (B) after 50%. volatilization 20

8. Infrared absorption spectra of films of 2/1, methyl methacrylate-methyl acrylate copolymer: (—) undegraded; (---) after 50% volatilization. 21

9. Production of carbon dioxide during degradation of 7·7/1 methyl methacrylate-methyl acrylate copolymer. 27

10. Relationship between carbon dioxide production and chain scission during degradation of methyl methacrylate-methyl acrylate copolymers: (o) 112/1; (•) 26/1; (□) 7·7/1; (■) 2/1. 29

11. Relationship between volatilization and chain scissions during degradation of 26/1 methyl methacrylate-methyl acrylate copolymers: (o) 282°C; (•) 294°C; (■) 326°C. 31

12. Dependence of rate of production of carbon dioxide on size of polymer sample for methyl methacrylate -methyl acrylate copolymers. 34

13. Relationship between rate of chain scission and methyl acrylate content for methyl methacrylate -methyl acrylate copolymers. 35

14. Arrhenius plot of chain scissions during degradation of methyl methacrylate-methyl acrylate copolymers. 36

15. Extent of volatilization in 30 min at various temperatures: (o) poly(methyl methacrylate); (■) methyl methacrylate-methyl acrylate copolymer (26/1); (▲) methyl methacrylate-methyl acrylate copolymer (7·7/1). 46

16. Change in molecular weight with volatilization for photodegradation of methyl methacrylate-methyl acrylate copolumers at 170°C: (□) 112/1; (■) 26/1; (▲) 7·7/1; (△) 2/1. 48

17. Volatilization-time curves for the photodegradation of poly(methyl methacrylate) and methyl methacrylate -methyl acrylate copolymers at 170°C: (o) PMMA; (□) MMA/MA,112/1; (■) MMA/MA,26/1; (▲) MMA/MA, 7·7/1; (△) MMA/MA,2/1. 50

18. Relationship between chain scissions and volatilization in the photodegradation of methyl methacrylate-methyl acrylate copolymers at 170°C: (■) 26/1; (▲) 7·7/1; (△) 2/1. 52

19. Time dependence of chain scission in the photodegradation of methyl methacrylate-methyl acrylate copolymers at 170°C: (□) 112/1; (■) 26/1; (▲) 7·7/1; (△) 2/1. 53

20. The sealed tube technique. 59

21. Molecular weight plots. 62

22. Schematic diagram of the differential condensation T.V.A. (D.C.T.V.A.) 63

23. D.C.T.V.A. of a poly(methyl methacrylate) standard 69

24. D.C.T.V.A. of a 0·4 mole percent n-butyl acrylate copolymer 70

25. D.C.T.V.A. of a 3·9 mole percent n-butyl acrylate copolymer. 71

26. D.C.T.V.A. of a 16·3 mole percent n-butyl acrylate copolymer. 72

27. D.C.T.V.A. of a 50·0 mole percent n-butyl acrylate copolymer. 73

28. D.C.T.V.A. of a 52·4 mole percent n-butyl acrylate copolymer. 74

29. D.C.T.V.A. of an 82·2 mole percent n-butyl acrylate copolymer. 75

30. D.C.T.V.A. of a 93·4 mole percent n-butyl acrylate copolymer. 76

31. Programmed (5°C/min.) T.G.A. traces of a series of copolymers. The figures in brackets give copolymer composition as mole percent n-butyl acrylate. 81

32. First order plot for a 3·9 mole percent n-butyl acrylate copolymer, 83

33. Activation energy plot from initial rate data for a poly(methyl methacrylate) standard. 85

34. Activation energy plot from initial rate data for a 0·4 mole percent n-butyl acrylate copolymer. 86

35. Activation energy plot from initial rate data for a 3·9 mole percent n-butyl acrylate copolymer. 87

36. Activation energy plot from initial rate data for a 16·3 mole percent n-butyl acrylate copolymer. 88

37. Activation energy plot from initial rate data for a 52·4 mole percent n-butyl acrylate copolymer. 89

38. G.L.C. trace for a 50·0 mole percent n-butyl acrylate copolymer degraded at 313°C for 11 hours. Column run isothermally at 40°C for 3 min. then programmed at 5°C/min. 93

39. Room temperature g.l.c. of a 16·3 mole percent n-butyl acrylate copolymer degraded at 313°C for 16 hours. 94

40. Room temperature g.l.c. of the permanent gas fraction from the degradation of a 52·4 mole percent n-butyl acrylate copolymer pyrolyzed at 313°C for 24 hours. 95

41. (a) But-1-ene standard. (b) Product gases from a 16·3 mole % n-butyl acrylate copolymer degraded for 12 hours at 313°C. 97

42. Infra-red spectrum of a 93·4 mole percent n-butyl acrylate copolymer degraded for 12·5 hours at 313°C. 99

43. G.L.C. trace of the liquid degradation products from the breakdown of a 50·0 mole percent n-butyl acrylate copolymer heated at 313°C for 4 hours. 102

44. G.L.C. trace from G.C.M.S. of liquid degradation products. 103

45. Mass spectrum of component 1 in Fig. 44 (n-butanol). 104

46. Mass spectrum of component 2 in Fig. 44 (methyl methacrylate) 105

47. Mass spectrum of component 3 in Fig. 44 (toluene) 106

48. Mass spectrum of component 4 in Fig. 44 (n-butyl acrylate. 107

49. Mass spectrum of component 5 in Fig. 44 (n-butyl methacrylate) 108

50. Infra-red calibration curves for but-1-ene and carbon dioxide. 119

51. Gas pressure plots for a 16·3 mole percent n-butyl acrylate copolymer degraded at 313°C. 120

52. Gas pressure plot for a 3·9 mole percent n-butyl acrylate copolymer degraded at 313°C. 122

53. Gas pressure plots for a 50·0 mole percent n-butyl acrylate copolymer degraded at 313°C. 123

54. Gas pressure plots for an 82·2 mole percent n-butyl acrylate copolymer degraded at 313°C. 124

55. Gas pressure plots for a 93·4 mole percent n-butyl acrylate copolymer degraded at 313°C. 125

56. Gas pressure plots for a 50·0 mole percent n-butyl acrylate copolymer degraded at 332°C. 126

57. Gas pressure plots for a 93·4 mole percent n-butyl acrylate copolymer degraded at 332°C. 127

58. Gas evolution plots for copolymers degraded at 313°C. 139

59. Gas evolution plots for copolymers degraded at 313°C. 140

60. Gas evolution plot for a 93·4 mole percent n-butyl acrylate copolymer degraded at 313°C. 141

61. Gas evolution plot for a 50·0 mole percent n-butyl acrylate copolymer degraded at 332°C. 142

62. Gas evolution plot for a 93·4 mole percent n-butyl acrylate copolymer degraded at 332°C. 143

63. Residue and liquid volatile plots for a 3·9 mole percent n-butyl acrylate copolymer degraded at 313°C. 153

64. Residue and liquid volatile plots for a 16·3 mole percent n-butyl acrylate copolymer degraded at 313°C. 154

65. Residue and liquid volatile plots for a 50·0 mole percent n-butyl acrylate copolymer degraded at 313°C. 155

66. Residue and liquid volatile plots for an 82·2 mole percent n-butyl acrylate copolymer degraded at 313°C. 156

67. Residue, chain fragment, and liquid volatile plots for a 93·4 mole percent n-butyl acrylate copolymer degraded at 313°C. 157

68. Liquid volatile and chain fragment plots for a 50·0 mole percent n-butyl acrylate copolymer degraded at 332°C. 158

69. Residue plot for a 50·0 mole percent n-butyl acrylate copolymer degraded at 332°C. 159

70. Liquid volatile and chain fragment plots for a 93·4 mole percent n-butyl acrylate copolymer degraded at 332°C.

71. Residue plot for a 93·4 mole percent n-butyl acrylate copolymer degraded at 332°C. 161

72. G.L.C. trace of the liquid degradation products from a 50·0 mole percent n-butyl acrylate copolymer pyrolyzed at 313°C for 16 hours. 162

73. n-Butanol production as a percentage of the total liquid products at 313°C. 166

74. n-Butanol production as a percentage of the total liquid products for a 93·4 mole percent n-butyl acrylate copolymer. 167

75. Plots of methyl methacrylate production at 313°C. 168

76. Plots of methyl methacrylate and n-butanol production at 313°C. 169

77. Plots of n-butanol production for a 93·4 mole percent n-butyl acrylate copolymer. 170

78. Infra-red spectra of an 82·2 mole percent n-butyl acrylate copolymer. 178

79. U.V. spectra of an 82·2 mole percent n-butyl acrylate copolymer degraded for the times shown. 181

80. N.M.R. of a 50·0 mole percent n-butyl acrylate copolymer degraded at 313°C for 16 hours. (Run in carbon tetrachloride solution.) 182

81. Molecular weight versus percentage volatilization plots. 184

82. Effect of composition on gel formation at 329°C. 186

83. Effect of molecular weight on gel formation at 329°C. 187

84. Effect of temperature of degradation on gel formation in poly(n-butyl acrylate) $\bar{M}_n$870,000. 188

85. Carbon dioxide evolution versus chain scission plot for a 52·4 mole percent n-butyl acrylate copolymer degraded at 237°C. 195

86. Mass spectra (20ev) of products from the degradation of a 52·4 mole percent n-butyl acrylate copolymer for seven hours at 237°C. 196

87. G.L.C. trace of short chain fragments from the degradation of a 50·0 mole percent n-butyl acrylate copolymer at 313°C for 11·5 hours. 197

TABLES

1. Nuclear Magnetic Resonance spectral analyses. 8

2. Reactivity ratios. 10

3. Composition of volatile products of degradation. 16

4. Colour and absorption maxima for conjugated ethylene structures. 22

5. Data on sequence distribution in the copolymers. 23

6. Summary of carbon dioxide-chain scission data. 30

7. Zip lengths. 32

8. Chain scissions and permanent gases. 37

9. Rate exponents for various reaction mechanisms 40

10. Photodegradation data obtained at 170°C. 47

11. Molar composition of monomeric products (MMA/MA) 49

12. Chain scission and the production of carbon dioxide. 49

13. Zip lengths for depolymerization 51

14. Copolymer composition and molecular weight data. 58

15. G.L.C. columns used for investigation of degradation products 64

16. Dependence of TVA rate maxima on the composition of methyl methacrylate/n-butyl acrylate copolymers. 77

17. Orders of reaction. 82

18. Activation energies for degradation of methyl methacrylate/n-butyl acrylate copolymers. 82

19. Activation energy from initial rate measurements. 90

20. G.L.C. data for hydrocarbon products. 96

21. G.L.C. data for isomeric butenes. 96

22. G.L.C. data for permanent gases. 96

23. Mass spectral data. 98

24. Assignments of the infra-red absorptions shown in Fig. 42. 100

25. G.L.C. data for liquid products. 101

26. Mass spectral data for liquid products. 109

27. Mechanism of fission in the mass spectrometer. 113

28. Mass spectra of liquid products. 114

29. G.L.C. data for a 50·0 mole percent n-butyl acrylate copolymer degraded at 313°C for 11 hours. 116

30. G.L.C. data for a 16·3 mole percent n-butyl acrylate copolymer degraded at 313°C for 16 hours. 117

31. Data for a 52·4 mole percent n-butyl acrylate copolymer degraded at 313°C for 24 hours. 117

32. Gas evolution data for a 16·3 mole percent n-butyl acrylate copolymer degraded at 313°C. 121

33. Gas evolution data for a 3·9 mole percent n-butyl acrylate copolymer degraded at 313°C. 128

34. Gas evolution data for a 50·0 mole percent n-butyl acrylate copolymer degraded at 313°C. 129

35. Gas evolution data for an 82·2 mole percent n-butyl acrylate copolymer degraded at 313°C. 130

36. Gas evolution data for a 93·4 mole percent n-butyl acrylate copolymer degraded at 313°C. 132

37. Gas evolution data for a 50·0 mole percent n-butyl acrylate copolymer degraded at 332°C. 134

38. Gas evolution data for a 93·4 mole percent n-butyl acrylate copolymer degraded at 332°C. 136

39. Molar ratios of carbon dioxide and but-1-ene. 144

40. Molar ratios of but-1-ene and n-butyl acrylate. 144

41. Data for the degradation of a 3·9 mole percent n-butyl acrylate copolymer at 313°C. 146

42. Data for the degradation of a 16·3 mole percent n-butyl acrylate copolymer at 313°C. 147

43. Data for the degradation of a 50·0 mole percent n-butyl acrylate copolymer at 313°C. 148

44. Data for the degradation of an 82·2 mole percent n-butyl acrylate copolymer at 313°C. 149

45. Data for the degradation of a 93·4 mole percent n-butyl acrylate copolymer at 313°C. 150

46. Data for the degradation of a 50·0 mole percent n-butyl acrylate copolymer at 332°C. 151

47. Data for the degradation of a 93·4 mole percent n-butyl acrylate copolymer at 332°C. 152

48. G.L.C. data for liquid products. 163

49. G.L.C. data for liquid products. 163

50. Analysis of the liquid degradation products. 165

51. Analysis of the liquid degradation products. 171

52. Mass balance data. 173

53. Yields of n-butyl acrylate and n-butyl methacrylate. 175

54. Change in elemental analysis during reaction. 183

55. Polymers examined by sol-gel analysis. 185

56. Sol-gel analysis data for poly(n-butyl acrylate). 190

57. Sol-gel analysis data for poly(n-butyl acrylate). 190

58. Sol-gel analysis data for a 93·4 mole percent n-butyl acrylate copolymer $\overline{M}_n$ 76,500, degraded at 329°C. 191

59. Sol-gel analysis data for a 93·4 mole percent n-butyl acrylate copolymer, $\overline{M}_n$ 3,160,000, degraded at 329°C. 191

60. Sol-gel analysis data for a 52·4 mole percent n-butyl acrylate copolymer, $\overline{M}_n$ 1,330,000, degraded at 313°C. 191

61. Data for the degradation of a 52·4 mole percent n-butyl acrylate copolymer at 237°C. 194

62. Sequence distribution data for copolymers of n-butyl acrylate and methyl methacrylate. 203

63. Sequence distribution data for copolymers of methyl methacrylate and methyl acrylate. 205

CHAPTER 1

INTRODUCTION

The presence of a small amount of a second monomer copolymerised into a homopolymer can have a profound effect upon the stability of the homopolymer. In some cases the effect is to enhance the stability, in others the copolymer is less stable. Since copolymers are being increasingly applied commercially and industrially it is important to understand, at a fundamental chemical level, the reasons for these differences in stability so that they may be taken into account, along with the other physical and chemical properties of the material, in choosing materials most effectively for new applications.

The introduction of a few per cent of an acrylate comonomer has long been recognised as an effective method of stabilising poly(methyl methacrylate) although the precise chemical mechanism of this effect is not clearly understood. The degradation reactions of a number of polymethacrylate homopolymers have been thoroughly investigated (1) so that a consistent unified picture of the reactions which occur in the whole series has emerged. The acrylate series has also recently similarly been studied (2) and since a variety of both acrylates and methacrylates are available the large number of possible copolymers provides a fertile field for detailed study of comonomer stabilisation mechanisms and the influence on them of successive small changes in the structures of the constituent comonomers.

The present report describes detailed investigations of thermal degradation processes which occur in the methyl methacrylate/ methyl acrylate and methyl methacrylate/ n-butyl acrylate copolymer systems and the photodegradation reactions which occur in the former.

In order to obtain the maximum benefit from work of this kind it is essential to be able to prepare copolymers of precisely known composition. However, since the chemical natures of the constituent monomers are so similar, considerable

difficulties have been encountered in deducing the structures of the copolymers using conventional analytical methods. Although values for the reactivity ratios of the methyl methacrylate/ methyl acrylate system were available in the literature it was considered necessary to derive more reliable values. N.M.R. was found to be particularly valuable for this purpose and Chapter 2 is devoted to a description of the measurement of reactivity ratios for the copolymerisation of a number of acrylate monomers with methyl methacrylate. Chapters 3 and 4 describe various aspects of the thermal degradation of the methyl methacrylate/methyl acrylate system and Chapter 5 demonstrates how the reactions are modified by photoinitiation.

Although some thermal analysis data are presented for the methyl methacrylate/ methyl acrylate system in Chapter 3 a very much more sophisticated form of the thermal volatilisation analysis (TVA) equipment had become available when the methyl methacrylate/ n-butyl acrylate system was being studied and Chapter 6 is devoted to this. In Chapters 7 and 8 a detailed description of the thermal degradation of the methyl methacrylate/ n-butyl acrylate system is given and the report closes with a general survey and discussion of the results (Chapter 9).

CHAPTER 2

REACTIVITY RATIOS FOR THE COPOLYMERISATION OF ACRYLATES AND METHACRYLATES BY NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

INTRODUCTION

Few values of reactivity ratios for pairs of acrylate and methacrylate monomers have been reported. This is principally due to the fact that the similarities of the structures of the components make analysis of the copolymers difficult. Elemental analysis cannot be made accurate enough for the purpose (3) and the application of i.r. or u.v. spectroscopic methods would require the two monomers to have absorbing structures which are significantly different.

The gas-liquid chromatographic analysis of pyrolysis products has been applied but may be of doubtful quantitative validity (3). Radiometric (4) and isotopic (5) methods are the only ones to have been used successfully but, being time consuming and requiring elaborate experimental technique, have only been applied to a few isolated systems.

This chapter shows how nuclear magnetic resonance spectroscopy can be successfully used for such monomer pairs, although this method also has its limitations. It has previously been used to determine the monomer content of vinyl acetate-ethylene copolymers (6,7) but reactivity ratios were not calculated. The method is clearly widely applicable to copolymer analysis and is particularly valuable for its rapidity and simplicity.

EXPERIMENTAL

Monomer purification

Methyl methacrylate (MMA) (I.C.I. Ltd.), methyl acrylate (MA) (B.D.H. Ltd.), butyl acrylate (BuA) (Koch Laboratories), ethyl acrylate (EA) (Light and Co.), ethyl methacrylate (EMA) (I.C.I. Ltd.)

and propyl acrylate (PrA) (prepared by alcoholysis of methyl acrylate (8)) were washed with caustic soda solution to remove inhibitor, subsequently with distilled water, and dried over calcium chloride. The monomers were vacuum distilled and stored at -18°C.

Polymerisation

Copolymers of MMA with MA, EA, PrA, BuA and EMA were studied.

After degassing and distillation in vacuum, monomer mixtures of known composition were polymerised in bulk under vacuum to about five per cent conversion. The pair MMA-MA was polymerised at 65°C with 0·075 per cent w/v azoisobutyronitrile as catalyst. All other pairs were polymerised at 60°C with 0·18 per cent w/v catalyst.

The copolymers were precipitated three times from chloroform solution by methanol and dried in a vacuum oven for 24 hours at 50°C.

Copolymer analysis

N.m.r. spectra were obtained using a Perkin-Elmer R10 60 Mc/s spectrometer with integrator using 20 mg copolymer samples dissolved in 1 ml of $CDCl_3$. Ten integrals were obtained for each sample and the average used for the calculation of copolymer composition.

RESULTS AND DISCUSSION

In the n.m.r. spectra of the copolymers MMA-EA, MMA-PrA, MMA-BuA and MMA-EMA the peak due to the $-O-CH_3$ protons (in MMA) was resolved from those due to the $-O-CH_2-$ protons (in the second monomer) as shown for a representative example in Figure 1. The monomer compositions of the copolymers were calculated from the ratios of the areas under those peaks, as measured by the integral curves, the areas being proportional to the number of protons contributing to the peaks. Thus

$$I\text{-}OCH_2- \propto 2 \text{ (number of second monomer units in chain)}$$

$$I\text{-}OCH_3 \propto 3 \text{ (number of MMA units in chain)}$$

in which $I\text{-}OCH_2-$ and $I\text{-}OCH_3$ are the integrals of the $-OCH_2-$ and $-OCH_3$ peaks respectively.

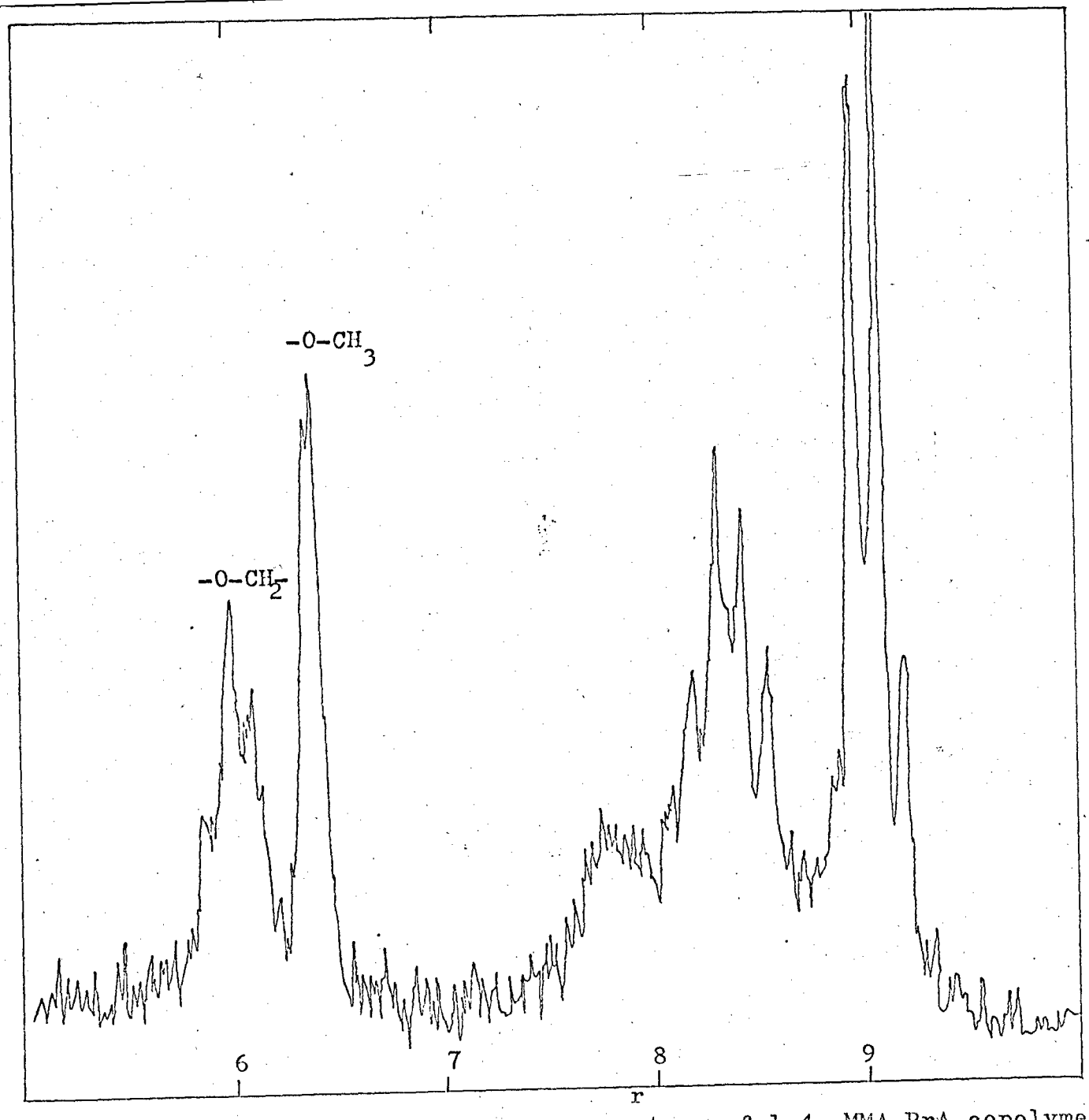


Figure 1. Nuclear magnetic resonance spectrum of 1-4, MMA-PrA copolymer

If X is molar ratio MMA/second monomer in copolymer, then

$$I\text{-}OCH_2\text{-}/I\text{-}OCH_3 = 2/3X$$

No characteristic peaks could be distinguished for MMA-MA copolymers, MA and MMA both contain $-O-CH_3$ groups and the absorptions due to the tertiary protons in MA and the methylene protons overlap as illustrated in Figure 2. Thus the total proton difference (8 from MMA, 6 from MA) between the two monomers had to be used here to calculate copolymer composition. Thus, if X = molar ratio MMA/MA in copolymer, then

$$I_{total}/I\text{-}O\text{-}CH_3 = Y = (8X + 6)/(X + 1)3$$

Therefore

$$X = (3Y - 6)/(8 - 3Y)$$

The ratios obtained by averaging ten determinations of the appropriate integrals when applied to the appropriate equations above gave the values for copolymer compositions shown in Table 1(a) and (b).

From the values of M_1/M_2 and X shown in Tables 1(a) and (b), reactivity ratios were calculated by the method of Mayo and Lewis (9) using the equation

$$r_2 = (M_1/M_2)\{(1/X)[1 + (M_1/M_2)r_1] - 1\}$$

r_1 versus r_2 plots for the systems under investigation are illustrated in Figure 3. In estimating r_1 and r_2 values from the data the intersections of adjacent lines were discounted, and the reactivity ratios obtained are shown in Table 2. These values are seen to be in good agreement with those calculated from Q and e data (10) for these monomers (11,12) with the exception of the MMA-EA system.

The last column in Table 2 shows the only other results obtained directly for the radical copolymerisation of these systems. The values for MMA-MA were obtained by the use of deuterated monomer (5) (polymerisation temperature 130°C) while the MMA-EMA system was studied by the use of radioactive tracers (4), and both are in reasonable agreement with the present results.

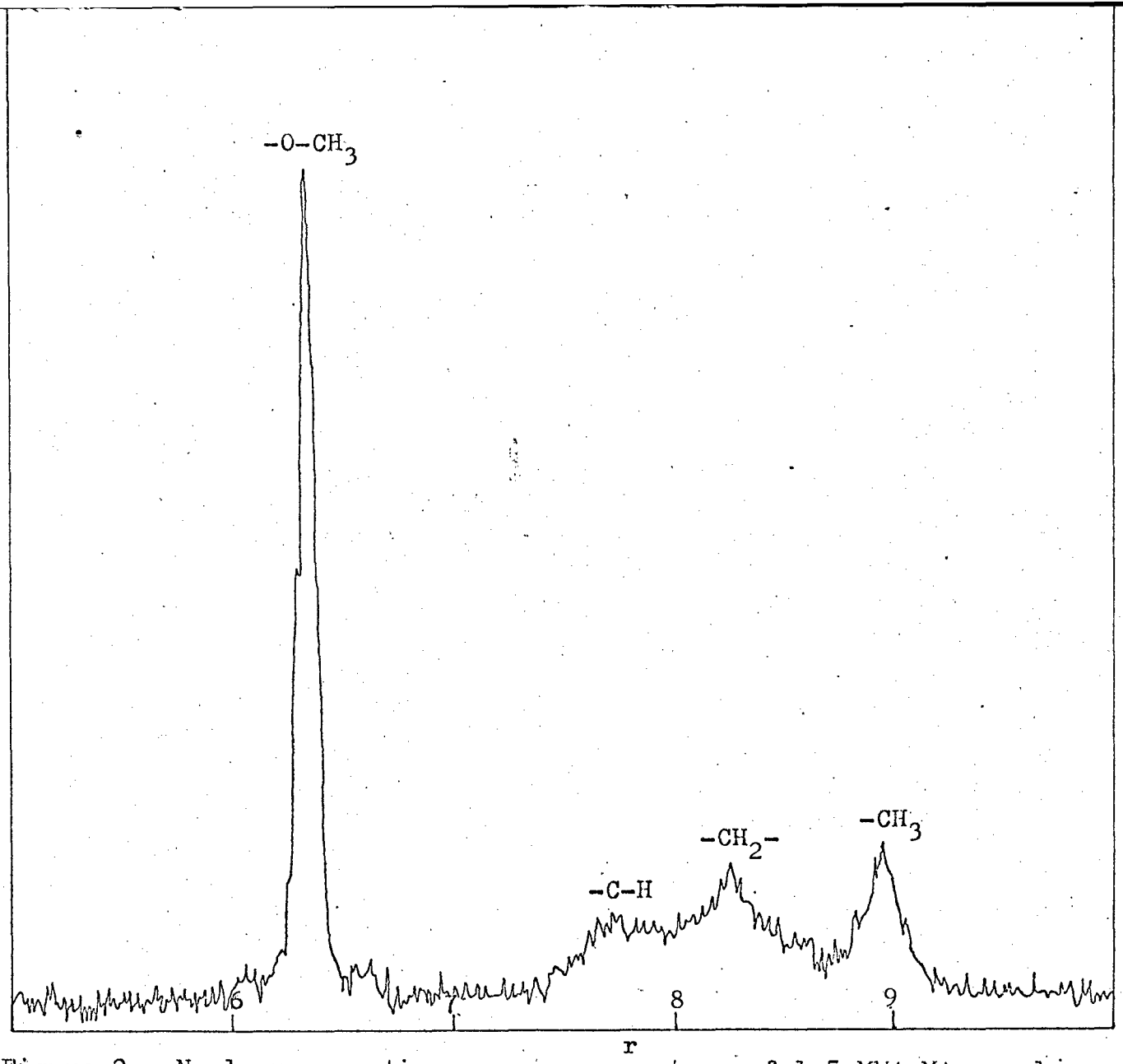


Figure 2. Nuclear magnetic resonance spectrum of 1-5 MMA-MA copolymer

Table 1. Nuclear Magnetic resonance spectral analyses

(a)

Monomer pair M_1	M_2	Molar ratio in monomer mixture (M_1/M_2)	$\frac{I\text{-}OCH_2\text{-}}{I\text{-}OCH_3}$	Molar ratio in copolymer (X)
MMA	EA	4·05	0·08	8·76
		2·02	0·15	4·45
		1·01	0·23	2·78
		0·52	0·47	1·39
		0·25	0·67	0·78
MMA	PrA	4	0·09	7·41
		2	0·20	3·33
		1	0·32	2·0
		0·5	0·63	1·06
		0·25	0·97	0·69
MMA	BuA	4	0·09	7·41
		2	0·17	3·92
		1·2	0·26	2·56
		1	0·34	1·96
		0·25	1·01	0·66
		0·125	2·86	0·23
MMA	EMA	4	0·15	4·44
		2	0·29	2·39
		1	0·67	1·0
		0·5	1·27	0·53
		0·25	2·53	0·26

(b)

Monomer pair M_1	M_2	Molar ratio in monomer mixture (M_1/M_2)	$\frac{3I_{total}}{I\text{-}O\text{-}CH_3}$	Molar ratio in copolymer (X)
MMA	MA	5·2	7·77	7·7
		1·0	7·32	1·94
		0·85	7·33	2·0
		0·38	6·86	0·76
		0·20	6·78	0·64

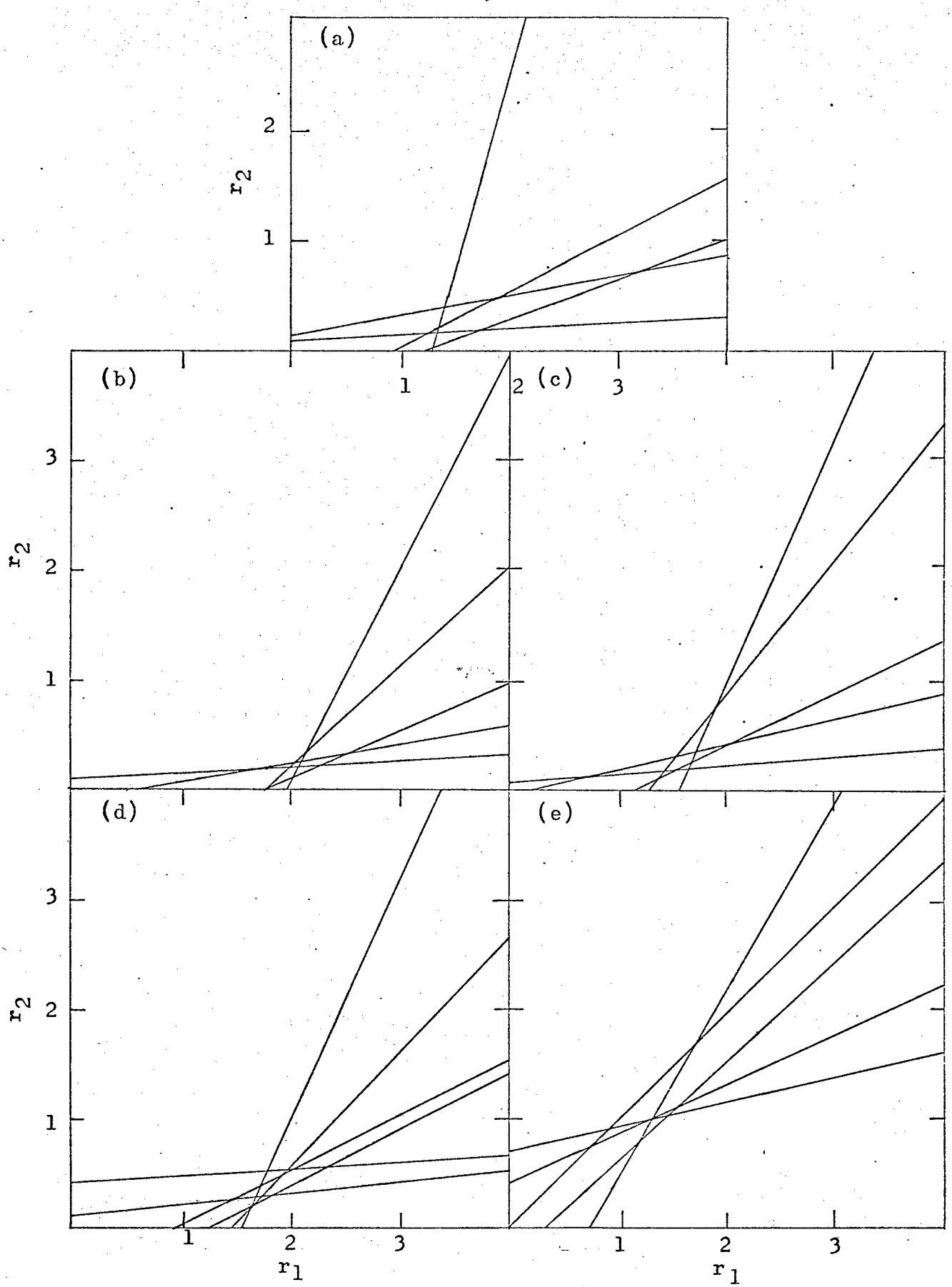


Figure 3. r_1 versus r_2 plots for (a) MMA-MA; (b) MMA-EA; (c) MMA-PrA; (d) MMA-BuA; (e) MMA-EMA

Table 2. Reactivity ratios

Polymerisation temperature. °C	Monomer pair M_1	M_2	Experimental r_1	r_2	Q-e values r_1	r_2	Other experimental values r_1	r_2
65	MMA	MA	1·8±0·4	0·35±0·1	1·9	0·5	2·3±0·5 (at 130°C)	0·47±0·1
60	MMA	EA	2·03±0·12	0·24±0·12	1·43	0·73	-	-
60	MMA	PrA	1·61±0·1	0·29±0·1	-	-	-	-
60	MMA	BuA	1·8±0·1	0·37±0·1	1·86	0·37	-	-
60	MMA	EMA	1·09±0·1	0·98±0·1	1·08	0·96	0·92	1·08

Thus nuclear magnetic resonance spectroscopy offers a general method of analysis of copolymers with an accuracy comparable with that achieved by other analytical methods. It has the additional advantages that it is rapid and can cope with monomer pairs whose similarity in structure makes other analytical methods inapplicable. It is clearly of maximum use among the acrylates and methacrylates where one of the monomers does not incorporate the $-O-CH_2-$ structure. It is still useful, although less accurate when this is not so, provided the constituent monomers have different numbers of protons as in the MMA-MA system. It cannot be readily applied, however, when both monomers incorporate $-O-CH_2-$ groups and the same number of protons, as for example, the system ethyl methacrylate-propyl acrylate.

CHAPTER 3

THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND METHYL ACRYLATE. A. PRODUCTS AND GENERAL CHARACTERISTICS OF THE REACTION

INTRODUCTION

A recent series of papers (13-16) has been concerned with the study of degradation processes in copolymers. In a summary of this and previous work (17) it was shown that this kind of investigation not only helps to clarify the degradation processes which occur in the homopolymers of the constituent monomers but also to demonstrate the mechanism whereby a small amount of a comonomer may influence the stability of a polymer either favourably or adversely.

Acrylates are used commercially in this way to stabilise poly(methyl methacrylate). The small concentrations used have no significant influence on the useful physical properties of the parent polymer. The mechanism of this stabilisation and the way in which the acrylate units influence the ultimate breakdown process have not been reported upon. This and the following chapter (18) represent the first stage of a study of the degradation properties of methacrylate-acrylate systems.

EXPERIMENTAL

Preparation of Copolymers

Methyl methacrylate (MMA) (I.C.I. Ltd.) and methyl acrylate (MA) (B.D.H. Ltd.) were purified by standard methods involving washing with caustic soda solution to remove inhibitor, washing with distilled water to remove residual caustic soda, drying over anhydrous calcium chloride, and distilling under vacuum, the first and last 10% being eliminated. Thereafter the monomers were stored in the dark at -18°C until used. The polymerisation initiator, 2,2'-azoisobutyronitrile was purified by recrystallisation from methanol.

The reactivity ratios, $r_a = 1{\cdot}8$, $r_b = 0{\cdot}35$ (where A is MMA; B is MA), whose determination by nuclear magnetic resonance spectroscopic methods (19) was described in Chapter 2, were used to calculate the proportions of the monomers required to prepare polymers of appropriate composition. The monomers, purified as above, were distilled twice more under vacuum before distilling into dilatometers, containing 0·075% (w/v) of initiator, which were sealed off under vacuum. Copolymerisations were carried to approximately 5% conversion in a thermostat at 65°C. The resulting copolymers were precipitated three times from chloroform solution by methanol, dried in a vacuum oven at 50°C for 24 hr. and ground to a fine powder (120 mesh). Copolymers with MMA and MA in the molar ratios 112/1, 26/1, 7·7/1, and 2/1 were thus prepared.

Degradation Techniques

Degradations were carried out in the apparatus illustrated in Figure 4. Samples of the powdered copolymers (2-4 mg.) were spread evenly on the bottom of glass tube A, which was a Quickfit FG 35 flange with the end sealed and flattened. It was heated by immersion in an electrically heated and thermostatted Wood's metal bath. The temperature of the inside surface of the degradation tube was calibrated against the bath temperature by checking the melting points of pellets of pure tin, bismuth and antimony (232, 271, and 327°C respectively). The water-cooled copper coil B, protected the grease of the flange from the heat of the bath.

The volume of the section bounded by taps T_1, T_2, and T_3, including the Macleod gauge, and of the reaction vessel to T_1, were measured by the standard method of expanding a known volume of gas, in a reservoir attached to the apparatus, into these sections in turn and observing the change in pressure. The total volume to T_2 and T_3 was of the order of 325 ml, varying with the various tubes, A, which were used from time to time.

Permanent gases formed during degradation were estimated from the increase in pressure observed during degradation with T_2 closed and C immersed in liquid nitrogen. They were analysed for carbon monoxide, hydrogen, and methane by methods previously described (20). With C at -78°C the additional pressure was due to carbon dioxide which was checked by absorption on soda asbestos (B.D.H. Ltd., microanalytical reagent) in D. Products not volatile at -78°C but volatile at room temperature were distilled into the calibrated

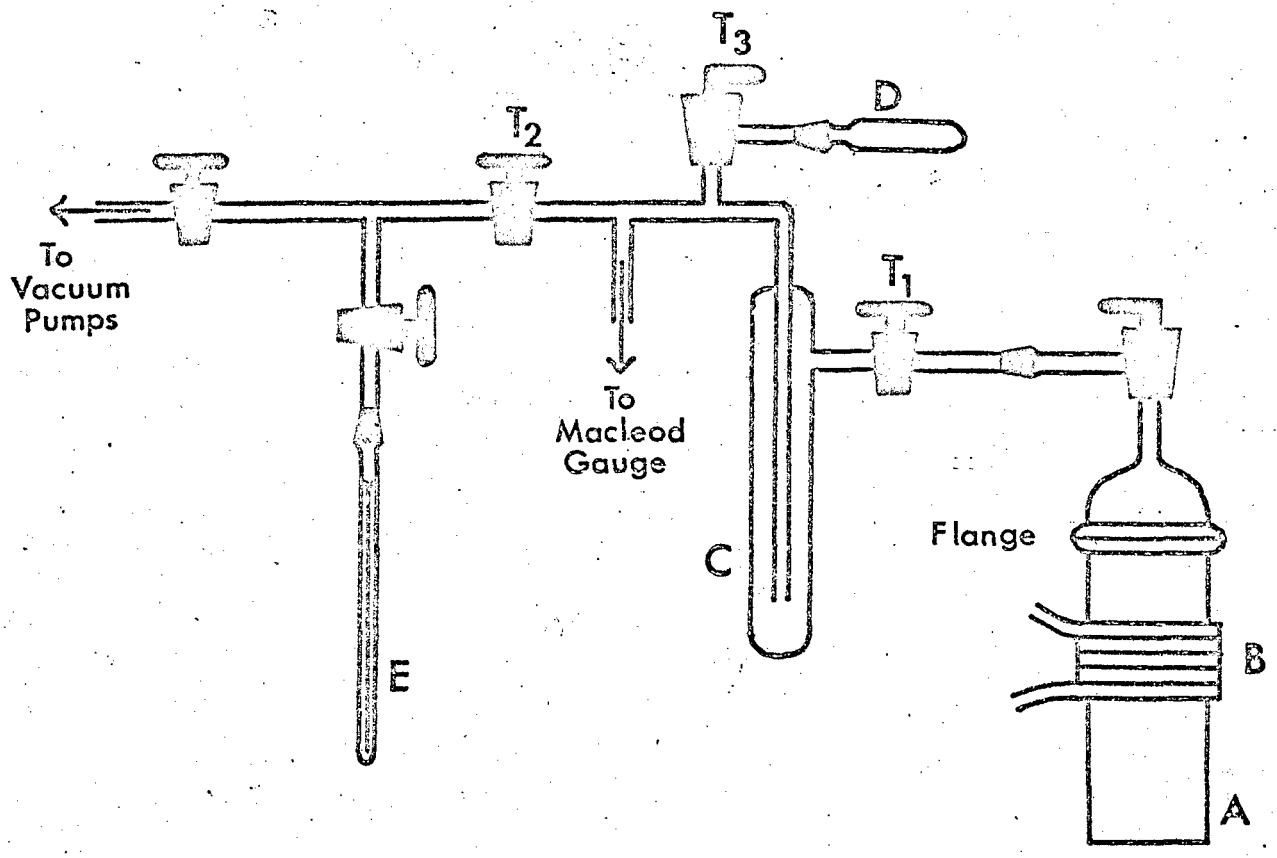


Figure 4. Degradation apparatus

capillary E and stored at -18°C. They consisted of the monomers and were analyzed by standard gas-liquid chromatography techniques by use of a Perkin-Elmer Fractometer. Methanol was sought in this fraction but never found. Products involatile at room temperature, which had condensed on the area of the reaction vessel cooled by B, were estimated by weighing the reaction vessel before and after their removal by solvent.

Thermal volatilization analyses were carried out on equipment which has already been described in detail by McNeill (21).

Molecular Weights

Number-average molecular weights were measured by using a Mechrolab high-speed membrane osmometer. The molecular weights of the poly(methyl methacrylate) (PMMA) and the 112/1, 26/1, 7·7/1 and 2/1 copolymers were 82 x 10^4, 60 x 10^4, 60 x 10^4, 42·5 x 10^4, and 37 x 10^4, respectively.

Spectroscopic Measurements

Infrared spectra were obtained by using a Perkin-Elmer 237 spectrophotometer. Materials of lower MA content were used in the form of a film mounted between brass rings to prevent warping. For copolymers of higher acrylate contents and for degradation residues, films were deposited on NaCl plates from chloroform solution, the last traces of solvent being removed by heating at 50°C in a vacuum oven for 24 hr.

Ultraviolet spectra were obtained by using a Unicam model SP800 spectrophotometer with the polymer either in the form of film or in chloroform solution.

RESULTS AND DISCUSSION

Thermal Volatilization Analysis

Thermal volatilization analysis thermograms for 25 mg. samples of PMMA and the four copolymers are compared in Figure 5. Below 200°C the evolution of occluded volatile material is observed as the polymer melts and softens. At higher temperatures there are two obvious trends in the characteristics of evolution of volatile products of degradation as the MA content of the copolymer is increased.

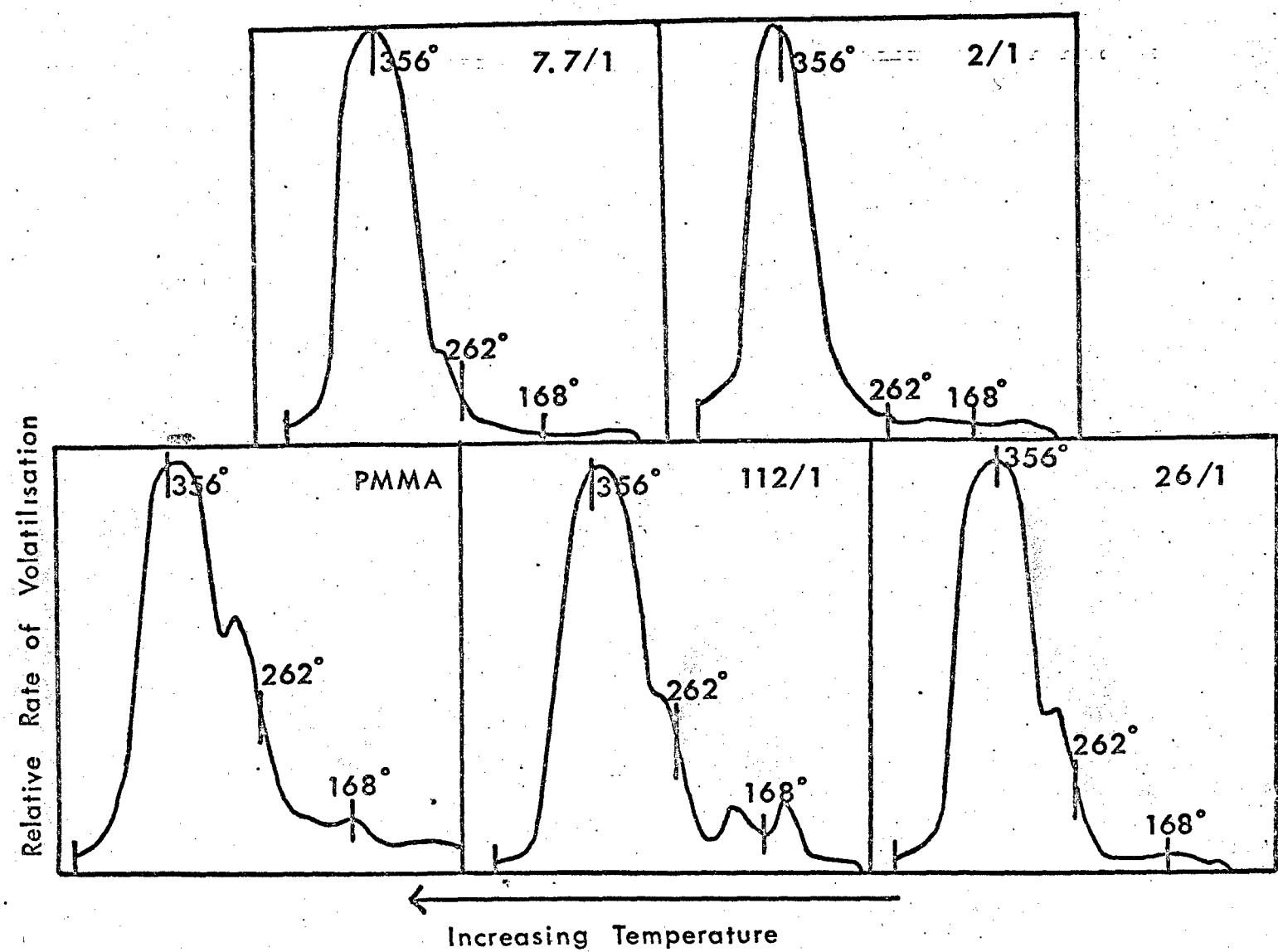


Figure 5. Thermal volatilization analysis thermograms of poly(methyl methacrylate) and methyl methacrylate-methyl acrylate copolymers.

First, the peak in the vicinity of 280°C progressively decreases. Second, the maximum of the main peak moves to higher temperatures. It is obvious from these thermograms that volatilization occurs at an appreciable rate at temperatures above 260°C, so that the temperature range 260-300°C may be most convenient for isothermal studies.

The volatilization thermogram for PMMA, in Figure 5, has previously been accounted for (21,22) in terms of the known degradation properties of this material. The lower temperature peak is the result of depolymerization initiated at unsaturated terminal structures. The peak at higher temperature is the result of depolymerization initiated by random scission of the polymer molecules.

In the light of previous work on the influence of comonomers on the degradation properties of PMMA (14-16) there are two possible explanations of the progressive decrease in the amount of chain terminally initiated depolymerization as the MA content of the copolymer is increased. The first and most obvious explanation is that, as in MMA copolymers with acrylonitrile (15), units of the second monomer block the passage of chain depolymerization. Blocking of this kind is certainly not complete since monomeric MA does appear among the reaction products. The constant ratio throughout the range of copolymer compositions studied, of one MA unit in four being liberated as monomer (see Table 3) may be some measure of the blocking efficiency in the temperature range of the randomly initiated reaction. The blocking efficiency at the lower temperature at which the terminally initiated reaction occurs should be very much greater as in acrylonitrile copolymers (16).

Table 3. Composition of Volatile Products of Degradation

Polymer	Composition, % by weight of total volatiles					
	CO_2	Permanent gases	Methanol	MMA	MA	Chain fragments
PMMA	-	-	-	>96	-	-
112/1	Trace	-	-	>96	-	Trace
26/1	1	Trace	-	93	0·8	5
7·7/1	1	0·1	-	87	2·5	10
2/1	3	0·4	-	64	7·0	25
PMA[a]	7·5	1	15	-	0·76	75

[a] Data of Madorsky (25)

It is not possible to make quantitative deductions from monomer ratio data alone, however, since the MA-terminated radical which results from this kind of blocking must ultimately undergo some further reaction which may complicate the situation.

The second explanation of the suppression of the terminally initiated reaction is that, as in the copolymerization of MMA and styrene (14,23), the presence of the second monomer favours combination rather than disproportionation as the termination step. In this way the proportion of terminally unsaturated structures is drastically reduced even in copolymers containing quite small proportions of styrene. An assessment of this possibility cannot be made for the MMA-MA system, however, since the relevant copolymerization data are not available. The tendency for the high temperature peak to move to higher temperatures with increasing MA content favours the first theory. Thus it can be accounted for in terms of a progressive decrease in the amount of monomer produced per initiation. This chain or zip length for depolymerization should not vary with copolymer composition if the second theory applies to the complete exclusion of the first.

Thus it is clear that the progressive suppression of the low temperature peak in the volatilization thermograms in Figure 5 can be accounted for qualitatively in terms of blocking by MA units, although some contribution to the effect by a decrease in the proportion of unsaturated chain ends formed during copolymerization cannot be entirely eliminated.

Changes in Molecular Weight

Figure 6 illustrates the changes which occur in the molecular weight of the 26/1 copolymer during degradation in the temperature range 282-326°C. The other copolymers behave similarly. Although this behaviour is characteristic of a random scission process it cannot be taken as evidence in favour of the random initiation reaction discussed above, since the large chain fragments which are seen in Table 3 to be a major product of degradation of the copolymers must be formed in transfer reactions of the type which also lead to chain scission during the thermal degradation of poly(methyl acrylate) (PMA).

All the copolymers remain completely soluble, even after extensive degradation, which contrasts with the tendency to gel formation in PMA (24).

A close association between chain scission and the production of carbon dioxide is demonstrated in the following chapter (18).

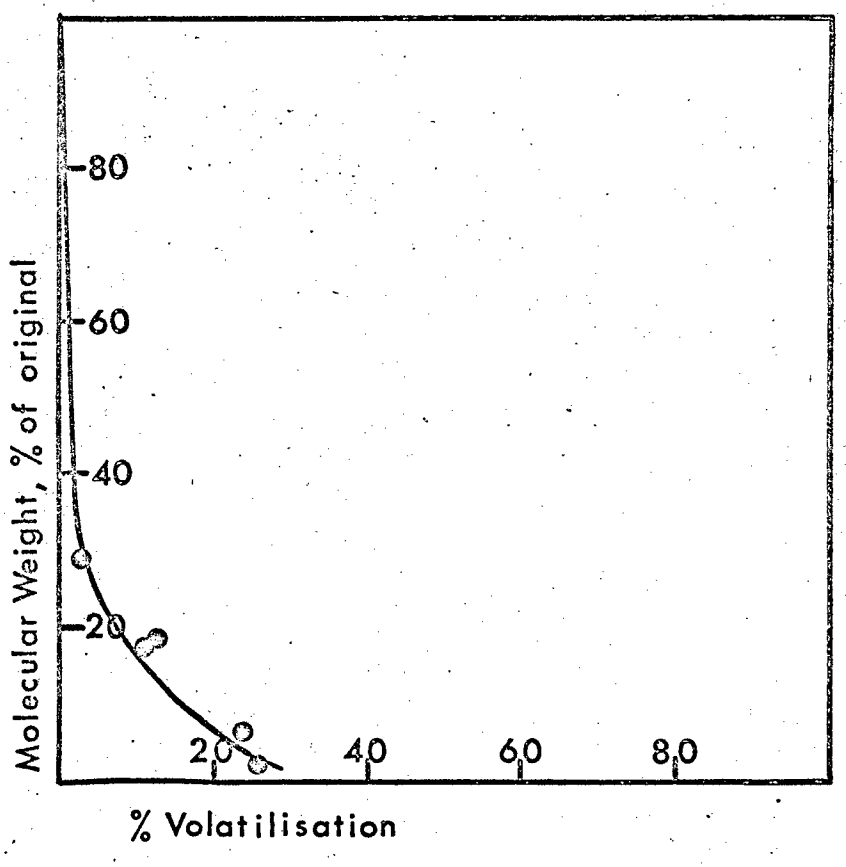


Figure 6. Molecular weight changes during degradation of 26/1 methyl methacrylate-methyl acrylate copolymer.

Volatile Products of Degradation

The compositions of the volatile products of degradation of the copolymers and the two homopolymers are compared in Table 3. Each of the results quoted represents an average of 3-5 experiments carried to relatively high extents of volatilization in the temperature range 260-300°C. The permanent gas fraction is found to consist of hydrogen with traces of methane and carbon monoxide.

The yields of chain fragments, carbon dioxide, and permanent gases are approximately as one would predict from the copolymer compositions and the behaviours of the homopolymers. There are, however, at least two major deviations between the pattern of products predicted in this way and the actual experimental results. First, no methanol is obtained from any of the copolymers in spite of the high yield from PMA. Thus, because the yield of carbon dioxide is proportional to the MA content, it seems that carbon dioxide and methanol are produced in two completely separable reactions. This is perhaps surprising, since the methanol and carbon dioxide must both be associated with decomposition of the ester group in the MA unit. Secondly, MA is obtained from the copolymers in larger amounts than might be expected from the behaviour of PMA. This was previously observed by Strassburger and his colleagues (26). It is obvious from the data in Table 3 that a fairly constant ratio of about 1 in 4 of the MA units in the 26/1, 7·7/1 and 2/1 copolymers are liberated as monomer. The amount produced from the 112/1 copolymer was too small to be detected.

Unsaturation in the Residual Copolymer

At higher extents of degradation, residual copolymer is coloured yellow. For comparable extents of volatilization the depth of colour increases with increasing MA content of the copolymer. Ultraviolet spectra show an increase in absorbance in the 2750-3750 Å region, as illustrated in Figure 7. Table 4 shows the colour to be expected and the wavelength of absorption for various lengths of carbon-carbon conjugation which suggests that conjugated sequences up to six units in length are present in the coloured material. The development of absorption at 1630 cm^{-1} in the infrared spectrum of degraded polymer, as in Figure 8, is confirmation of the appearance of ethylenic structures.

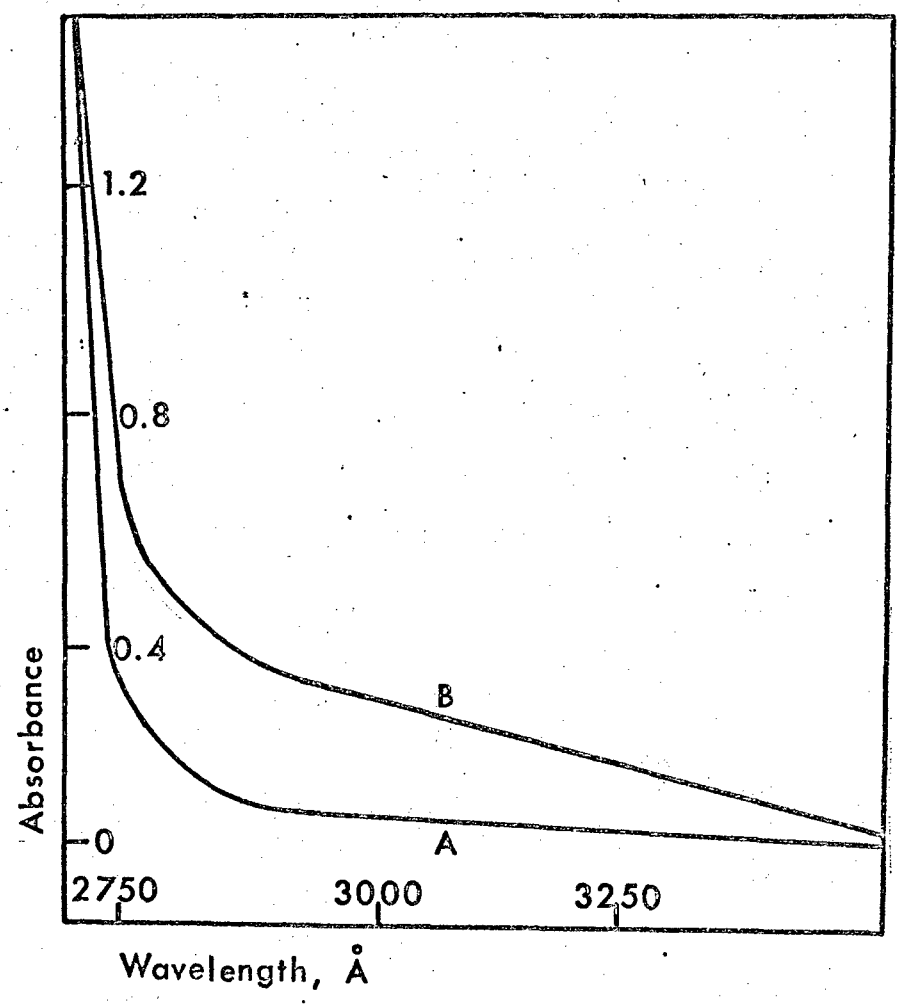


Figure 7. Ultraviolet absorption spectra of 2/1 methyl methacrylate-methyl acrylate copolymer in chloroform solution: (A) undegraded; (B) after 50% volatilization.

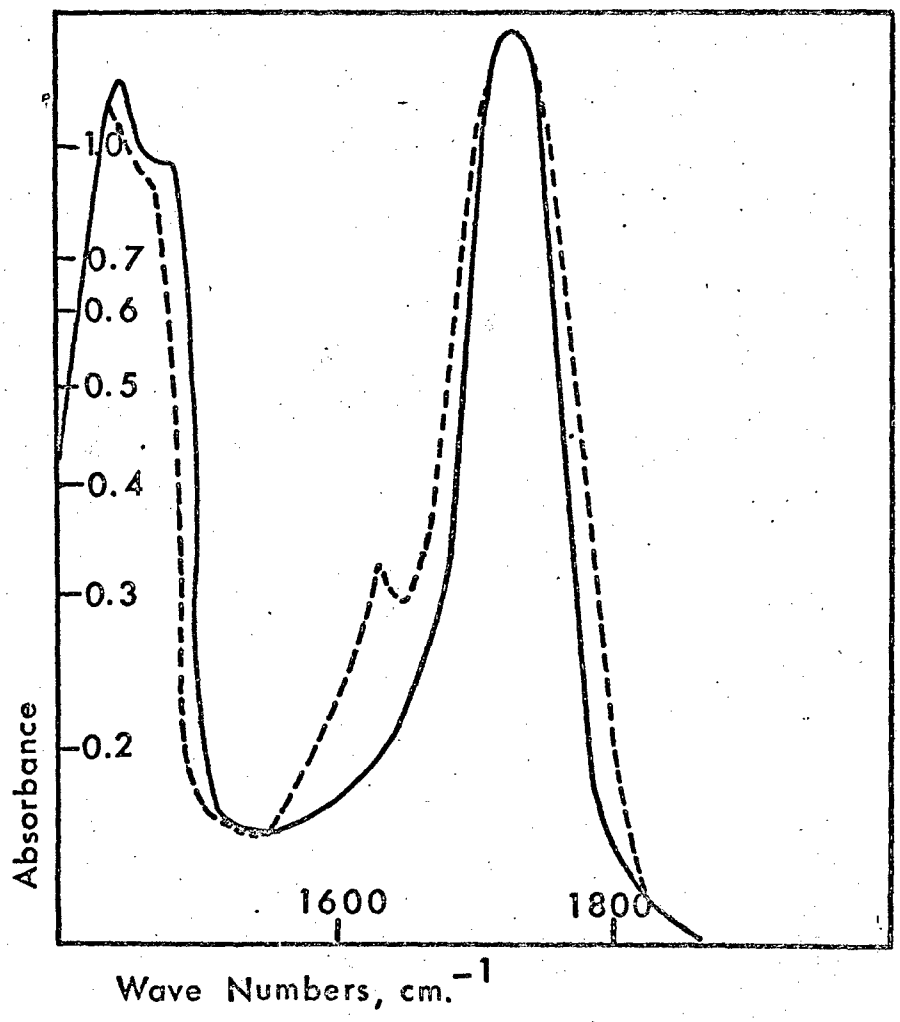


Figure 8. Infrared absorption spectra of films of 2/1, methyl methacrylate-methyl acrylate copolymer: (—) undegraded; (---) after 50% volatilization.

Table 4. Colour and Absorption Maxima for Conjugated Ethylenic Structures

Length of conjugation	Colour	Absorption maximum, Å
4	Pale yellow	2960
5	Pale yellow	3350
6	Yellow	3600
8	Orange	4150

The development of ethylenic conjugation is reminiscent of the degradation behaviour of polyvinyl esters which liberate the corresponding acid in a chain process which progresses along the polymer molecule. The ability of polymers to develop this kind of conjugation, presumably by the liberation of hydrogen, has been demonstrated for polyethylene (27) and polystyrene (28) under high energy and ultraviolet irradiation, respectively. It has been suggested (29) that once a radical is produced on the polymer chain the reaction may proceed in these polymers by a mechanism strictly analogous to the radical mechanism which has been proposed for the degradation of poly (vinyl chloride) (30):

$$\sim\!\sim CH_2-\dot{C}H-CH_2-CH_2-CH_2-CH_2\sim\!\sim \rightarrow$$
$$\sim\!\sim CH_2-CH=CH-CH_2-CH_2-CH_2 + H\cdot \rightarrow$$
$$\sim\!\sim CH_2-CH=CH-\dot{C}H-CH_2-CH_2\sim\!\sim + H_2 \qquad [1]$$

A comparable reaction in MMA-MA copolymers would involve the evolution of one or more of the products hydrogen, methane and methyl formate and could account for at least some of the hydrogen and methane which have been shown above to appear among the volatile products. In the present instance, the initial radicals would be produced in the kind of transfer reactions which lead to large volatile fragments and chain scission in the degradation of PMA (eq. [2]).

$$R\cdot + \sim\!\sim CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\overset{H}{|}}{C}}\sim\!\sim \rightarrow RH + \sim\!\sim CH_2-\underset{\underset{COOCH_3}{|}}{\overset{\cdot}{C}}\sim\!\sim \qquad [2]$$

Absence of Methanol among the Reaction Products

The complete absence of methanol from the volatile products of degradation of all four copolymers is an unexpected feature of the reaction in view of its prominence among the products from PMA. It would appear that while methanol production is a property of long sequences of methyl acrylate units, it is not a property of isolated units and in this connection it is clearly of interest to obtain information about the distribution of MA units in the various copolymers under discussion. Harwood (31) has shown how the sequence distribution of monomer units in copolymers can be predicted provided reactivity ratios and monomer mixture or copolymer composition are known. By using Harwood's methods, the data in Table 5 have been calculated for the four copolymers. The first five columns in Table 5 are self-explanatory. The data in the last column represent the relative percentage concentrations of MA units in the middle of MA triads whose immediate environment is thus comparable with the environment of a MA unit in a PMA molecule.

Table 5. Data on Sequence Distribution in the Copolymers

Copolymer omposition (MMA-MA)	MMA-MMA bonds in copolymer, %	MMA-MA bonds in copolymer, %	MA-MA bonds in copolymer, %	Fraction z of MA in middle units of MA triads	Z x % MA in copolymer
112/1	98·234	1·762	0·004	0·000020	0·000017
26/1	92·675	7·25	0·075	0·0004	0·0015
7·7/1	77·95	21·1	0·95	0·0069	0·08
2/1	42·3	48·8	8·9	0·073	2·43

In order to be able to discuss the whole question of methanol production in a completely satisfactory way it will clearly be necessary to study copolymers covering the whole composition range. However, the fact that no detectable amounts of methanol were obtained from any of the copolymers under discussion allows a few observations to be made. For example, it is clear that methanol production is not even a property of pairs of MA units since measurable amounts of methanol would have been produced from the 2/1 copolymer, 8·9% of whose chain linkages are between pairs of methyl acrylate units. Only 2·43% of all chain units are in an environment comparable with PMA chain environment. Thus by comparison with PMA (Table 3) one would expect methanol to comprise about

0·36 % of the total products which is at the limit of the analytical methods used. These results therefore indicate that sequences of at least three MA units are necessary for the evolution of methanol. This conclusion is in accord with the thermal degradation behaviour of ethylene-MA copolymers (32). Thus block copolymers produce methanol in the quantities expected from the MA content while random copolymers produce very much less.

Apparently conflicting results have been reported for pyrolysis-gas-liquid chromatography studies on MMA-MA copolymers (26) when it was found that a 4/1 copolymer yielded methanol. However, in the preparation of this copolymer the conversion of the monomer mixture was carried to 100% so that in the later stages of the copolymerization virtually pure PMA was being formed. It was also reported, however, that an equivalent mixture of the two homopolymers gave a much higher yield of methanol than a copolymer of the same overall composition.

Production of Methyl Acrylate and Chain Fragments

Although the principal products of degradation of PMA and PMMA are so different, the reactions have been explained in terms of a single chain depolymerization mechanism in which there are two competing steps, namely depropagation and intramolecular transfer (1). In PMMA the former predominates so that high yields of monomer are obtained, while in PMA the latter predominates to give long chain fragments as the principal product. It is clear from Table 3 that as one would expect, a high proportion of the MM in the copolymers is accounted for as monomer among the products. Table 3 also shows that the yields of MA and chain fragments both increase in proportion to the concentration of MA in the copolymers. The constant ratio, throughout the copolymer composition range studied, of one MA unit in four being liberated as monomer is therefore a measure of the relative probabilities of depropagation and transfer occurring at a long chain radical terminated by a MA unit. In copolymers containing higher proportions of MA in which a higher proportion of the MA units will occur in groups, depropagation will be inhibited as in PMA, and these relationships will undoubtedly break down.

Production of Carbon Dioxide

Carbon dioxide is not produced in significant quantities during the thermal degradation of PMMA. On the other hand, the data in Table 3 demonstrate that the yields of carbon dioxide

from the copolymers are approximately in proportion to the MA content so that liberation of carbon dioxide may be a property of individual MA units. In view of a possible association of chain scission with MA units it seems that carbon dioxide might also be closely associated with chain scission. It is also clear that since chain scission plays such a vital part in this degradation process its mechanism will have to be clarified if a satisfactory picture of the overall reaction is to be given. It has therefore been found convenient to devote the following chapter to carbon dioxide production and chain scission leading to a discussion of mechanism and kinetics.

CONCLUSIONS

The high rates of monomer production from PMMA due to chain terminal initiation are suppressed in the copolymers due to the blocking of the depropagation process by the MA units. Thus degradation occurs in the copolymers only at temperatures at which PMMA molecules devoid of terminal unsaturation degrade. This involves random scission followed by depropagation. When depropagation reaches an isolated unit of MA, there is competition among deprogagation, intramolecular transfer, and intermolecular transfer which results in MA monomer, large chain fragments and chain scission, respectively. Depropagation is unlikely to occur from a radical chain end which comprises a sequence of more than one MA unit so that only the transfer processes can occur. During the course of the reaction the copolymers become yellow, the rate of coloration being greater the greater the MA content of the copolymer. This has been associated with the formation of carbon-carbon conjugation in the chain backbone. It seems possible that hydrogen and methane, which appear as minor products of the reaction, are being liberated from adjacent units in the polymer molecules in a chain reaction which is initiated by the intermolecular transfer process mentioned above and which is therefore in competition with chain scission.

The fact that methanol does not appear among the volatile products of degradation of any of the copolymers demonstrates that at least three adjacent units of MA are necessary in the polymer chain for its formation.

CHAPTER 4

THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND METHYL ACRYLATE. B. CHAIN SCISSION AND THE MECHANISM OF THE REACTION

INTRODUCTION

It was suggested in the previous chapter (33) that there may be a link between the chain scission and the production of carbon dioxide which occur during thermal degradation of methyl methacrylate-methyl acrylate (MMA-MA) copolymers. In the present chapter it is demonstrated that over the range of copolymer compositions studied one molecule of carbon dioxide is liberated for each chain scission. It is therefore possible to use carbon dioxide production as a measure of chain scission and thus to study the relationship between chain scission and certain other features of the reaction in a very much more sensitive way and to larger extents of reaction than is possible by use of the more conventional measurement of molecular weight.

EXPERIMENTAL

The polymers referred to and the experimental methods applied in the present chapter are those described in the previous chapter (33).

RESULTS AND DISCUSSION

Chain Scission and Carbon Dioxide Production

A typical series of curves for the production of carbon dioxide over a range of temperatures is illustrated in Figure 9. During the initial period of low reaction rate, which is more pronounced the lower the temperature, the copolymer retains its powdery appearance and has clearly not attained the temperature of the reaction vessel. The point of transition to the higher rate can be seen to be associated with the conversion of the polymer to a transparent film. This may be loosely termed melting. The mobility of the "molten" polymer thereafter will

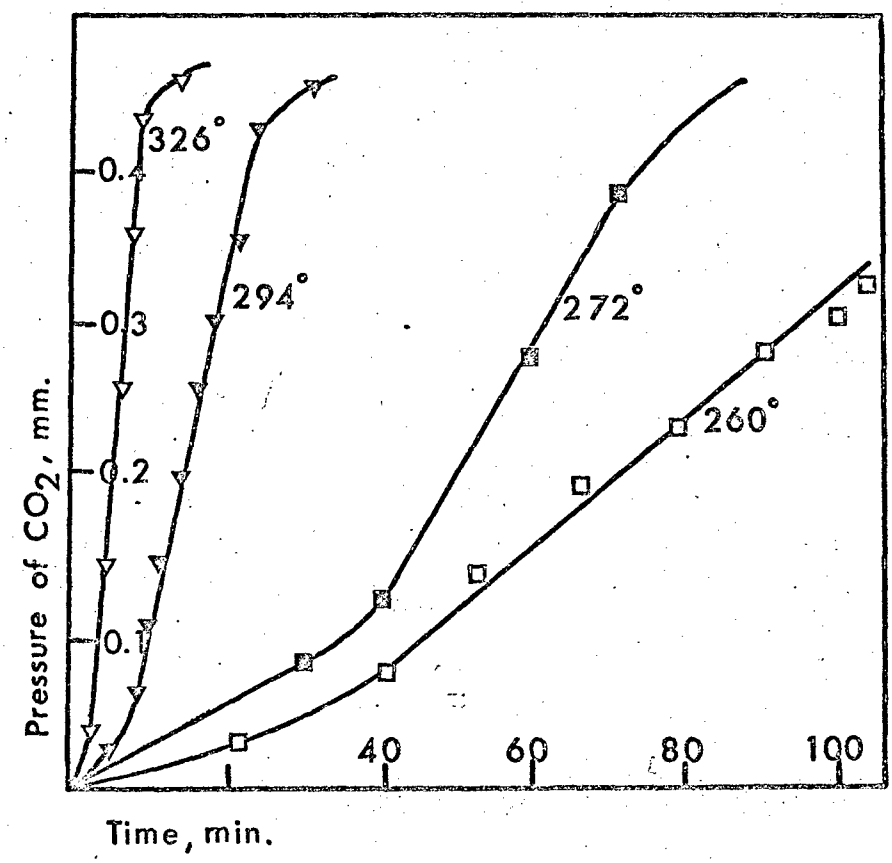


Figure 9. Production of carbon dioxide during degradation of 7·7/1 methyl methacrylate-methyl acrylate copolymer.

ensure that its temperature rises rapidly to that of the reaction vessel and the subsequent high rate may be taken as a reliable measure of the rate at the temperature quoted. By heating copolymer samples slowly it was confirmed by visual observation that the "melting points" are all in the range 240-260°C whereas pure PMMA "melted" at 160-170°C.

It has previously been shown (13) that the number of chain scissions N which has occurred per molecule of copolymer is given by equation [3],

$$N = [M_0(1 - x)/M] - 1 \qquad [3]$$

in which M_0 and M are the original molecular weight and the molecular weight at an extent of volatilization x, respectively. In Figure 10 chain scissions per molecule of polymer calculated in this way are plotted against molecules of carbon dioxide produced per molecule of polymer at a variety of temperatures for various extents of degradation of the four copolymers (see Table 6, columns 5 and 6). The straight line in Figure 10 has been drawn with a slope of 45°. It is obvious that within experimental error and over the range of experimental conditions represented in Figure 10, each chain scission in all four copolymers is associated with the production of one molecule of carbon dioxide. Beyond about 45% volatilization there is some deviation from this relationship, but this is due to the fact that polymer molecules are then disappearing from the system in appreciable quantities by complete unzipping so that equation [3] no longer applies. Since the molecular weight decreases so rapidly during degradation and since the measurement of low molecular weight is inaccurate owing to diffusion effects in the osmometer, the measurement of the production of carbon dioxide is very much more reliable at all but the lowest extents of degradation. For this reason, all chain scission data quoted in the following sections of this chapter were calculated from carbon dioxide production data.

Volatilization, Chain Scission, and Zip Length

The previous chapter (33) has shown the reaction to consist essentially of chain scission followed by three competing reactions, namely, depropagation to monomer, intramolecular transfer giving large chain fragments, and intermolecular transfer which may lead to further chain scission or, to a lesser extent, to conjugated unsaturation in the polymer backbone. It seems, therefore, that there should be at least

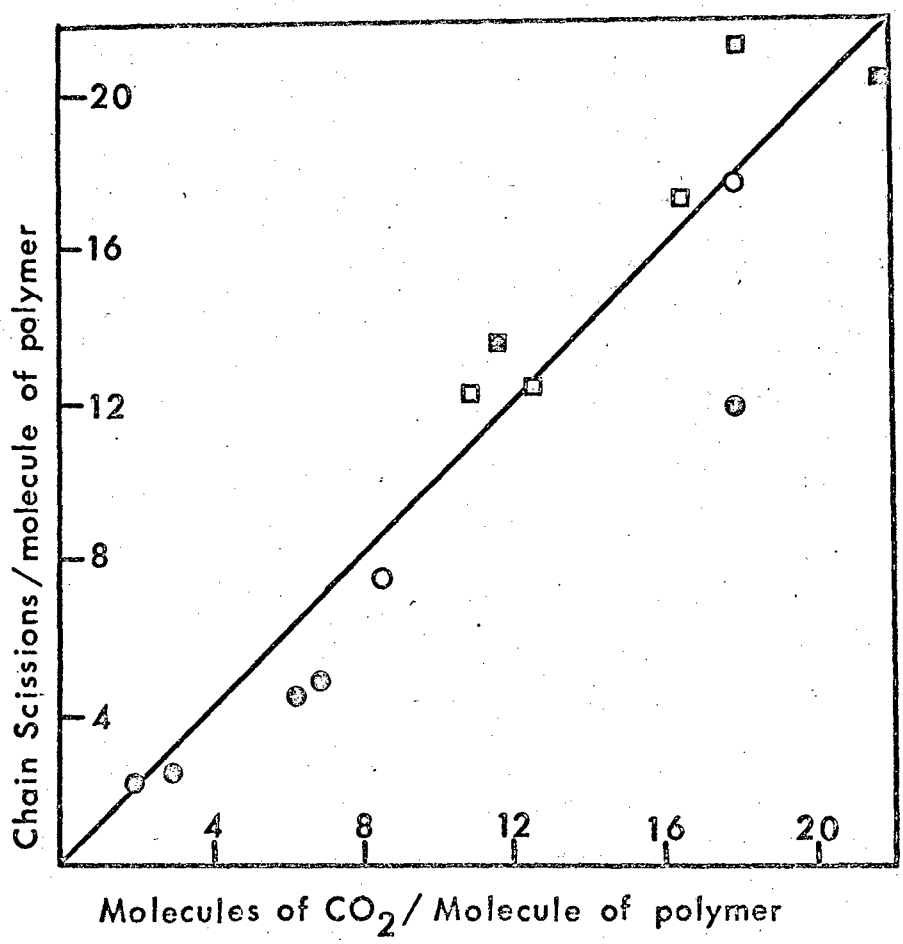


Figure 10. Relationship between carbon dioxide production and chain scission during degradation of methyl methacrylate-methyl acrylate copolymers; (○) 112/1; (◑) 26/1; (□) 7.7/1; (▣) 2/1.

Table 6. Summary of Carbon Dioxide-Chain Scission Data

›polymer	Degradation temperature, °C	Volatilization, %	MW of residue	Scissions/molecule	Molecules CO_2/molecule
112/1	294	6·6	66,000	7·46	8·2
	282	22·5	-	-	7·2
	294	31·5	58,000	6·21	11·6
26/1	282	26·0	15,000	28·6	24·5
	282	62·0	-	-	52·4
	282	79·5	-	-	66.0
	294	2·3	175,000	2·34	2·8
	294	23·6	40,000	11·8	17·6
	272	-	190,000	2·2	1·9
	294	12·5	115,000	4·8	6·0
	326	11·0	110,000	4·68	6·6
7·7/1	282	16·4	27,000	12·1	10·5
	282	25·0	23,600	12·5	12·4
	282	31·4	13,000	21·3	17·8
	294	17·3	20,000	17·5	16·1
	294	32·2	-	-	18·0
	294	50·3	-	-	30·0
	326	74·7	-	-	35·5
2/1	294	13·9	15,000	20·3	22·0
	310	5·3	24,000	13·6	11·2
	310	15·4	16,800	17·7	17·7
	310	27·3	-	-	35·5
	310	45·2	-	-	48·0
	310	53·4	-	-	60·0

a qualitative correlation between the number of monomer units liberated per chain scission, the zip length, and copolymer composition and the pattern of products described in the previous chapter.

On plotting representative data from Table 6 as in Figure 11, it is clear that over a large part of the reaction a constant amount of volatilization occurs per chain scission for each copolymer, which is consistent with the reaction mechanism outlined above. From the slopes of plots, as in Figure 11, the zip length for each copolymer can be calculated as in Table 7. Although there may be considerable experimental error in these values of zip length, they are undoubtedly correct to within 10%.

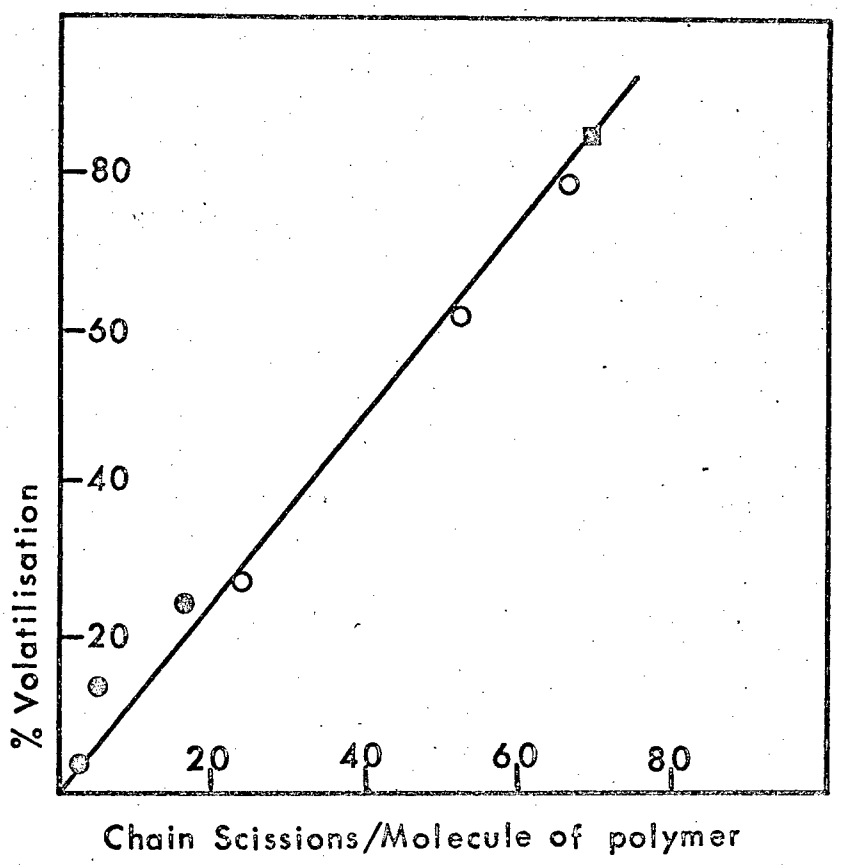


Figure 11. Relationship between volatilization and chain scissions during degradation of 26/1 methyl methacrylate - methyl acrylate copolymers: (○) 282°C; (●) 294°C; (▣) 326°C.

Table 7. Zip Lengths

Copolymer	Slope A	Initial MW, M_o	MW lost/ scission ($M_oA/100$)	Average wt. of monomer unit B	Zip Length ($M_oA/100B$)
112/1	2·9	600,000	17,320	100.0	173
26/1	1·22	600,000	7,320	99·5	74
7·7/1	1·68	425,000	7,150	97·2	74
2/1	0·88	370,000	3,260	95·3	34

Table 5 in the previous chapter indicates that in the 112/1 copolymer the proportion of adjacent MA units is extremely small, and indeed there must be relatively few MA units even in the close vicinity of each other. Thus there should be expected to be relatively little intramolecular transfer and this is confirmed by the absence of any significant amount of chain fragments. In the previous chapter it was shown that approximately one in four of the methyl acrylate units areliberated as monomer so it may be assumed that at least for single MA units there is a 1 in 4 chance that depropagation will pass through them. For the 112/1 copolymer this will lead to an average zip length of approximately 150 $[112 + (112/4) + (112/4^2) + \ldots]$ which is in satisfactory agreement with the value of 173 in Table 7.

As the MA content of the copolymers is increased so that a greater proportion of the MA units form adjacent sequences, monomer production is increasingly suppressed and intramolecular transfer with the production of chain fragments plays an increasing part. Since the zip length values in Table 7 become proportionately greater compared with the monomer ratios in the copolymers and since the zip length includes chain fragments based as it is on total weight loss, it is obvious that a radical terminated by a sequence of MA units is very much more likely to undergo intramolecular than intermolecular transfer. The present experimental data only allow these qualitative observations to be made. A more quantitative analysis will only be possible when a precise analysis of the chain fragments can be carried out.

Chain Scission and Copolymer Composition.

In view of the possibly important part which MA units may play in the chain scission process it is important to

investigate the dependence of rate of chain scission upon MA content as a step towards the establishment of the overall reaction mechanism. The rates of carbon dioxide evolution after "melting" of the polymer (see Figure 9) were taken as a measure of rate of chain scission. Owing to the considerable potential experimental error and the possibility of the sample size influencing measured rates, rates of carbon dioxide production were measured for samples of various sizes for each copolymer. Results are illustrated in Figure 12, which demonstrates no consistent trend with sample size. The horizontal lines indicate average values of rate. Figure 13 illustrates the relationship between rate and MA content for the 26/1, 7·7/1 and 2/1 copolymers at 294 and 272°C. The slopes of the straight lines through these points are 0·42 and 0·33 respectively. Although the limited number of experimental data makes the probable error fairly high, taking the two sets of data together it may reasonably be claimed that the rate of chain scission is proportional to less than the half power of the MA content of the copolymer.

Activation Energy for Chain Scission

The data for the 26/1 and 7·7/1 copolymers in Figure 12 are represented in Figure 14 in the form of an Arhennius plot from which a value of 23·5 ± 2 k.cal/mole may be deduced for the energy of activation of chain scission. This is also the value for the energy of activation for volatilization, since volatilization has been shown to be a linear function of chain scission for each copolymer. It is low compared with the values for the initial volatilization of PMMA (34) and PMA (25) which are 32 and 34 K.cal/mole, respectively. Both the low exponent in the relationship between rate of chain scission and MA content and this low value of energy of activation are evidence in favour of the involvement of chain scission as an integral part of a radical chain process.

Chain Scission and the Production of Permanent Gases

It was reported in the previous chapter that permanent gases, particularly hydrogen, are produced during the reaction although in quantities very much less than carbon dioxide. It was also suggested that these permanent gases might be associated with the colouration which occurs, the radical resulting from intermolecular transfer acting as a centre of initiation for two competing reactions, the first resulting

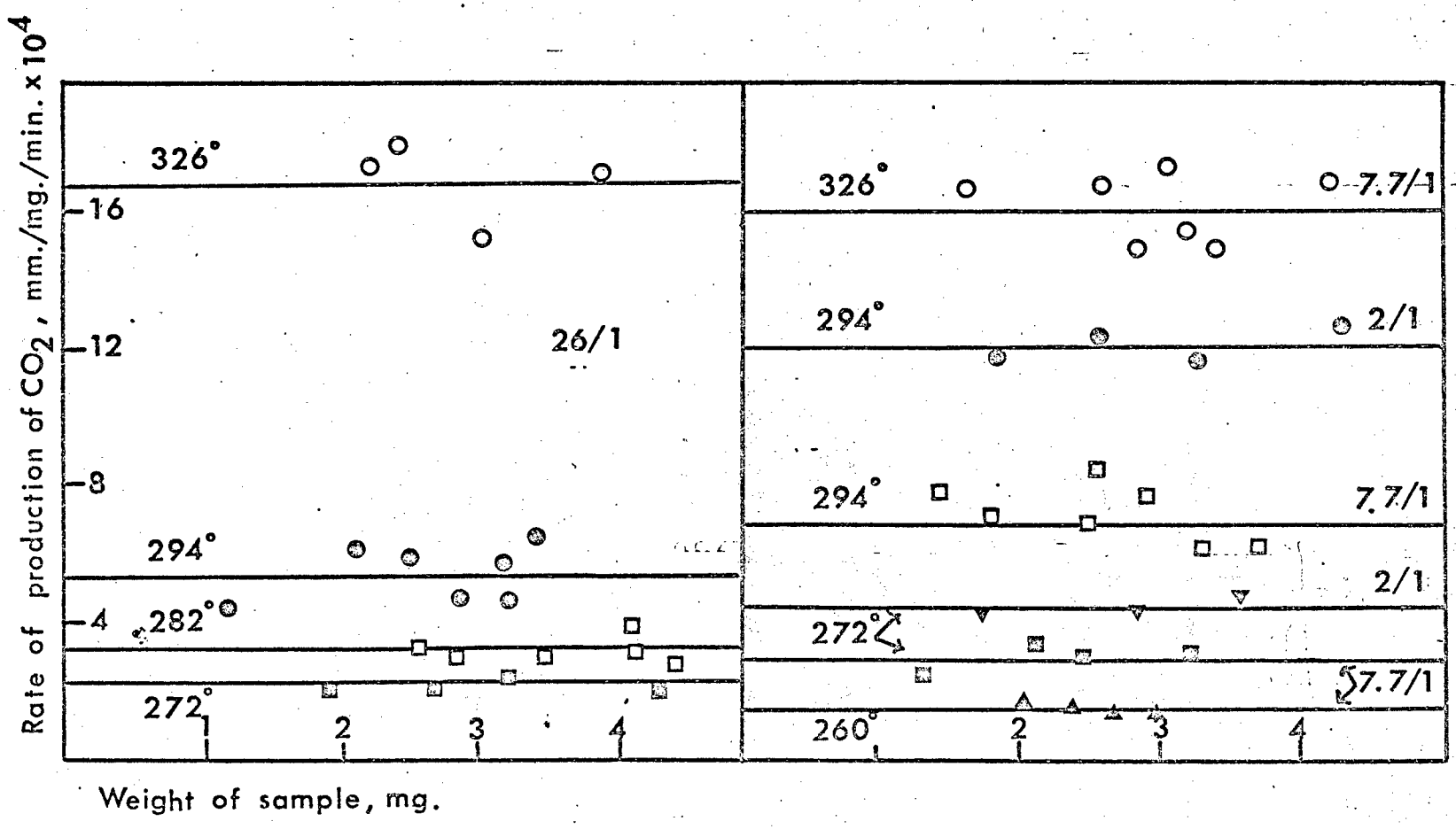


Figure 12. Dependence of rate of production of carbon dioxide on size of polymer sample for methyl methacrylate-methyl acrylate copolymers.

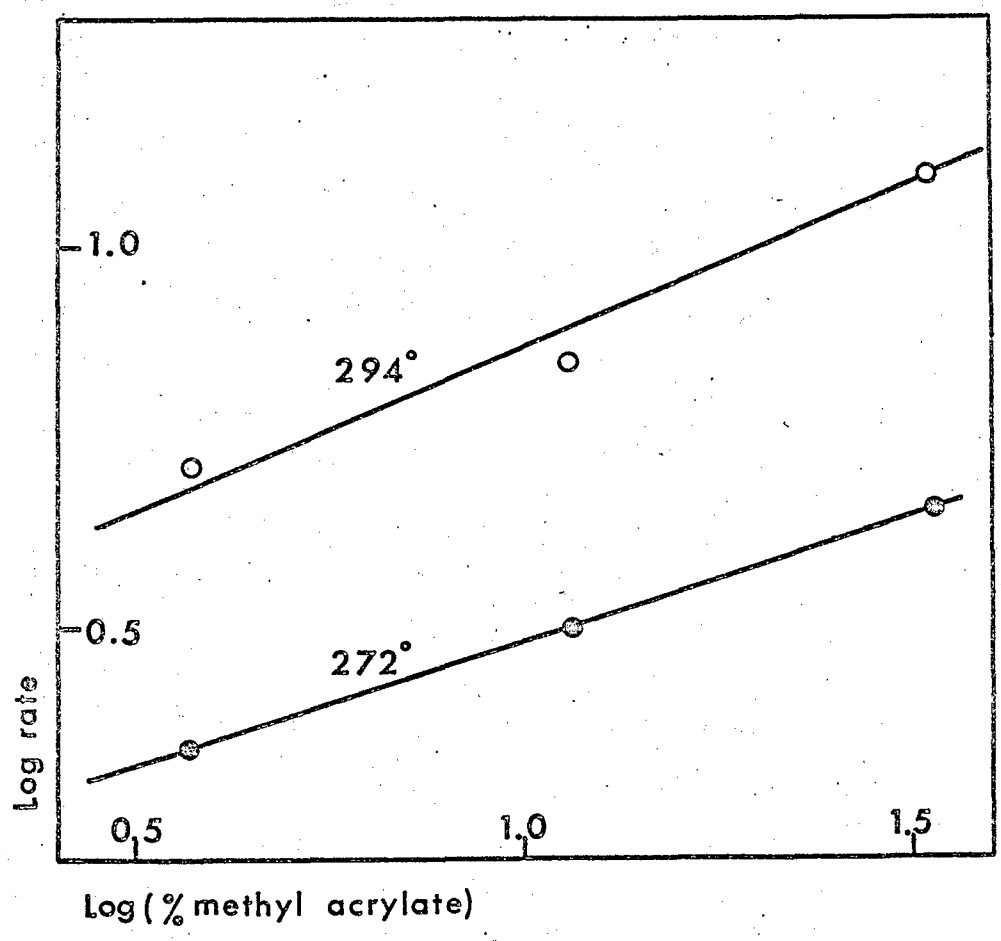


Figure 13. Relationship between rate of chain scission and methyl acrylate content for methyl methacrylate-methyl acrylate copolymers.

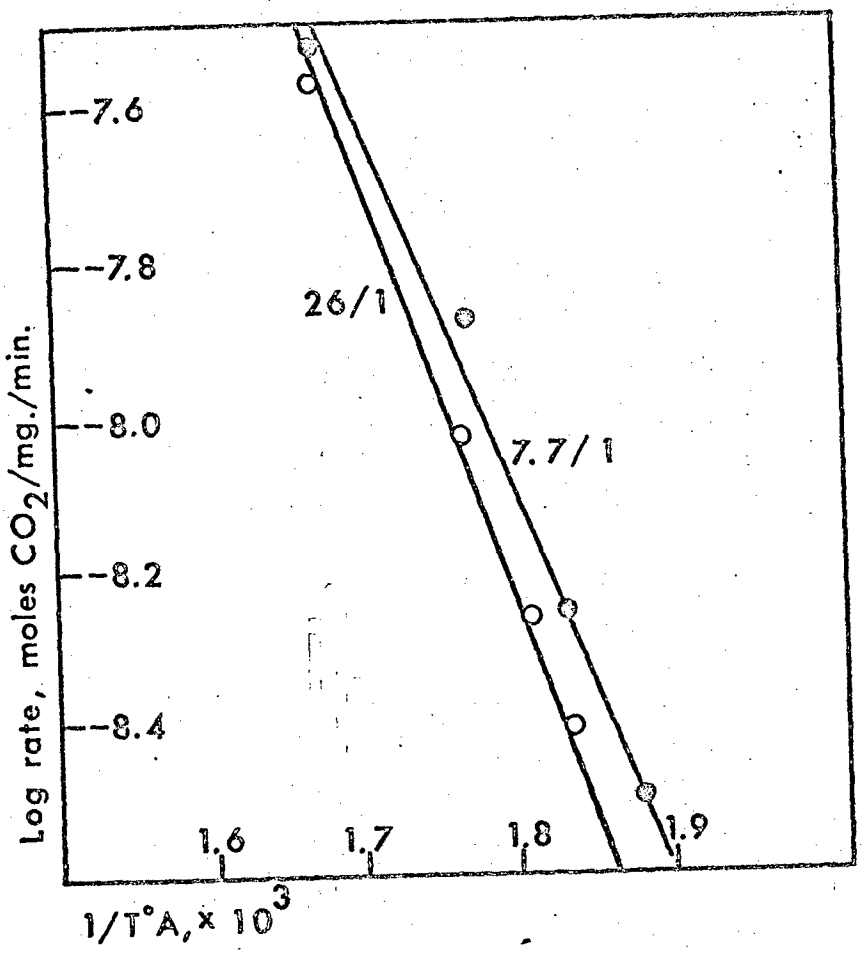


Figure 14. Arrhenius plot of chain scissions during degradation of methyl methacrylate-methyl acrylate copolymers.

directly in chain scission and the second in the evolution of hydrogen and methane in a chain process similar to that which has been suggested for the liberation of hydrogen chloride from poly(vinyl chloride) (30). If these conclusions are correct, they should provide a basis for the explanation of any relationship which exists between carbon dioxide and permanent gas production.

The data in Table 8 demonstrate that for a wide range of degradation temperatures and extents of reaction, the ratio of chain scissions to permanent gas production is constant for each copolymer but that the proportion of permanent gases increases with the MA content of the copolymer. This is in accordance with the mechanism outlined above. Thus the constant value for each copolymer demonstrates the close association of chain scission and permanent gas production throughout the whole course of the reaction. Also, because permanent gas production and colouration are associated with MA rather than MMA units, the chain reaction in which permanent gases are liberated is more likely to occur, the greater the probability that the transfer radical finds itself in the vicinity of MA units; that is, the greater the MA content of the copolymer.

Table 8. Chain Scissions and Permanent Gases.

Copolymer	Degradation temperature, °C	Volatilization, %	Chain scissions/ molecules of permanent gas	Average ratio
26/1	200	1	20	
	220	2	25	
	294	85	18	20
	294	85	17	
	326	80	20	
7·7/1	326	80	12	12
	326	1	12	
2/1	294	50	8	
	310	52	7	8
	310	60	8	

Mechanism and Kinetics of Chain Scission

In order to gain further information about the site of the initial chain scission and of the intermolecular transfer

process with which chain scission and carbon dioxide production are associated, these two processes may be regarded as the initiation and propagation steps of a chain reaction whose rate is measured by the rate of chain scission.

In view of the fact that the degradation reaction occurs in the copolymers at the same temperature as the randomly initiated phase of the degradation of PMMA, random initiation seems the most likely initiation process in this chain reaction. Thus the rate of initiation would be independent of the MA content of the copolymer and given by

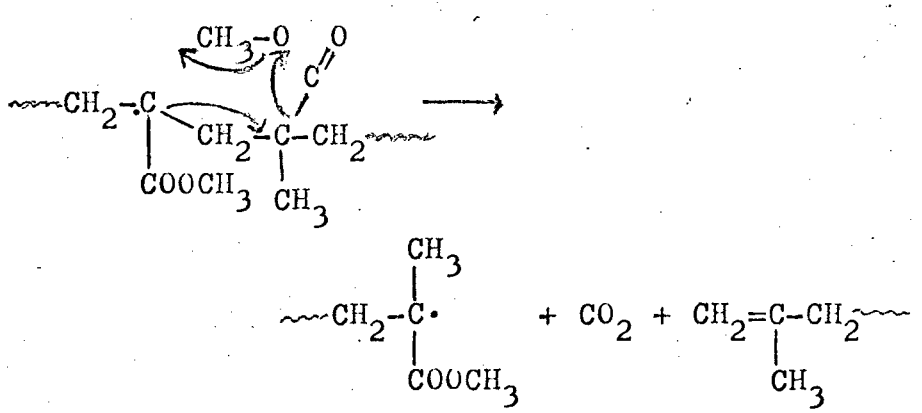
$$\text{rate of initiation} = k_i[M_n] \qquad [4]$$

in which k_i is the rate constant for initiation and $[M_n]$ the concentration of the copolymer which may be taken as constant throughout the range of copolymer composition studied.

The propagation step might reasonably be expected to involve the abstraction of a tertiary hydrogen atom from a methyl acrylate unit by a polymer radical, P•, thus

$$\text{rate of propagation} = k_p[P\bullet][MA] \qquad [5]$$

Chain scission and the production of carbon dioxide can be explained in terms of reaction of the resulting radical in a six-membered ring mechanism [eq. 6]



[6]

I

The radical I will liberate monomer and chain fragments and ultimately carry on propagation of the chain scission process by abstracting a further tertiary hydrogen atom.

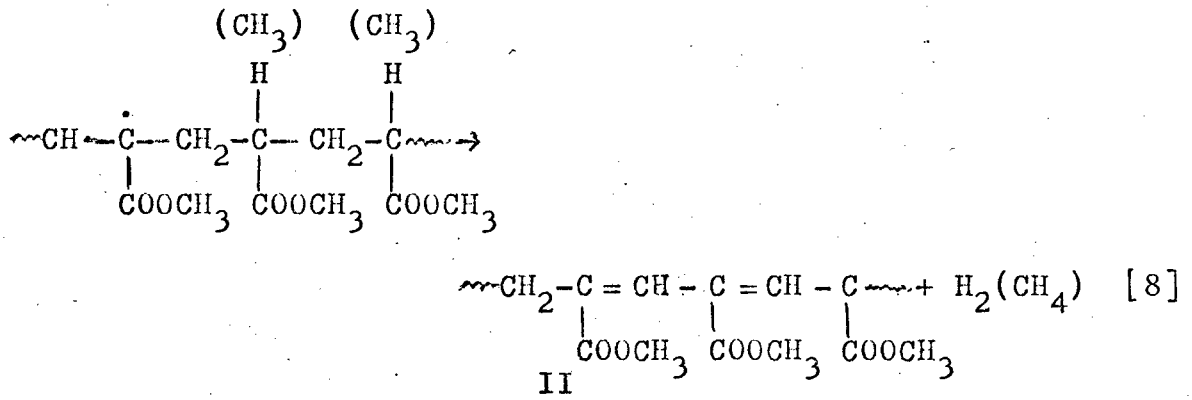
In accordance with experimental findings, one molecule of carbon dioxide is produced per chain scission in this mechanism if it can be assumed that the chain length is appreciable such that the number of initiation steps which occurs without production of carbon dioxide is negligible compared with the number of propagation steps. It may also be noted that a unit of MMA is formed in each act of scission which could explain the small proportion of MMA which is found among the volatile products of degradation of PMA (35,36).

Termination might reasonably be expected to occur by mutual destruction of pairs of radicals, so that

$$\text{rate of termination} = k_t[P\cdot]^2 \qquad [7]$$

On applying stationary-state kinetics to this mechanism it can easily be demonstrated that the rate of chain scission should be proportional to the first power of the MA content of the copolymer, which is not in accordance with the experimental values of less than 0·5.

It is possible, however, that initiation may be specifically associated with MA units and that the propagation step is random rather than specifically at MA units. Termination, on the other hand, may be associated with the hydrogen and methane loss reaction:



Thus conjugated radicals of type II may be so stable as to be incapable of continuing propagation by abstraction of a hydrogen atom in which case termination would become effectively first order with respect to radical concentration. Eight different combinations of initiation, propagation and termination are therefore possible, as in Table 9.

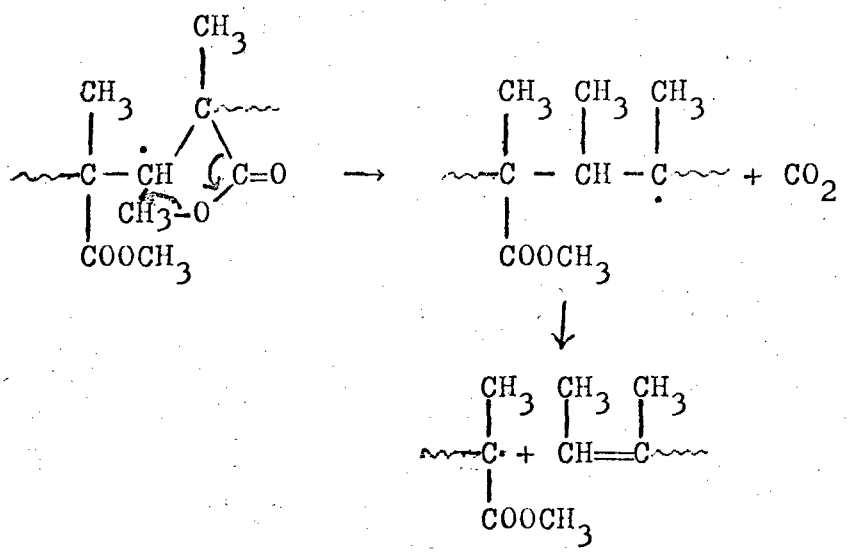
Table 9. Rate Exponents for Various Reaction Mechanisms

Initiation	Propagation	Termination	n
Random	Random	Pairs of radicals	0
Random	Random	Single radicals	0
Random	At MA units	Pairs of radicals	1
Random	At MA units	Single radicals	1
At MA units	Random	Pairs of radicals	$\frac{1}{2}$
At MA units	Random	Single radicals	1
At MA units	At MA units	Pairs of radicals	3/2
At MA units	At MA units	Single radicals	2

The exponent, n, in the relationship,

$$\text{Rate of chain scission} = K[MA]^n \qquad [9]$$

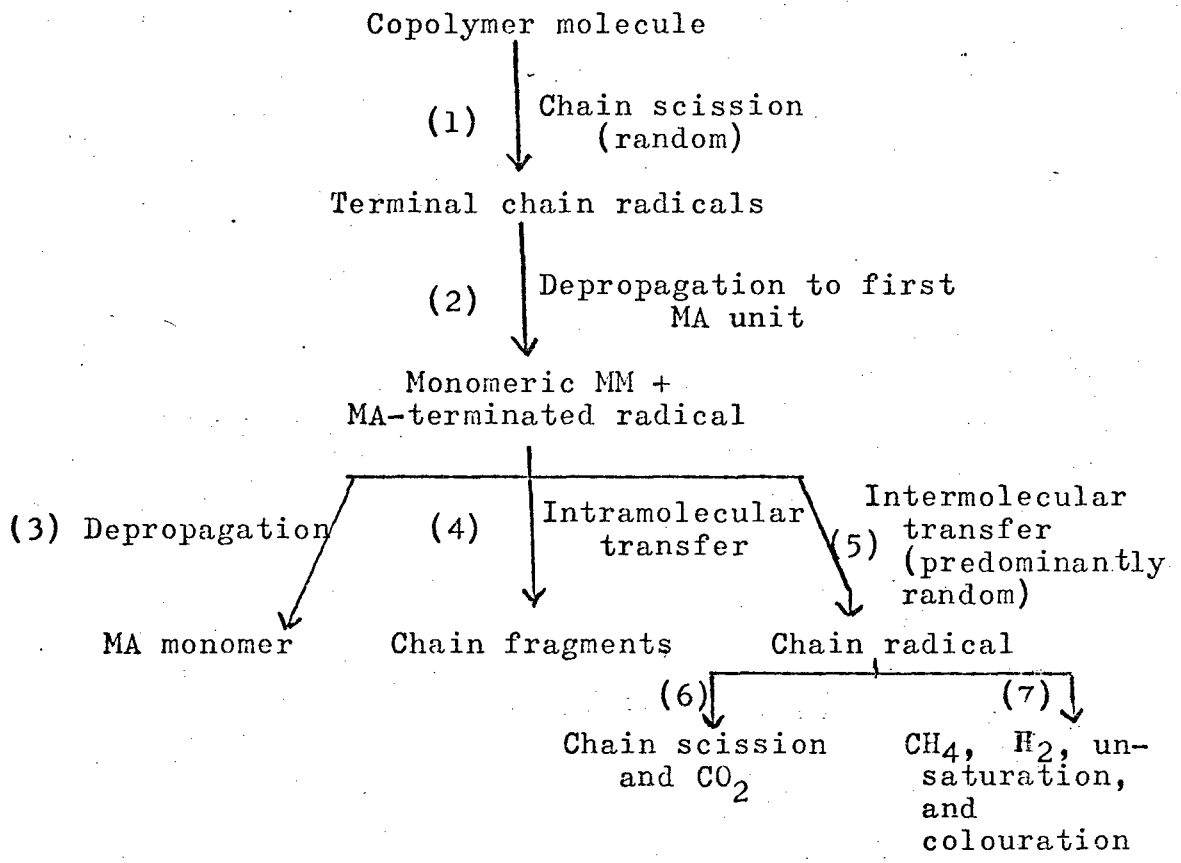
is given for each of these combinations in the final column of Table 9. Since the experimental value of n was found to be less than 0·5, it is clear that a significant proportion of both initiation and propagation must be random although it is not possible to say, on the basis of the kinetic evidence above, whether a proportion of initiation or propagation or both are associated with MA units. Since no bonds which are thermally more labile than the bonds already present in PMMA are introduced into the molecules by MA units and since the introduction of MA units does not lower the reaction temperature from that of the randomly initiated degradation of PMMA, it seems most unlikely that there can be a significant proportion of preferred initiation at MA units. However, the tertiary hydrogen atoms in MA will be much more liable to participate in the propagation step than the chain methylene groups whose reaction is implied by random propagation. The fact that transfer of methylene hydrogen atoms plays a significant part in presence of tertiary hydrogen atoms is explained by the very much higher concentration of the former. A reasonable mechanism for chain scission and the formation of carbon dioxide, following upon transfer at methylene groups, may be represented as in equation [10].



[10]

CONCLUSIONS

These relationships between chain scission and certain other features of the reaction together with the general reaction characteristics reportedin the previous paper lead to the following representation of the mechanism of the overall reaction



The evidence favours random scission in reaction (1) rather than preferential scission at MA units. It is the interplay of reactions (3),(4), and (5) which determines the principal characteristics of the overall reaction and their variation with copolymer composition. If the terminal MA resulting from reaction (2) is single, as would be predominantly so in the 112/1 copolymer, then only reactions (3) and (5) are possible. When the MA content is increased such that MA units occur increasingly in groups, then reaction (4) becomes significant and, by comparison with reaction (5), proves to be much faster than reaction (3). Although tertiary hydrogen atoms are undoubtedly more reactive in transfer processes than methylene hydrogen atoms, the very much higher concentration of the latter in the copolymers ensures that reaction (5) is predominantly a random process.

Although for any given copolymer the relative amounts of reactions (6) and (7) remain constant throughout the reaction, reaction (7) becomes relatively more important as the proportion of MA in the copolymer is increased. This is not surprising, since the principal permanent gaseous product, hydrogen, is to be expected from the MA units only, according to the mechanism proposed.

CHAPTER 5

PHOTODEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND METHYL ACRYLATE AT ELEVATED TEMPERATURES

INTRODUCTION

Recent publications (15,18,33) have demonstrated how the presence of the comonomers, acrylonitrile and methyl acrylate, influences the thermal degradation of poly(methyl methacrylate). In both systems the depolymerization reaction is initiated by random scission in the methyl methacrylate segments of the polymer chains. Like pure poly(methyl methacrylate) these copolymers also depolymerize at elevated temperatures under the influence of 2537 Å radiation. In the acrylonitrile polymer (16) however, the initiation process consists of chain scission specifically at acrylonitrile units, and the principal differences between the thermal and photo reaction have been accounted for in terms of the different sites of initiation and the influence of the temperature (280°C and 160°C for the thermal and photo reactions, respectively) and viscosity of the medium upon the relative rates of the subsequent constituent processes comprising the total reaction. In the present chapter the principal features of the photodegradation of the methyl methacrylate-methyl acrylate copolymer system are described and differences from the thermal reaction discussed.

EXPERIMENTAL

Copolymers

The four copolymers studied were those whose preparations have previously been described in chapters 3 and 4 (18,33). Their molar compositions are (MMA/MA) 112/1, 26/1, 7·7/1, 2/1.

Molecular Weights

Number-average molecular weights were measured by use of a Mechrolab high-speed membrane osmometer.

The amounts of material available for the measurement of molecular weights were of the order of only a few milligrams. Molecular weight measurements are therefore subject to considerable error and this accounts for the scatter of points in Figures 18 and 19.

Photodegradation Techniques

Photodegradations, except those involving the measurement of CO_2 produced, were carried out as previously described (16), the polymer (2-4 mg.), in the form of a thin transparent film, being irradiated in vacuo, through silica, by a source of 2 537 Å radiation.

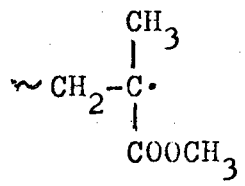
Because of the very small amounts of CO_2 involved it was found more convenient to make the CO_2 evolution measurements in the apparatus used for thermal studies with a suitably modified reaction vessel. The exit tube was situated at the side of the reaction vessel, being replaced at the top of the reaction vessel by a silica window through which the polymer was irradiated.

All product analyses were carried out exactly as described for the thermal reaction.

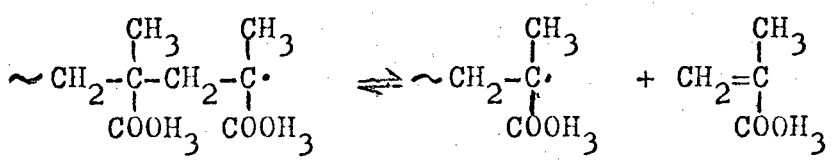
RESULTS

Influence of Temperature on Rate of Volatilization

The primary influence of ultraviolet radiation on poly (methyl methacrylate) is to cause chain scission, the radicals,



ultimately appearing in the system (37). The overall characteristics of the photolysis depends upon the subsequent reactions of these radicals, which in turn depends upon the temperature. At high temperatures, at which the polymer is in the liquid state, monomer produced in the equilibrium,



can easily escape, so that the reaction tends to the right and quantitative conversion to monomer occurs. On the other hand, at low temperatures when the polymer is in the form of a rigid solid, monomer can not readily escape, appreciable depolymerization does not occur, and the polymer radicals subsequently mutually destroy each other. At low temperatures, therefore, the photolysis is characterized by chain scission and at high temperatures by monomer production. It is the high-temperature reaction with which this chapter is concerned. Unfortunately, however, the range of temperature in which this reaction can be studied is restricted, the lower limit ($\simeq$150°C) being governed by the softening point of the polymer and the upper limit ($\simeq$200°C) by the onset of thermal degradation. Clearly, in this temperature range the viscosity of the polymer is changing rapidly with temperature, and since the viscosity could have a profound influence on the above equilibrium it is important to obtain some assessment of the influence of the viscosity on the overall reaction. The data in Figure 15 demonstrate that there is no significant change in the rate of photodegradation of PMMA in the temperature range 150-170°C. Since the reaction consists of photoinitiation followed by complete unzipping of the polymer chains the rate of the reaction should be governed by the rate of initiation and since photoinitiation should be associated with an activation energy close to zero, the constant rate is accounted for and in turn implies that there is no significant viscosity effect which should be expected to cause an increase in rate with temperature. In turn, it may be concluded that the increase in the rate of photodepolymerization of the two copolymers with temperature, illustrated in Figure 15, is not associated with a viscosity effect but is a direct manifestation of the modification of the overall reaction by the presence of the comonomer.

As a result of these experiments, 170°C was chosen as a suitable temperature for a general study of the reaction since an appreciable rate of reaction was obtained over the whole copolymer composition range without interference from thermal degradation. All subsequent data were obtained at this temperature and are summarized in Table 10. Chain scissions per molecule of polymer were calculated by using the formula

$$N = CL_o(1 - x)/CL - 1$$

in which CL_o and CL are the original chain length and the chain length at an extent of volatilization x, respectively. The number of chain scissions per unit length of chain, n, given by

$$n = N/CL_o = [(1 - x)/CL] - (1/CL_o)$$

must be used as a comparative measure of the extent of chain scission, however, since the copolymers have substantially different molecular weights.

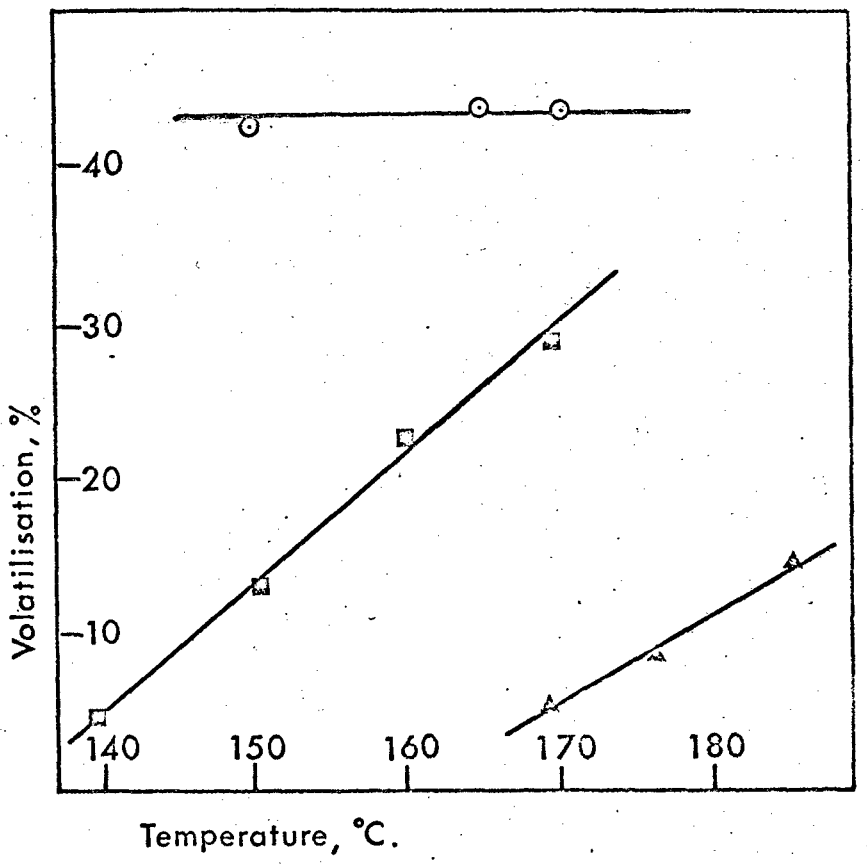


Figure 15. Extent of volatilization in 30 min at various temperatures: (o) poly(methyl methacrylate; (▣) methyl methacrylate-methyl acrylate copolymer (26/1); (▲) methyl methacrylate-methyl acrylate copolymer (7·7/1).

TABLE 10. Photodegradation Data Obtained at 170°C

Co-polymer	Time, min	Volatil-ization, %	MW of residue	Chain length of co-polymer (CL_o)	Scissions Per mole-cule (N)	Scissions Per chain unit ($n=N/CL_o$) x 10^4
112/1	0	0	600000	6000	0	0
	10	5·4	250000		1·27	2·11
	30	20·7	-		-	-
	60	41·4	237000		0·47	0·78
	90	53·6	-		-	-
	120	60·8	-		-	-
26/1	0	0	600000	6030	0	0
	5	1·7	376000		0·12	0·19
	15	4·0	248000		1·32	2·19
	23	13·4	229000		1·27	2·11
	30	30·4	172000		1·50	2·49
	45	34·2	180000		1·19	1·98
	60	36·2	145000		1·65	2·73
	90	46·2	118000		1·68	2·79
	120	54·0	125000		1·21	2·01
7·7/1	0	0	425000	4370	0	0
	5	1·5	411000		0·02	0·05
	15	2·9	321000		0·27	0·62
	23	4·4	181000		1·25	2·86
	30	5·2	263000		0·53	1·21
	45	16·2	168000		1·12	2·56
	65	20·3	144000		1·35	3·09
	75	22·3	157000		1·10	2·52
	90	27·8	150000		1·05	2·40
	120	29·8	140000		1·13	2·58
	300	40·0	81000		1·96	4·47
2/1	0	0	370000	3880	0	0
	30	1·75	149000		1·46	3·76
	60	5·8	78000		3·08	7·95
	150	13·9	49000		5·52	14·22
	300	28·2	45000		4·91	12·65
	600	39·6	47000		3·75	9·65

Molecular Weight Changes

The changes in molecular weight which occur during photodegradation are related to the extent of volatilization in Figure 16. Like the results of thermal degradation they are characteristic of a reaction in which random chain scission

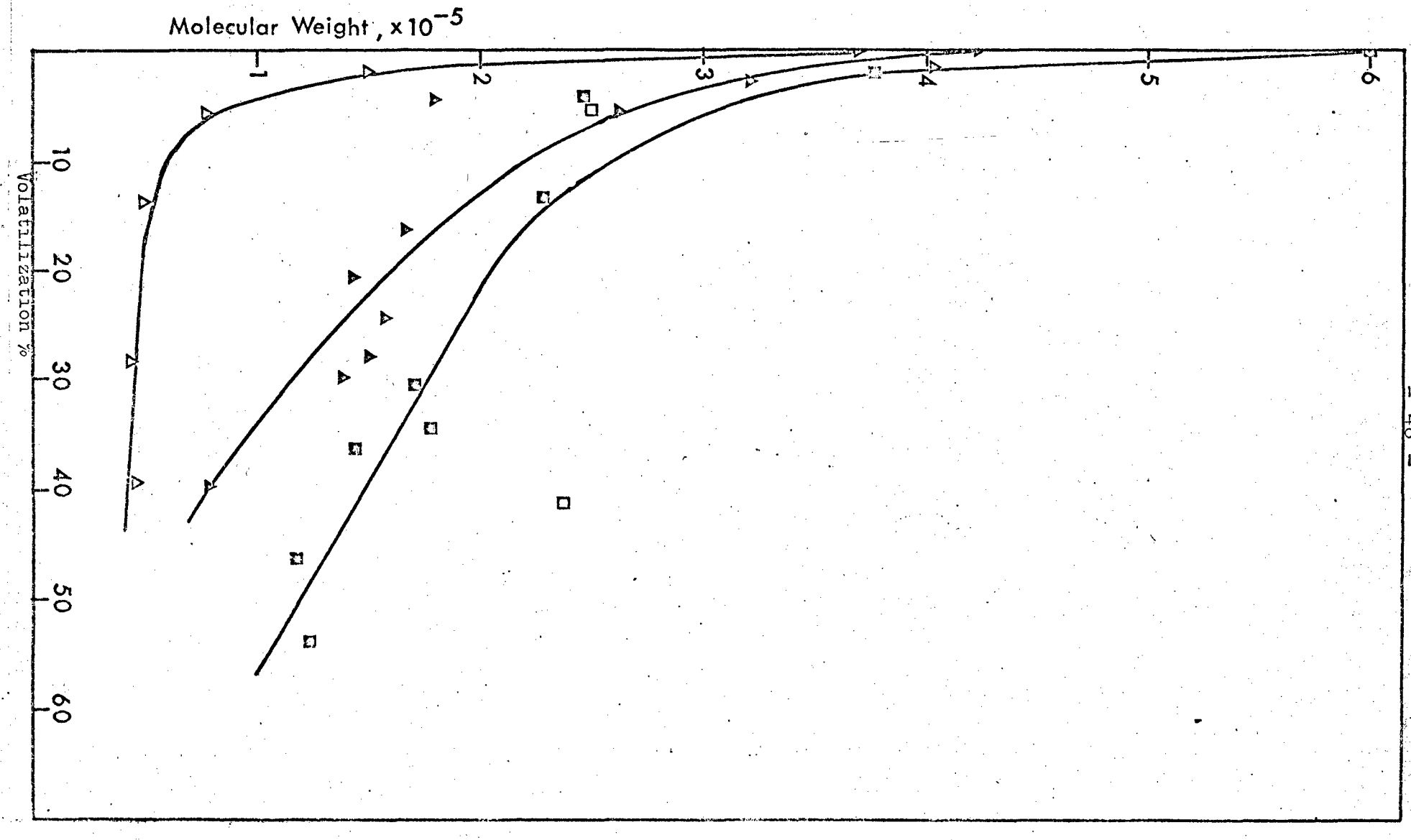


Figure 16. Change in molecular weight with volatilization for photodegradation of methyl methacrylate-methyl acrylate copolymers at 170°C: (□) 112/1; (■) 26/1; (◬) 7·7/1; (△) 2/1.

is involved. Even in the 2/1 copolymers there is no direct evidence of the crosslinking which is typical of poly(methyl acrylate), the residual material being completely soluble in all cases.

Volatile Products of Degradation

The pattern of volatile products is closely comparable with that produced in the thermal reaction. The only significant difference concerns the ratio of the monomers. The gas-liquid chromatographic analysis of the monomer fractions are presented in Table 11, from which it is clear that approximately one in ten of the MA units is liberated as monomer, compared with one in four in the thermal reaction.

TABLE 11. Molar Composition of Monomeric Products (MMA/MA)

Copolymer	Products
112/1	1000/1
26/1	320/1
7·7/1	80/1

Rates of Volatilization

Volatilization versus time curves for the four copolymers and PMMA are compared in Figure 17. It is obvious that, as in the thermal reaction, increasing concentrations of MA increasingly stabilize the copolymers.

Chain Scission and the Production of Carbon Dioxide

The data in Table 12 summarize the results of experiments designed to determine the relationship between chain scissions and CO_2 production.

TABLE 12. Chain Scission and the Production of Carbon Dioxide

Copolymer	Temp. °C	Volatilization, %	MW of residue	Scissions/molecule	CO_2/molecule	CO_2/scission
26/1	160	11·6	244,000	1·062	4·84	4·5
	170	11·5	292,000	0·82	4·46	5·4
7·7/1	170	24·8	118,000	1·71	5·15	3·0
	170	46·2	70,000	2·26	10·6	4·7
2/1	170	7·4	75,000	3·57	7·47	2·1

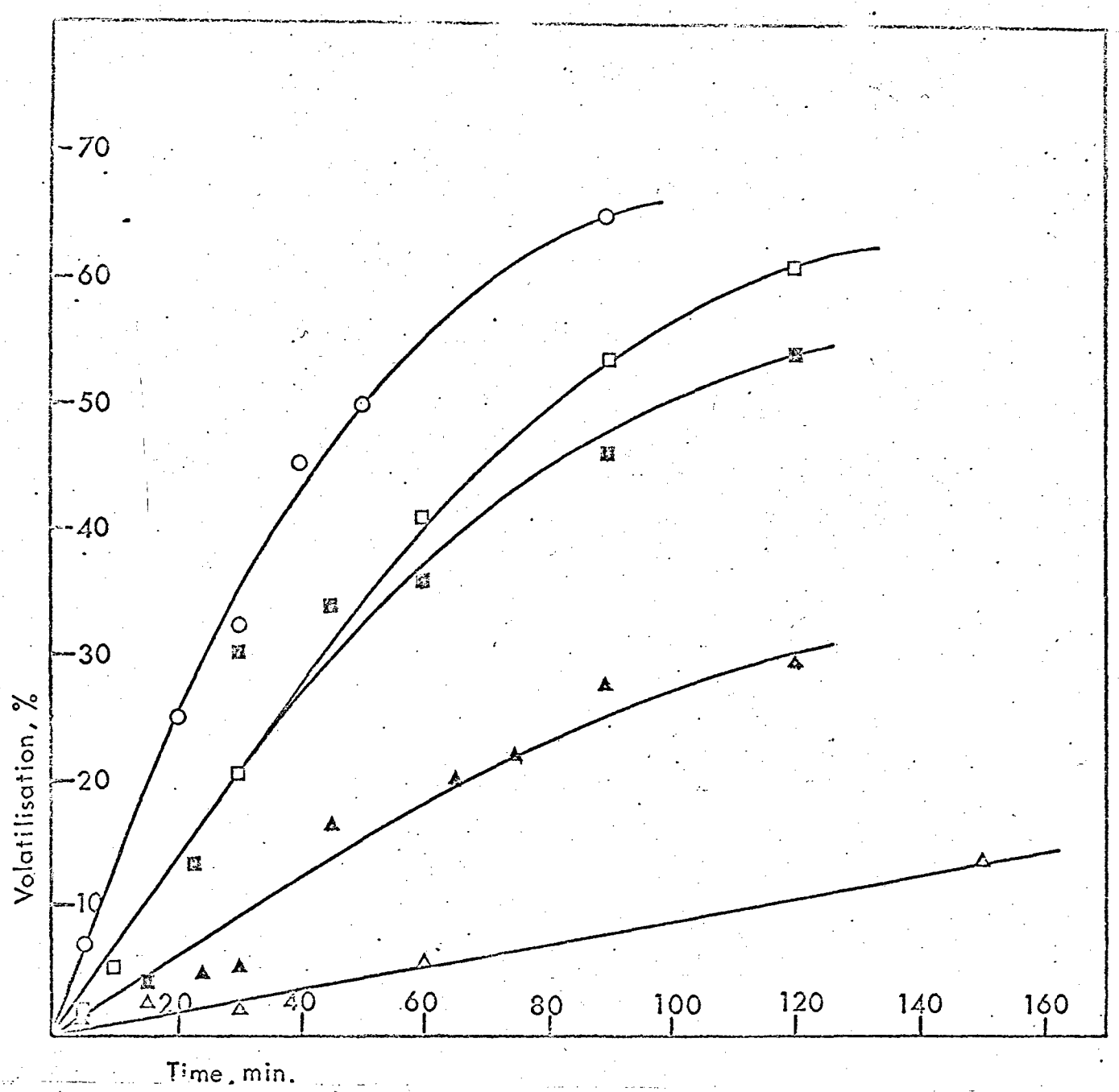


Figure 17. Volatilization-time curves for the photodegradation of poly(methyl methacrylate) and methyl methacrylate-methyl acrylate copolymers at 170°C: (o) PMMA; (□) MMA/MA, 112/1; (⊠) MMA/MA, 26/1; (▲) MMA/MA, 7·7/1; (△) MMA/MA, 2/1.

In the thermal reaction a strict 1/1 ratio was found throughout the polymer composition range which made it possible to use CO_2 production as a direct measure of chain scission. A mechanism for chain scission was proposed which accounted for these experimental observations. From the data in Table 12 it is clear that the CO_2/chain scission ratio is considerably greater than unity in the photo reaction. There appears to be some tendency for the ratio to fall as the MA content of the copolymer is increased, but the very small amounts of material available make it difficult to obtain values of molecular weight of sufficient accuracy to study the effect with high precision.

Chain Scission and Volatilization

The relationship between chain scission and volatilization is illustrated in Figure 18, the data in Table 10 being used. Once again, the scatter of the experimental points can be attributed to the difficulty of obtaining accurate values of molecular weight, but, taken as a whole, the results are best interpreted as demonstrating a linear relationship as represented in the figure. Thus it may be concluded that, as in the thermal reaction, radicals are formed as a direct result of chain scission and that volatilization occurs by depolymerization of these radicals. Zip lengths may be calculated as in Table 13, and the values are seen to be very much greater than those observed in the thermal reaction which are presented in the last column of Table 13. However, as before, blockage of the depropagation reaction by the MA units is clearly occurring, since zip lengths decrease with increasing MA content.

TABLE 13. Zip Lengths for Depolymerization

Co-polymer	Slope (Fig.18) A, % volatilization scission/molecule	MW	MW lost/ scission (MW x A)	Average wt. of monomer unit (B)	Zip Length	
					MW x A/B	Thermal
26/1	22	600,000	132,000	99·5	1327	74
7·7/1	17	425,000	72,000	97·2	741	74
2/1	5·5	370,000	20,300	95·3	214	34

Chain Scission and Copolymer Composition

The time dependence of chain scission for the four copolymers is represented in Figure 19. There is no clear trend with copolymer composition, and all the experimental points may be reasonably represented by a single straight line. Thus the rate of chain scission is independent of the MA content of the polymer.

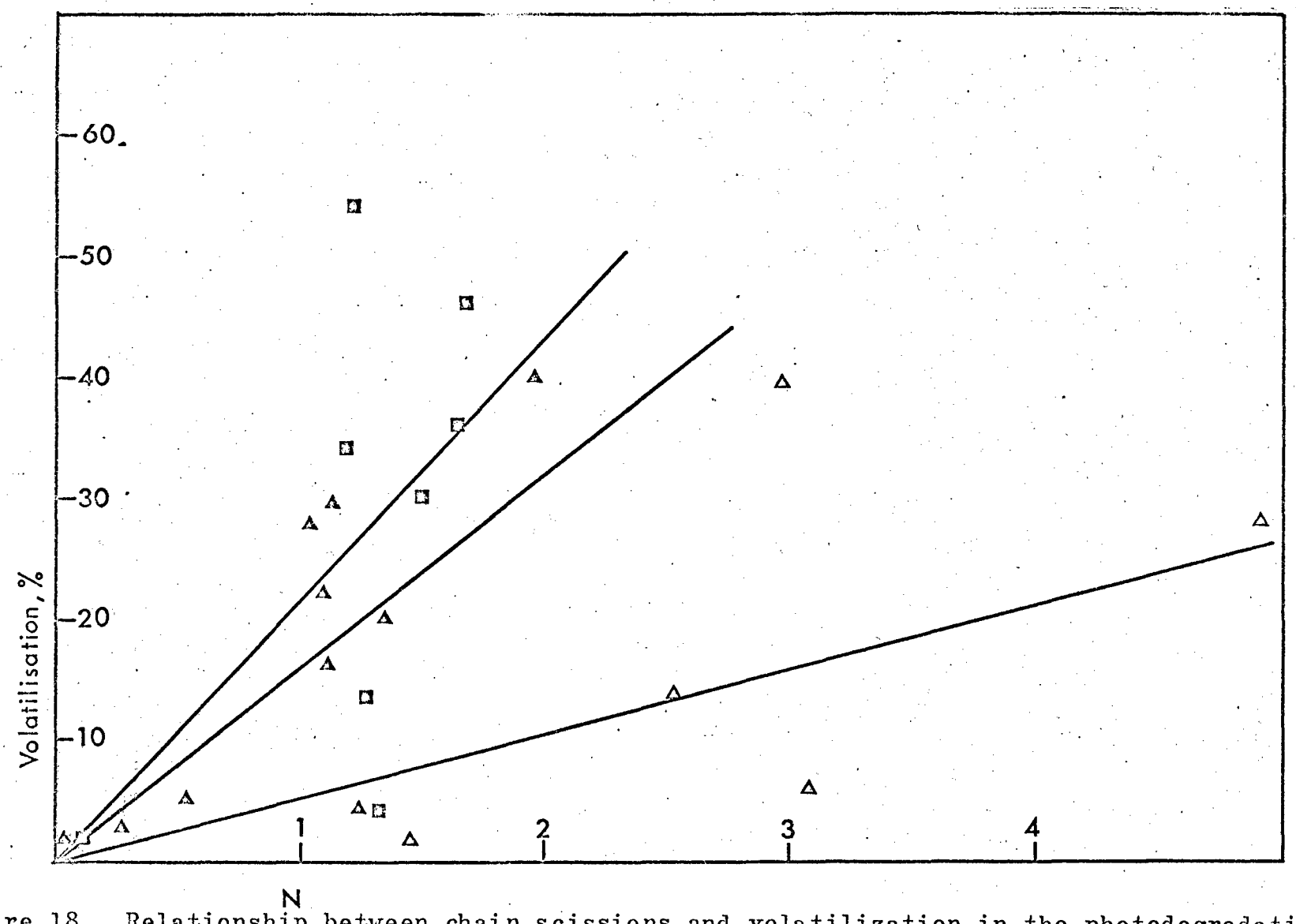


Figure 18. Relationship between chain scissions and volatilization in the photodegradation of methyl methacrylate-methyl acrylate copolymers at 170°C: (⊡) 26/1; (▲) 7·7/1; (△) 2/1.

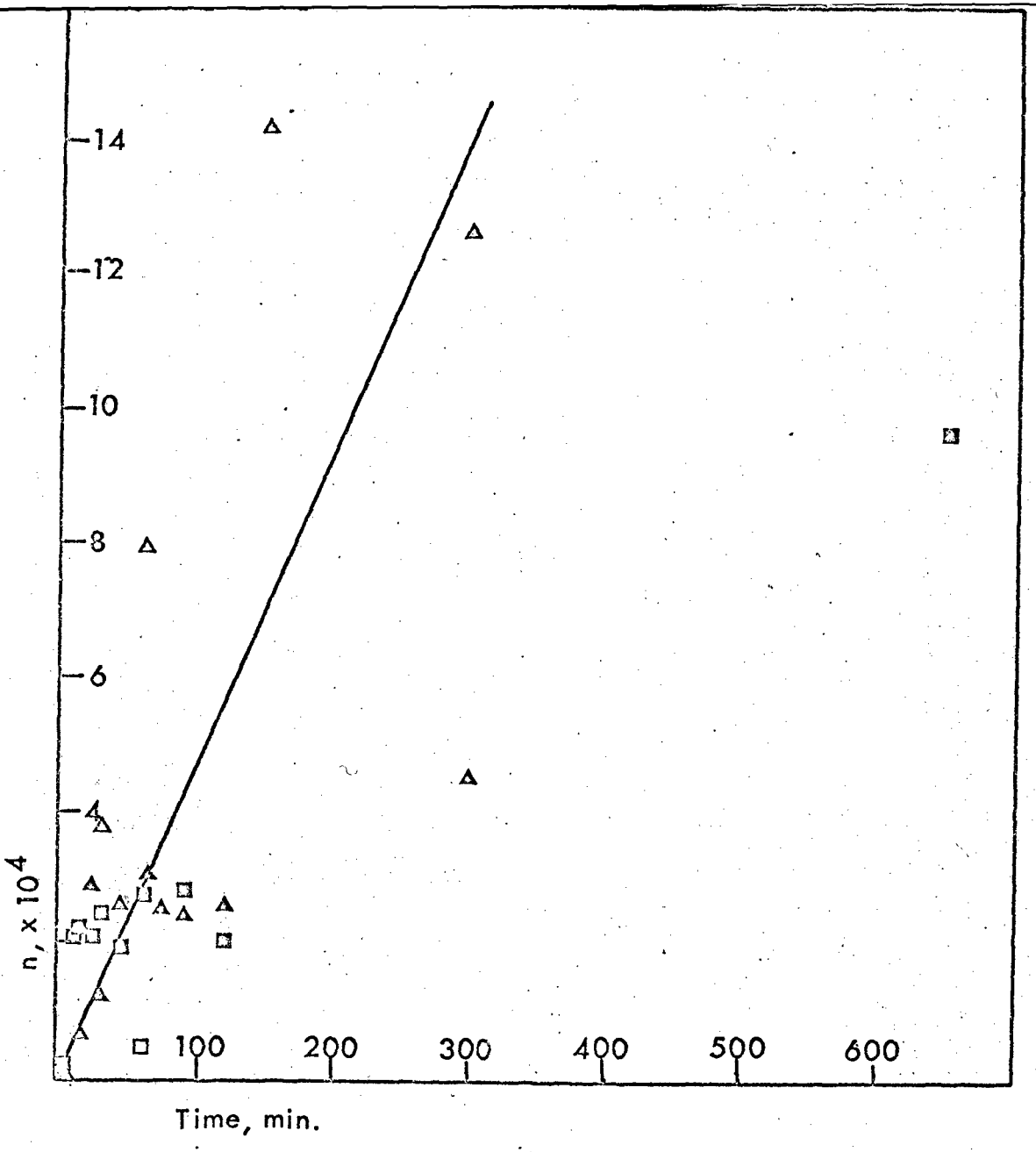


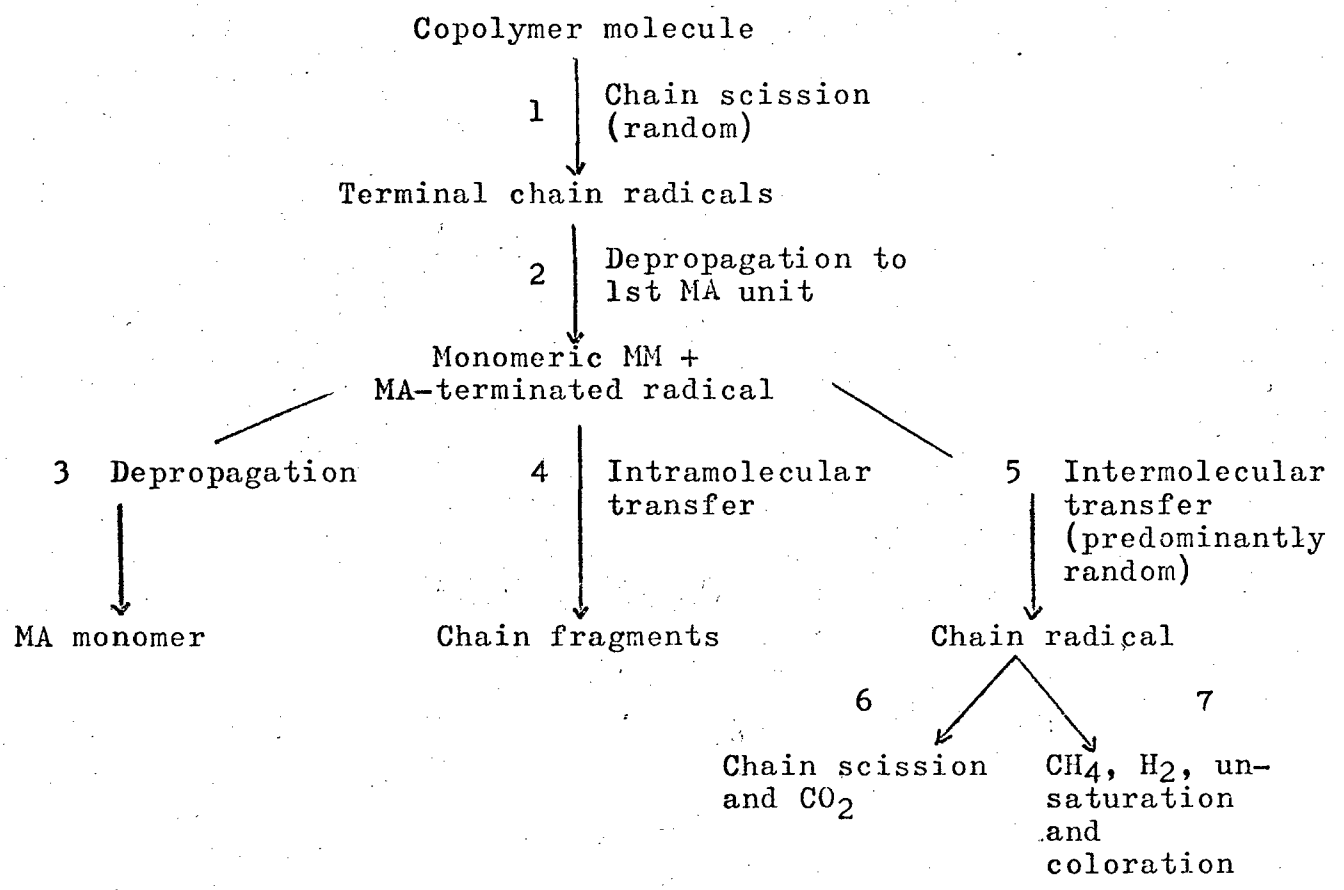
Figure 19. Time dependence of chain scission in the photodegradation of methyl methacrylate-methyl acrylate copolymers at 170°C: (□) 112/1; (▣) 26/1; (▲) 7·7/1; (△) 2/1.

DISCUSSION

Figure 16 demonstrates that the photolysis of MMA/MA copolymers at elevated temperatures involves the successive scissioning of the chain. Although the data in Figure 19 are of limited reliability, it is clear that the rate of chain scission is not strongly dependent upon MA content and thus that the scission reaction does not occur preferentially at MA units but rather at random. Since the rate of volatilization is progressively retarded by increasing MA content, it may be deduced that MA units block the monomer producing depropagation process. This blocking action is not complete, however, since small amounts of MA monomer do appear among the volatile products. In all these aspects the photo reaction is identical with the thermal reaction.

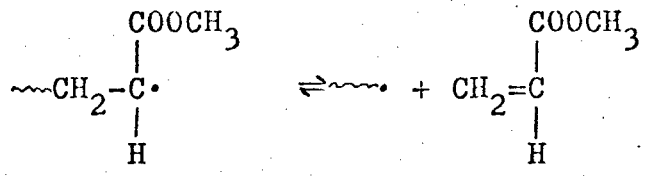
There are, however, some well defined differences between the two processes and the following are probably the most significant. Firstly, the zip length in the photo reaction is very much greater than in the thermal reaction. Secondly, the strict 1/1 ratio between CO_2 molecules produced and chain scissions in the thermal reaction does not apply to the photo reaction. In this case a very much higher proportion of CO_2 appears. Thirdly, a very much smaller proportion of the MA is liberated as monomer in the photo reaction - 1 in 10 units compared with 1 in 4 in the thermal reaction.

The reaction mechanism shown in Scheme I was presented previously to account for the principal features of the thermal reaction. The minor differences mentioned above between the thermal and photo reactions can be accounted for in terms of this mechanism bearing in mind the differences in the temperatures at which the two reactions were studied. These were 170°C and approximately 300°C for the photo and thermal reactions, respectively. In the present instance this difference in temperature may manifest itself through the direct influence of temperature on the relative rates of constituent reactions or these relative rates may be even more strongly influenced by the very great difference in the viscosity of the medium at the two temperatures. At 170°C the polymer is in the form of a highly viscous mass, while at 300° it is a relatively mobile liquid.

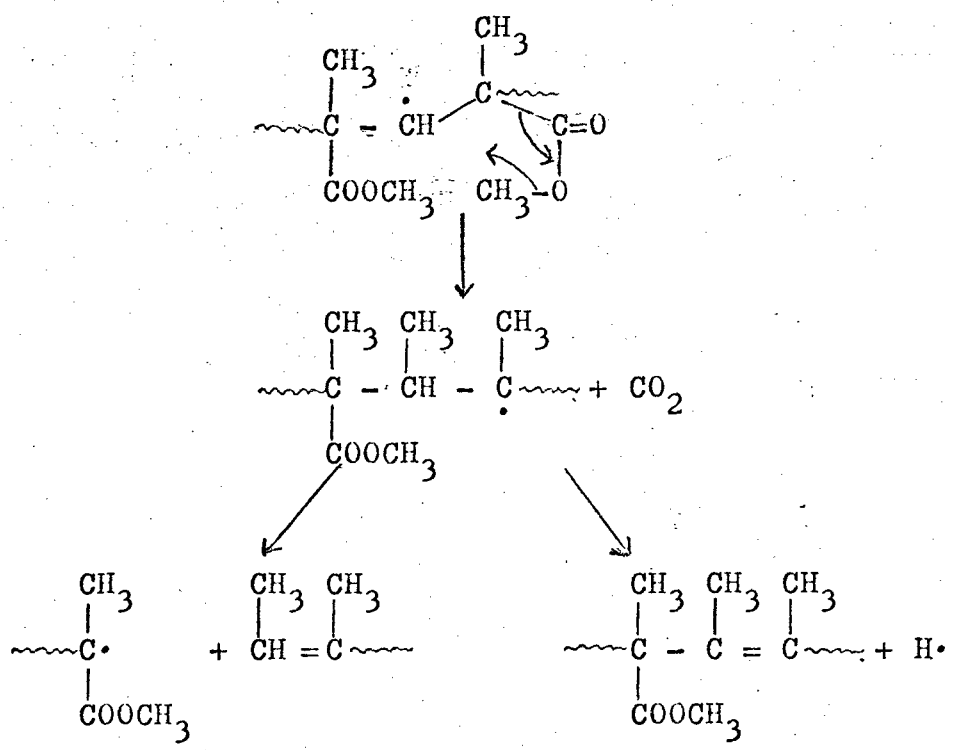


Scheme I.

Thus the greater zip length in the photo reaction can be accounted for by the fact that the more viscous medium, by suppressing thermal motion, should be expected to favour intramolecular transfer [reaction (4)] at the expense of intermolecular transfer [reaction (5)]. On the other hand, the greater CO_2/chain scission ratio in the photo reaction may result from the higher viscosity, favouring reaction (7) at the expense of reaction (6). These may be represented in more detail as shown in Scheme II, and the lower molecular mobility at the temperature of the photo reaction should be expected to favour separation of a mobile hydrogen atom at the expense of the diffusion apart of two long chain species. Finally the smaller relative amount of monomeric MA produced at the lower temperature may be a measure of the direct relative influence of temperature on reactions (3) and (4). Alternatively it may result from the greater viscosity of the medium inhibiting diffusion from the site of the reaction of monomer produced in depropagation. This would favour the back-reaction in the equilibrium,



and thus in turn favour reaction (4) at the expense of reaction (3).



Scheme II

CHAPTER 6

THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE.
A. EXPERIMENTAL METHODS.

SYNTHESIS OF COPOLYMERS

Methyl methacrylate (B.D.H. Ltd.), n-butyl acrylate (Koch-Light Laboratories Ltd.) and the initiator, 2,2'azoisobutyronitrile were purified, using the method described in chapter 3. The initiator concentration used was 0·17% weight/volume.

The volume of each of the comonomers required to obtain a copolymer of a given composition was calculated using the values of the reactivity ratios obtained as in chapter 2, namely, 1·8 for methyl methacrylate and 0·37 for n-butyl acrylate. These calculated volumes were then distilled under vacuum into a dilatometer containing the appropriate amount of initiator.

Polymerizations were carried out in bulk at 60°C to a maximum of 8% conversion. With copolymers of high acrylate content only 3 or 4% conversion could be reached because of the high viscosity of the reaction mixture. The contents of the dilatometers were then dissolved in Analar toluene and the copolymer precipitated by addition to excess Analar methanol. The copolymer was filtered and dried under vacuum. This procedure was repeated three times. Those polymers with a high methacrylate content precipitated as a fine powder, while acrylate rich samples came down as rubbery solids. All of the copolymers were finally freeze-dried from benzene solution.

In addition to seven copolymers covering the whole composition range, a methyl methacrylate homopolymer was synthesised. Homopolymers of n-butyl acrylate were also available so that it was possible to examine the degradative behaviour of the entire composition range.

Copolymer composition and molecular weight data are summarised in table 14.

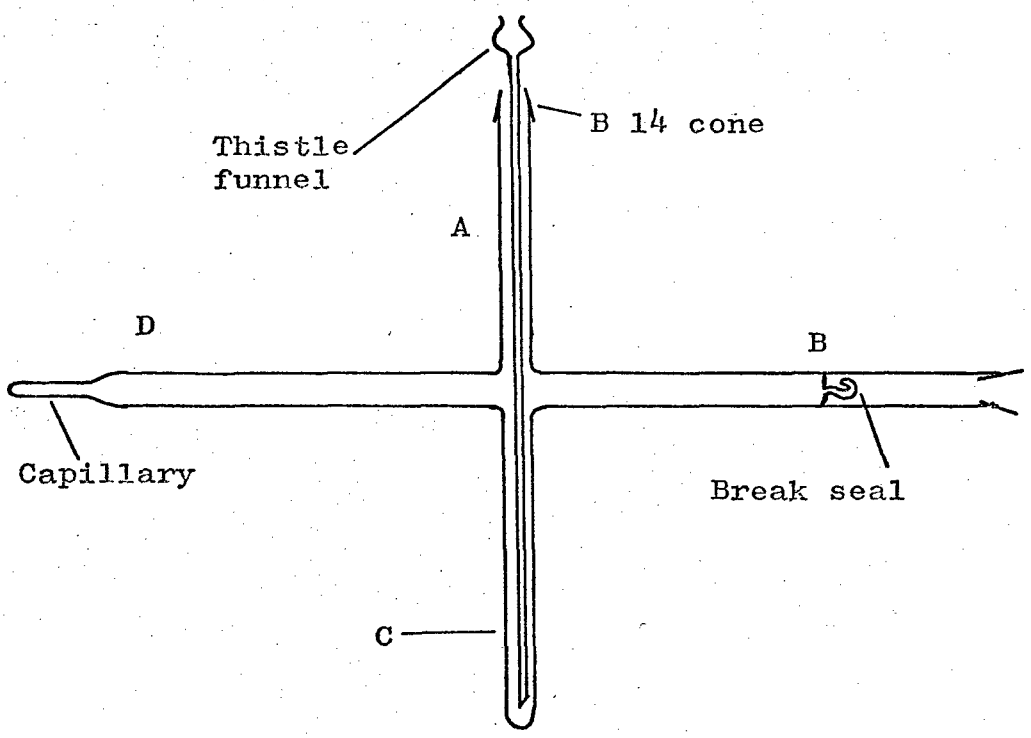
TABLE 14. Copolymer Composition and Molecular Weight Data

Composition (mole percent n-butyl acrylate)	Number Average Molecular Weight, $\bar{M}_n$
0	421,000
0·4	361,000
3·9	337,000
16·3	422,000
50·0	100,000
52·4	1,330,000
82·2	52,500
93·4	76,500

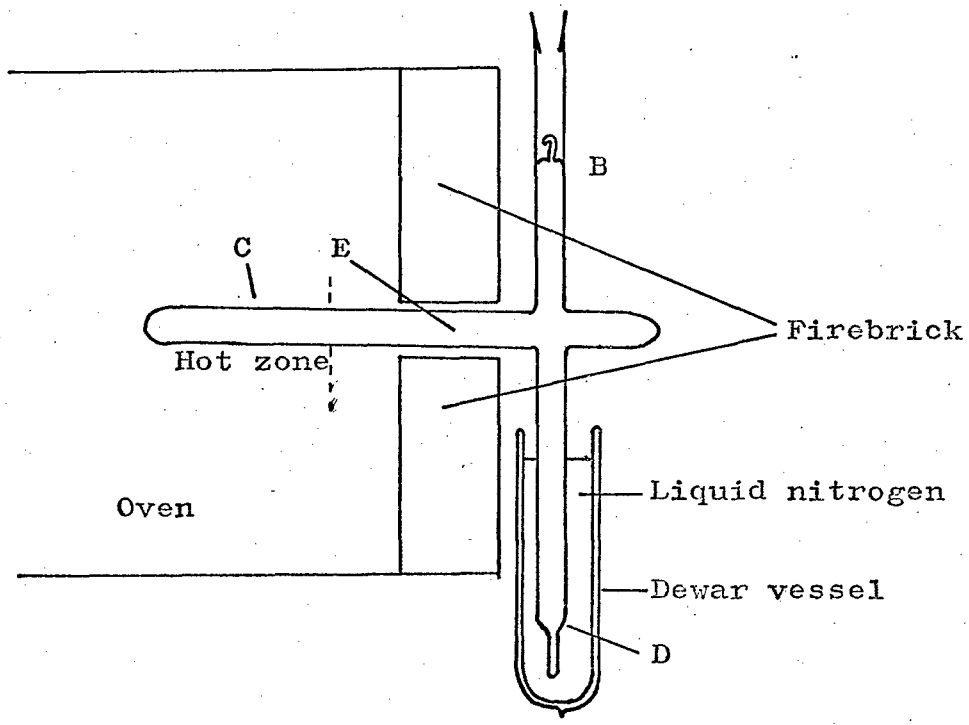
DEGRADATION APPARATUS

During this investigation two types of degradation apparatus were used namely the glass still which has already been described in Chapter 2 and the sealed tube.

The sealed tube is illustrated in figure 20. Copolymer solutions in Analar toluene (50 mg. per ml.) were pipetted into limb C. The toluene was removed under vacuum so that a film of copolymer was deposited on the walls of the tube at C. When all the solvent had been removed the tube was sealed off at A under sticking vacuum. Limb C was then placed in an oven at the required degradation temperature, while limb D was immersed in liquid nitrogen. Degradation products leaving the hot zone condensed either on the part of the tube passing through the furnace firebrick E or in limb D depending upon their volatility. When the degradation had proceeded for the required time, the sealed tube was removed from the furnace and stored at -18°C until required. The oven was a Catterson-Smith G31LX Electric Furnace controlled by an Ether Transitrol Controller, and its temperature could be maintained to ±1°C. This temperature was monitored throughout the degradation by a thermocouple sealed into an evacuated tube similar to the one containing the polymer sample and placed symmetrically with respect to it within the furnace. The thermocouple output was fed into a Honeywell Brown recorder so that any deviation of the furnace temperature from that required could be quickly noted and rectified.



(a) Filling sealed tube.



(b) Degradation by the sealed tube technique.

Figure 20. The sealed tube technique.

The sample size was normally in the range 100 to 500 mg, but when analysis of the small amount of permanent gases evolved was required, much larger samples, up to 1·5 g., were necessary. The fact that only small amounts of non-condensable material is produced renders invalid one criticism often levelled at degradation systems which are not continuously pumped, namely that diffusion of degradation products from the hot zone is inhibited by the increase in pressure in the system thus encouraging secondary reactions to take place. The sealed tube technique is particularly useful when the examination of decomposition products, including chain fragments, is to be carried out.

PRODUCT ANALYSIS

In this work the terms "gaseous products" and "gases" mean gases condensable at liquid nitrogen temperature, and do not normally include the permanent gases, which were found to be present in only very small quantities.

For the analysis of degradation products the sealed tube containing degraded polymer is attached to a vacuum line at B, and the capillary on limb D, in which the liquid degradation products have collected, is cooled in an ice-water bath. The break seal is then broken using a glass covered metal weight, and the gaseous decomposition products distilled for exactly one minute into a suitable receiver cooled in liquid nitrogen. The normal procedure followed was to distil the gases firstly into a constant volume manometer to make pressure measurements. From there they were distilled into an infra-red gas cell and then, a spectrum having been run, they were sealed in a glass sample vessel. This container was fitted with a break seal to enable the gases to be withdrawn for further examination if required, while avoiding the possibility of leaks or of the contents being absorbed on tap grease.

To obtain samples of the permanent gases produced in degradation a different procedure was used. The capillary part of the sealed tube was immersed in liquid nitrogen and the products remaining gaseous were collected in a sample bulb using a Topler pump.

The residue, chain fragments and liquid volatiles were separated by cutting the sealed tube in the appropriate places as they all collected in different parts, C, E and D

respectively (Fig. 20). The liquids were weighed, transferred to a suitable container by a Pasteur pipette, and stored at -18°C until required.

PRESSURE MEASUREMENT

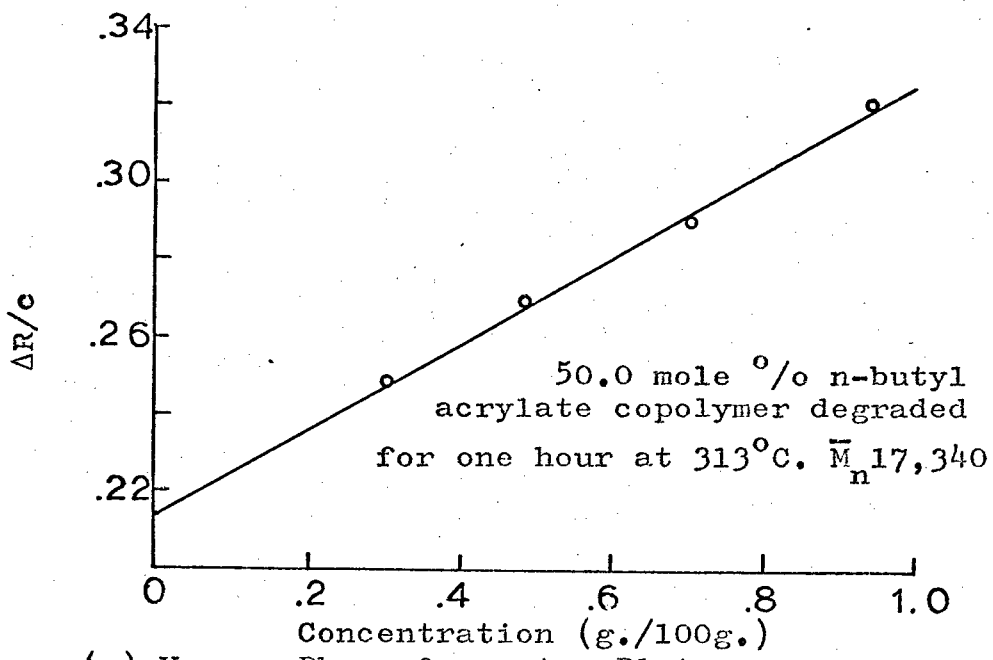
Two pressure measuring devices, a constant volume manometer and a McLeod gauge suitable for use in different pressure ranges were used in this work. When data on gas evolution at low percentage conversions were required, as in the investigation of the relationship between carbon dioxide production and chain scission, involving measurement of pressures of the order of 10^{-2}cm. the McLeod gauge was used. On the other hand, when polymers were degraded to higher conversions so that the pressures attained were of the order of several centimetres, use of the constant volume manometer was indicated.

MOLECULAR WEIGHT MEASUREMENTS

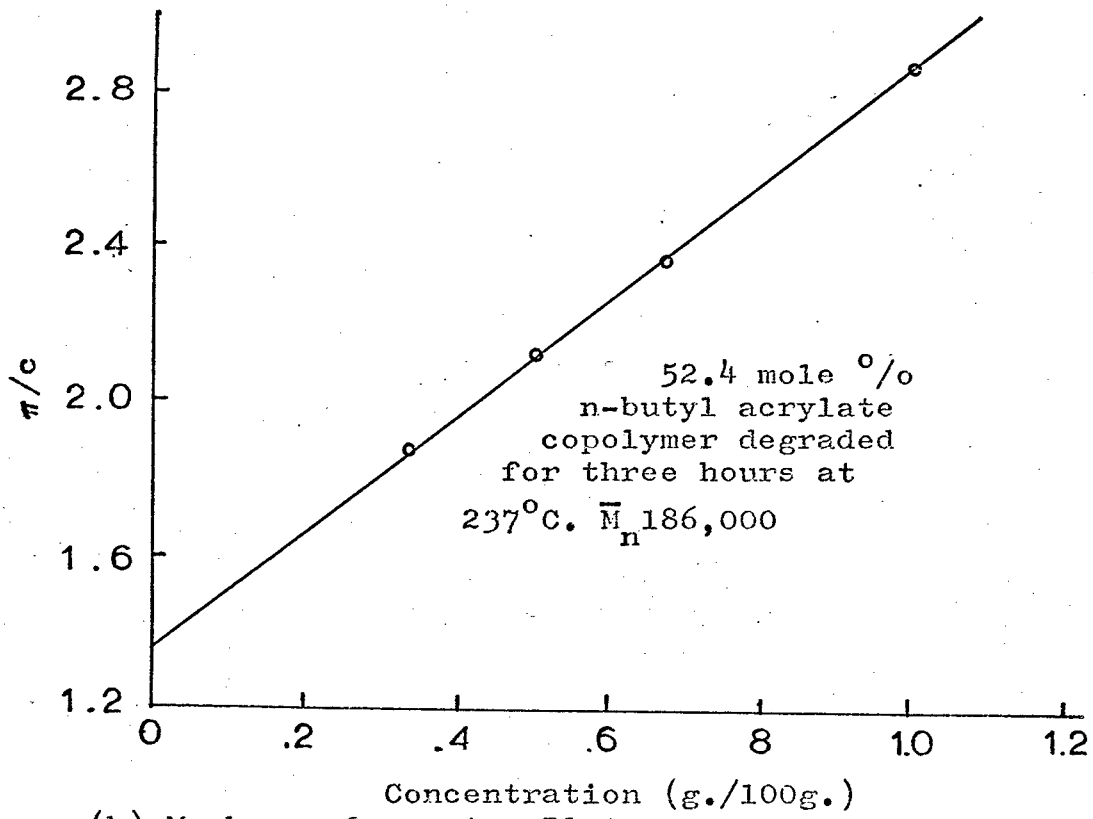
A model 301A Vapor Pressure Osmometer (Mechrolab Inc.) was used for the measurement of molecular weights up to 20,000. For the measurement of higher molecular weights the Mechrolab 501 High Speed Membrane Osmometer was used. Typical vapour pressure and osmotic pressure plots are illustrated in figure 21.

THERMAL METHODS OF ANALYSIS

The thermal volatilization analysis (T.V.A.) technique which was mentioned in chapter 3 was devised by McNeill (21). It measures the thermal conductivity of the volatile material evolved from a heated polymer sample which is being continuously pumped. The differential condensation T.V.A. apparatus (D.C.T.V.A.) (Fig. 22) is a modification of the original equipment which employs a series of traps maintained at different temperatures. After each trap is placed a Pirani gauge which measures the transient pressure of material not condensed by that particular trap. The Pirani outputs are fed into a multipoint recorder so that the traces produced are of Pirani response, which is a measure of the rate of volatilization, against time. The trace obtained gives an indication of the volatilities of the various products as well as the temperature at which they are produced.

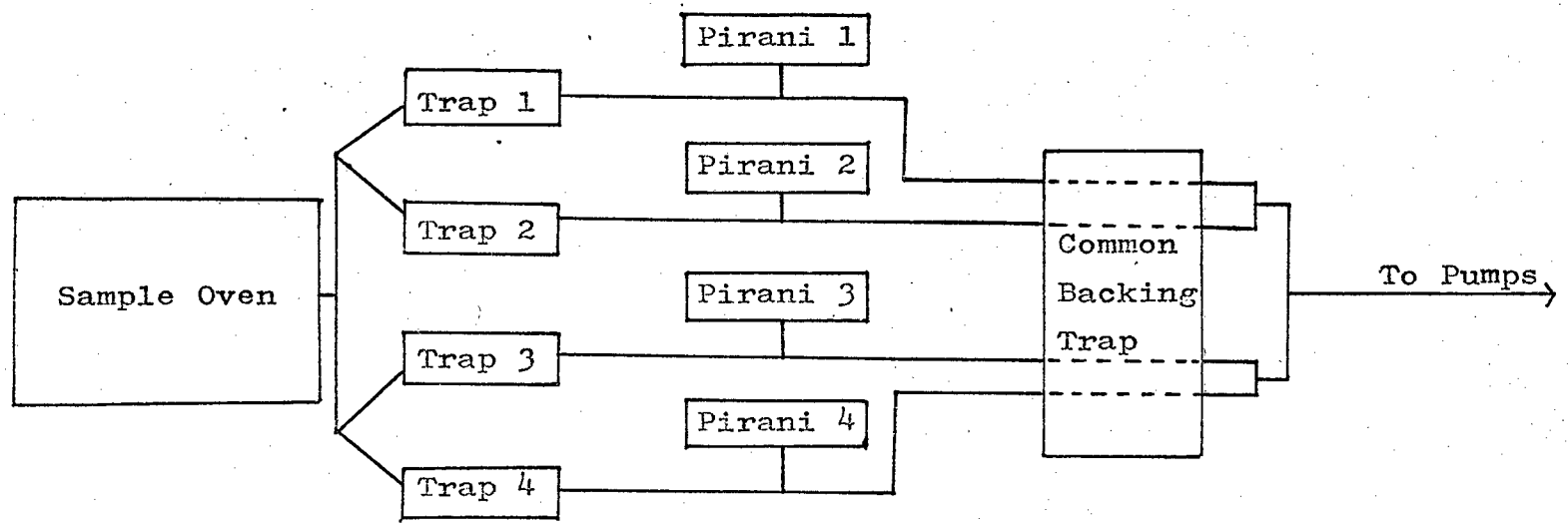


(a) Vapour Phase Osmometer Plot.



(b) Membrane Osmometer Plot.

Figure 21. Molecular weight plots.



Normal working temperatures :- Trap 1 -100°C
Trap 2 -75°C
Trap 3 -45°C
Trap 4 0°C

Figure 22. Schematic Diagram of the Differential Condensation T.V.A.(D.C.T.V.A.)

A separate temperature versus time trace is also recorded so that when a linear temperature programme is used, as is normal practice, any deviations of the heating rate from linearity may be checked.

For thermogravimetric analyses the DuPont 950 instrument was used.

GAS-LIQUID CHROMATOGRAPHY

For the most part g.l.c. data were obtained using a Microtek G.C.2,000R Research Gas Chromatograph equipped with a flame ionization detector. Since gases such as carbon monoxide and hydrogen cannot be detected by such flame ionization devices, analysis of the permanent gas fraction was carried out on a modified Gallenkamp chromatograph which had a thermal conductivity detector. A list of the columns employed and the conditions under which they were used is given in table 15

TABLE 15. G.L.C. Columns used for Investigation of Degradation Products

Column	Programme	Use	Detector
10 ft. ¼ inch diameter, 30-60 mesh silica gel	Isothermal at 40°C for 3 mins., then programme at 5°C/min. to 250°C.	General gas column.	Flame ionization
24 ft. 1/8 inch diameter 40% benzyl cyanide-silver nitrate	Isothermal at room temperature	Separation of C_4 olefins.	Flame ionization
20 ft. ¼ inch diameter, 30-60 mesh silica gel	Isothermal at room temperature	Permanent gas investigation	Thermal conductivity
10 ft. ¼ inch diameter, 1% S.E.30 on 100-120 mesh embacel. (S.E.30 is a silicone gum)	Isothermal for 6 mins. at 40°C, then programme at 5°C/min. to 250°C.	Liquid volatiles and short chain fragments.	Flame ionization
10 ft. ¼ inch diameter, 10% di-nonyl phthalate on 100-120 mesh embacel	Isothermal at 80°C	Liquid volatiles.	Flame ionization

Quantitative measurements were made on the liquid volatiles by adding a known weight of a suitable material as internal standard to a weighed quantity of liquid products. Several mixtures of pure samples of each of the products were made up with known amounts of the internal standard and run on the chromatograph to determine the sensitivities of the product compounds relative to the standard. Measurement of peak areas on g.l.c. traces was carried out by planimetry since the peak area for a particular substance is proportional to the weight present. If the sensitivity factor, k, for any product Y is defined as the ratio of the peak areas of product to standard when equal weights of both are considered, then the percentage by weight of Y in G grams of sample is given by:

$$\% \text{ Y} = \left(\frac{\text{peak area of Y}}{\text{peak area of standard}}\right)\left(\frac{100}{\text{G/weight of standard}}\right)\left(\frac{1}{k}\right)$$

A similar procedure was followed to determine the amounts of the various gases present, mixtures being made up by pressure rather than by weight, but as no internal standard was used in these cases, only relative rather than absolute measurements were possible.

MASS SPECTROMETRY

Mass spectra were run on an A.E.I. M.S.12 Mass Spectrometer and combined gas chromatography-mass spectrometry on an L.K.B. 9,000 A instrument.

Before examining the liquid degradation products on the combined instrument they were fractionated in order to remove high molecular weight materials which would contaminate the apparatus. This was done by distillation under high vacuum from a container at room temperature to a receiver cooled in liquid nitrogen.

A 10 ft. quarter inch diameter 1% S.E.30 column was used for the separation of the liquid products, run isothermally at 50°C.

SPECTROSCOPIC MEASUREMENTS

Infra-red spectra were obtained on a Perkin Elmer 257 Grating Infra-red Spectrophotometer. Prior to making any

measurements of gaseous products the infra-red detector was flushed with nitrogen so that quantitative analysis of the carbon dioxide present would not be interfered with by the presence of this gas in the atmosphere. Known pressures of pure samples of each of the product gases were measured by using the constant volume manometer, and infra-red spectra obtained over a wide pressure range. The optical density of the appropriate peaks was then plotted against pressure of the pure gas so that these traces could be used to determine the composition of the gaseous products of polymer breakdown.

A Unicam SP 800 Spectrophotometer was used for the measurement of u.v. visible spectra.

N.M.R. spectra were obtained on a Perkin Elmer R 10 60 Mc/s spectrometer, in carbon tetrachloride solution.

SOL-GEL ANALYSIS

The material remaining when copolymers of methyl methacrylate and n-butyl acrylate of high acrylate content, or homopolymers of n-butyl acrylate itself, are degraded is not completely soluble in organic solvents such as benzene in which they could be dissolved before decomposition. Sol-gel analysis was carried out on this residue using a Soxhlet extractor. Degradations were carried out by the sealed tube technique after which the portion of the tube containing residue was cut into short sections about one inch long. These were weighed and placed in a weighed glass sinter of porosity three. The whole assembly was then positioned in a Soxhlet extractor such that the solvent could wash, and drain easily from, every piece of the tube. Analar benzene was used as solvent and the extraction continued for a standard time of twenty hours. At the end of this time the tube pieces and glass sinter were removed, drained for a few minutes, then dried in a vacuum oven at 60°C for three hours, after which they were allowed to cool and were reweighed. The difference in weight of the sinter, ΔS, gives the weight of any insoluble material trapped, while the difference in weight of the tube pieces, ΔP, less ΔS, gives the weight of soluble residue. This latter weight was also determined by distilling off benzene from the solvent reservoir after extraction, and determining the concentration of a known volume of this solution. The sealed tube sections were immersed in soap solution overnight, cleaned of all insoluble material, dried and reweighed. The difference in weight

before and after this last operation, ΔQ, when added to ΔS is the weight of the insoluble residue. Thus the total weight of residue, the weight of soluble residue and the weight of insoluble residue have been found and are given by $(\Delta P+\Delta Q)$, $(\Delta P-\Delta S)$, and $(\Delta Q+\Delta S)$ respectively.

CHAPTER 7

THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. B. THERMAL ANALYSIS

INTRODUCTION

The techniques dealt with in this chapter may be generally applied to a polymer as a preliminary to a thorough investigation of its breakdown. From the results of such investigations an overall picture of the decomposition pattern of the n-butyl acrylate-methyl methacrylate copolymers was obtained and a temperature range selected in which to examine their degradation in some detail under isothermal conditions.

THERMAL VOLATILIZATION ANALYSIS

Collection of T.V.A. Data

All samples were run as films cast from 1 ml. of a 50 mg./ml. Analar toluene solution and heated at 10°C/min. from ambient to 500°C. The traces obtained are shown in Figs. 23-30 and the temperatures at which rate maxima occur are listed in Table 16.

It is clear that the position of the lowest temperature peak (A) is independent of the n-butyl acrylate content of the copolymer and that it decreases in size relative to the main peak (B) as the acrylate content of the copolymer increases, becoming a point of inflection when the acrylate content is 16·3 mole percent and disappearing altogether at 50 mole percent n-butyl acrylate. This low temperature peak may be ascribed to the products of depolymerization from unsaturated methacrylate chain end structures (22,38).

The second and main peak (B) moves to higher temperatures as the n-butyl acrylate content of the copolymer is increased. It is associated with depolymerization initiated by random scission of the main polymer chain.

The position of peak (C) appears to be composition independent but it is difficult to locate the exact position of this peak maximum for some of the copolymer samples. This peak is due to materials not condensable at -100°C in a

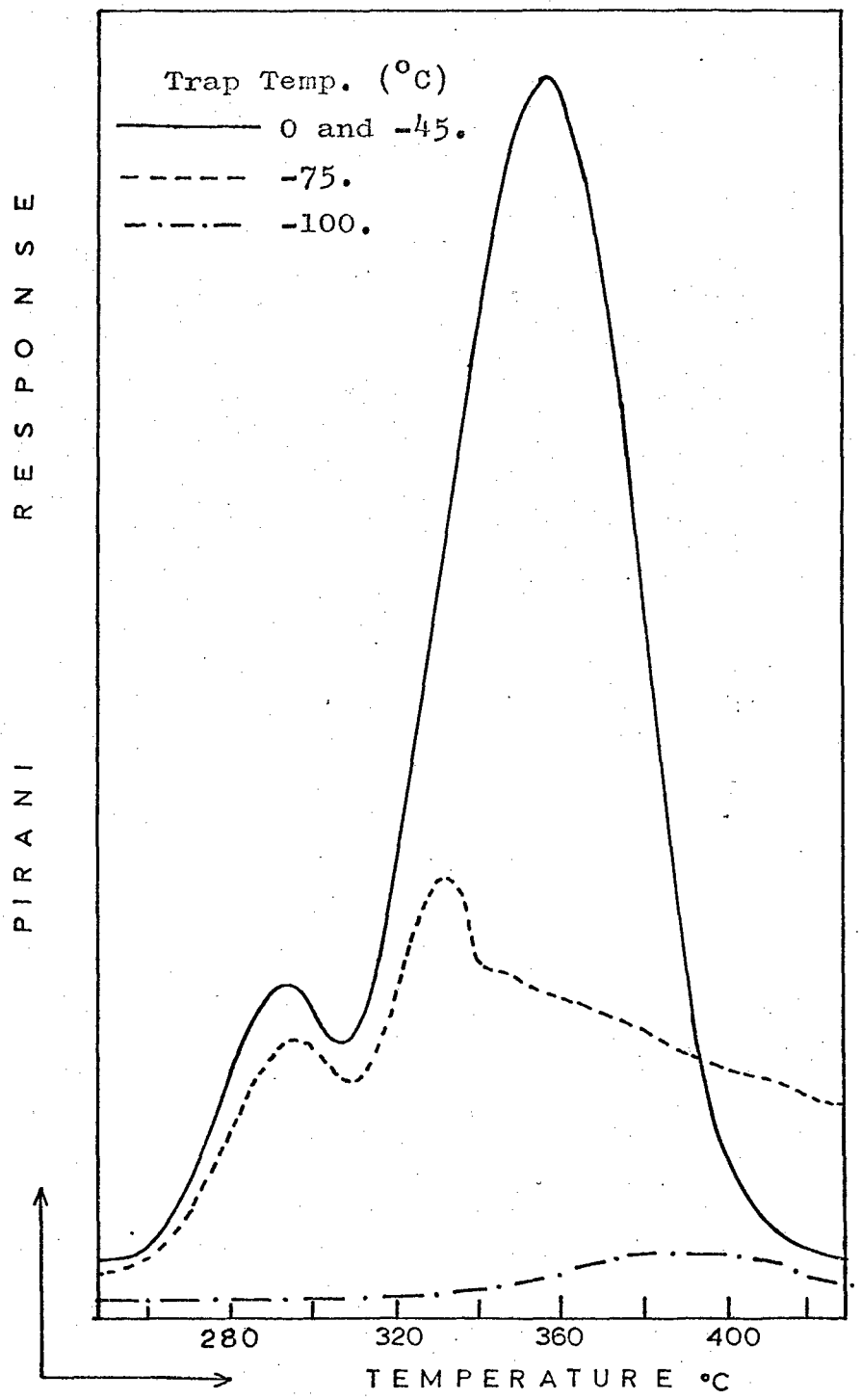


Figure 23. D.C.T.V.A. of a polymethylmethacrylate standard.

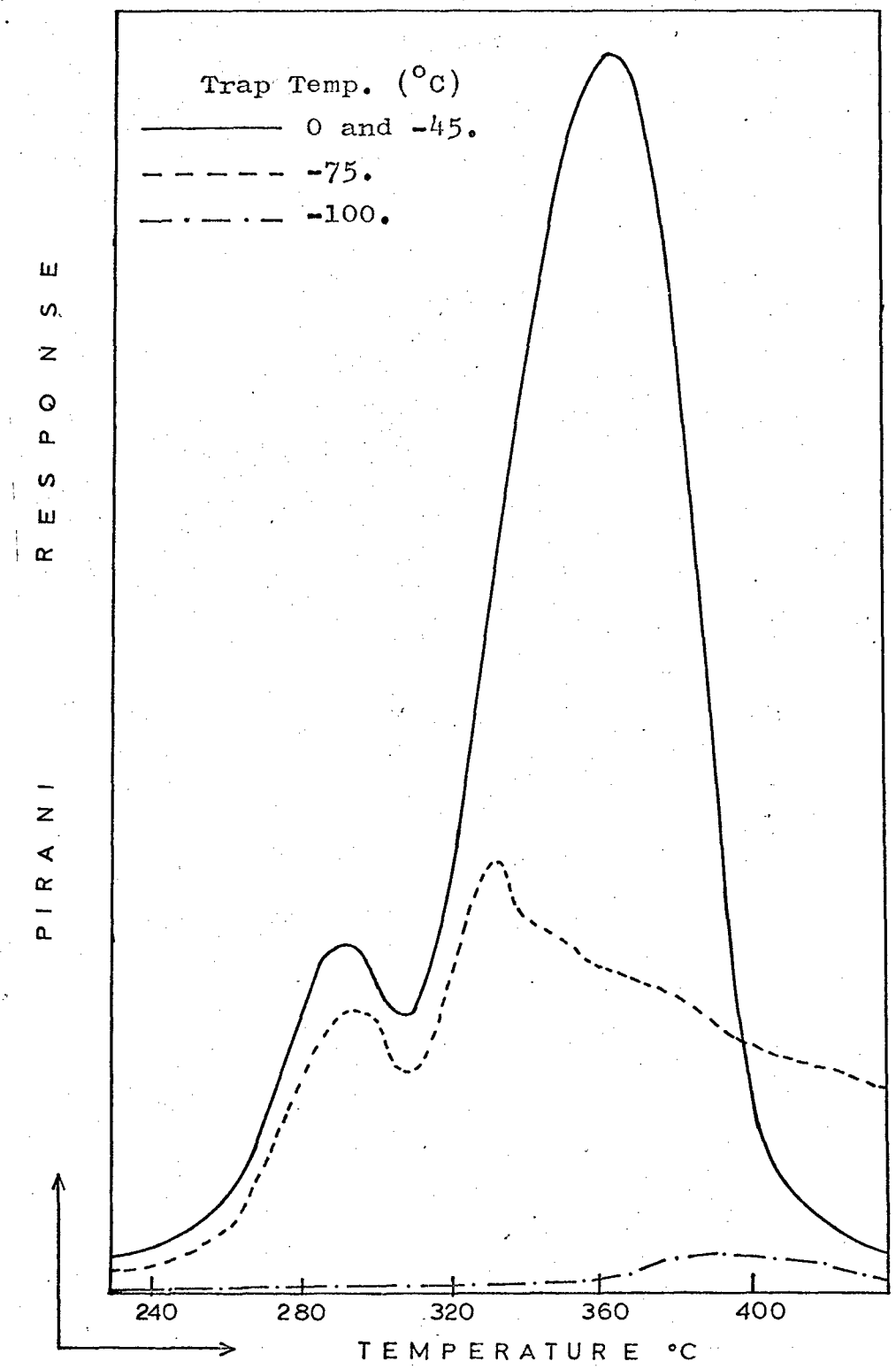


Figure 24. D.C.T.V.A. of a 0.4 mole percent n-butyl acrylate copolymer.

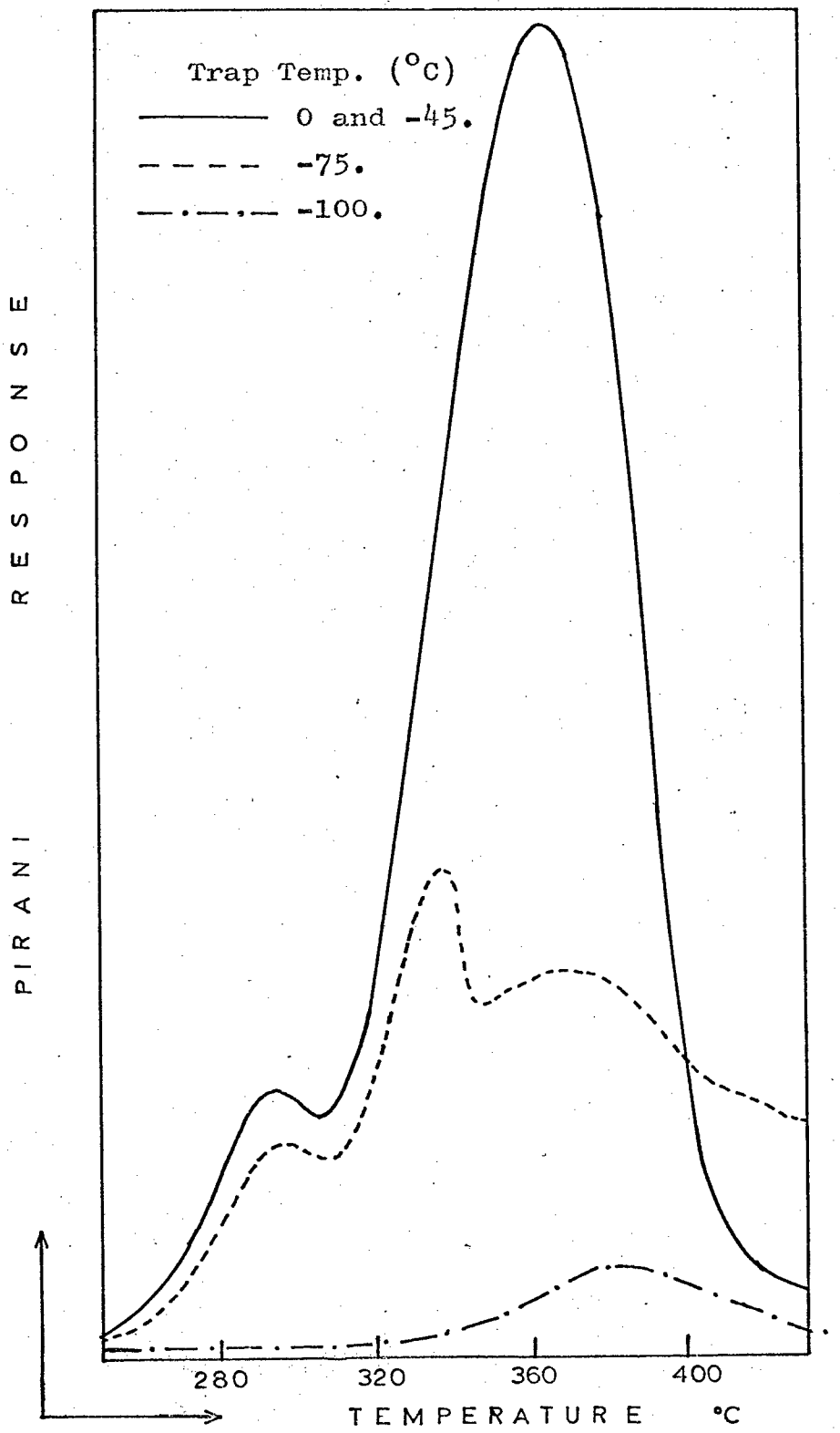


Figure 25. D.C.T.V.A. of a 3.9 mole percent n-butyl acrylate copolymer.

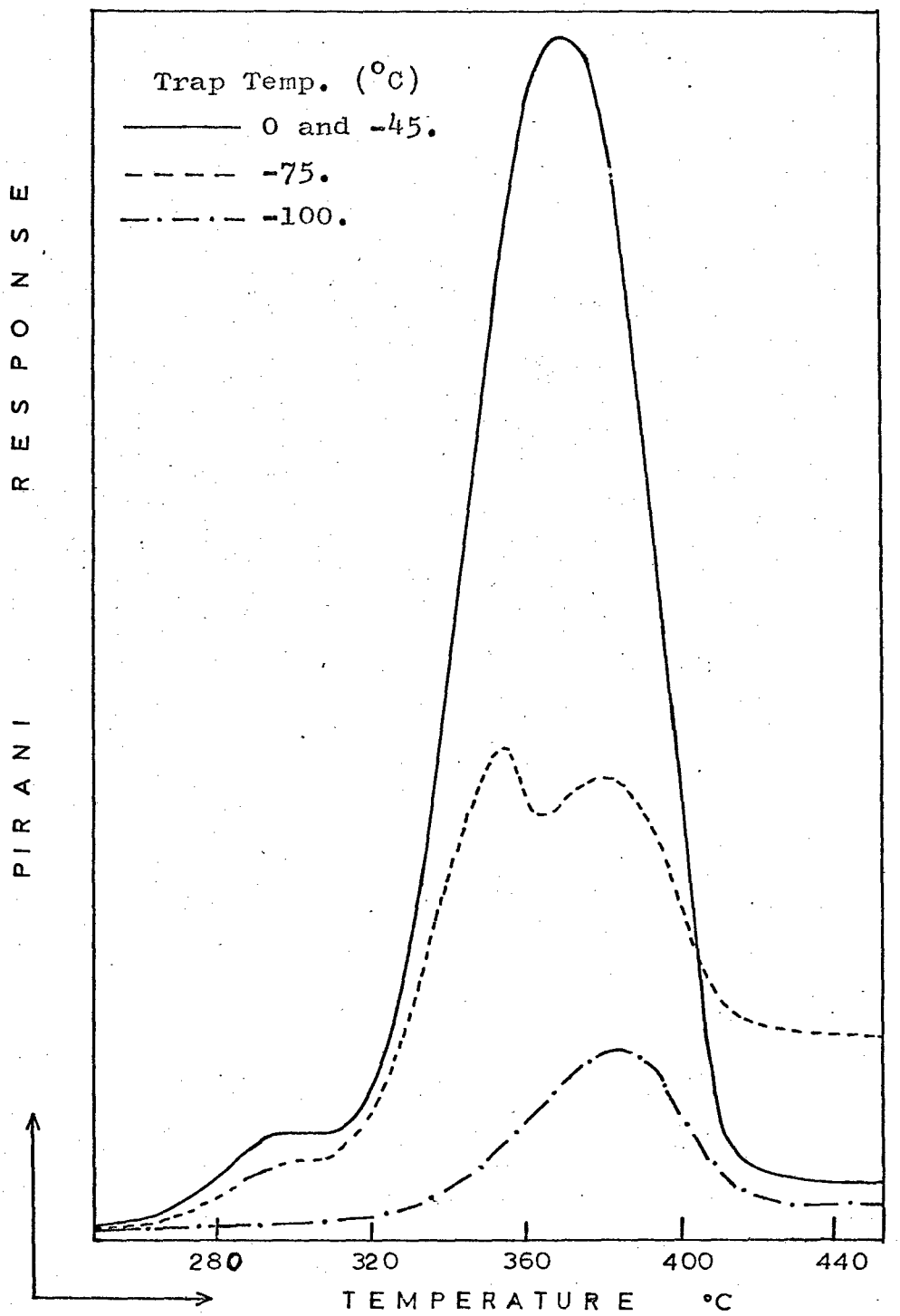
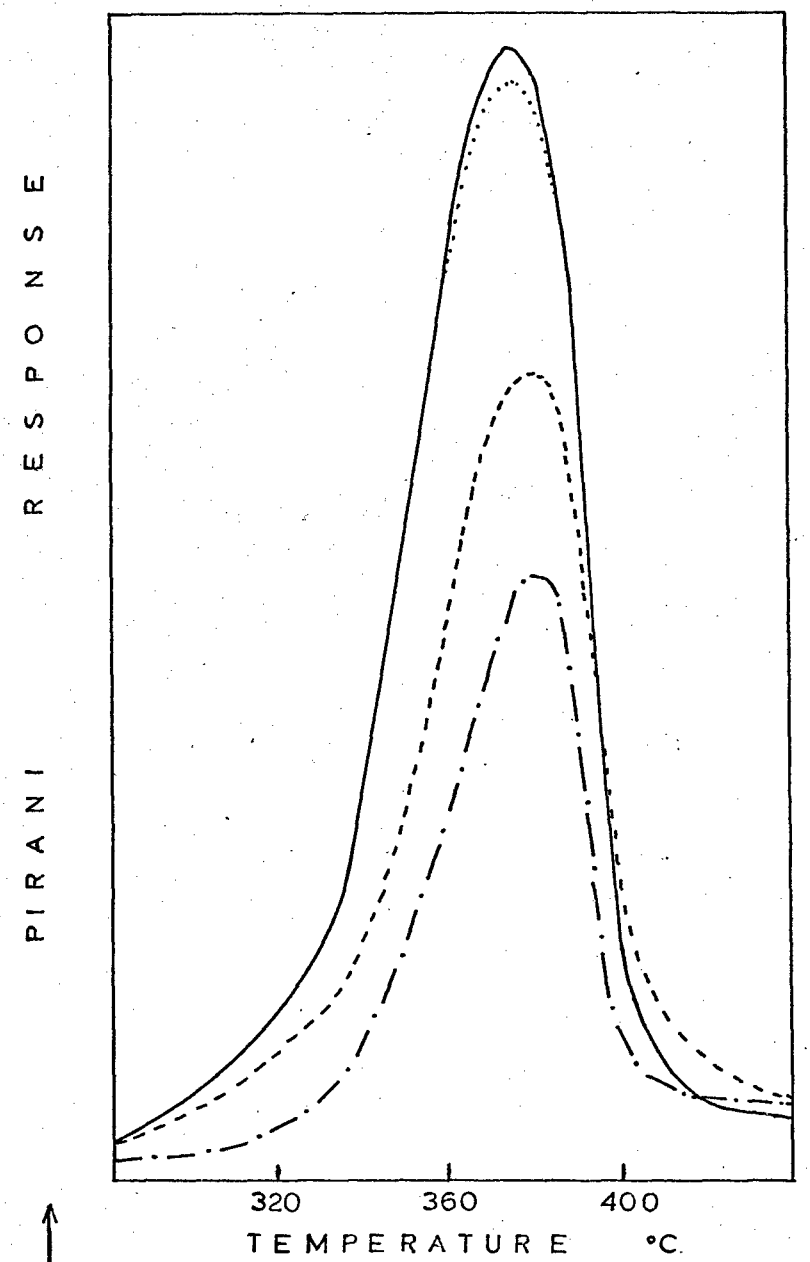


Figure 26. D.C.T.V.A. of a 16.3 mole percent n-butyl acrylate copolymer.



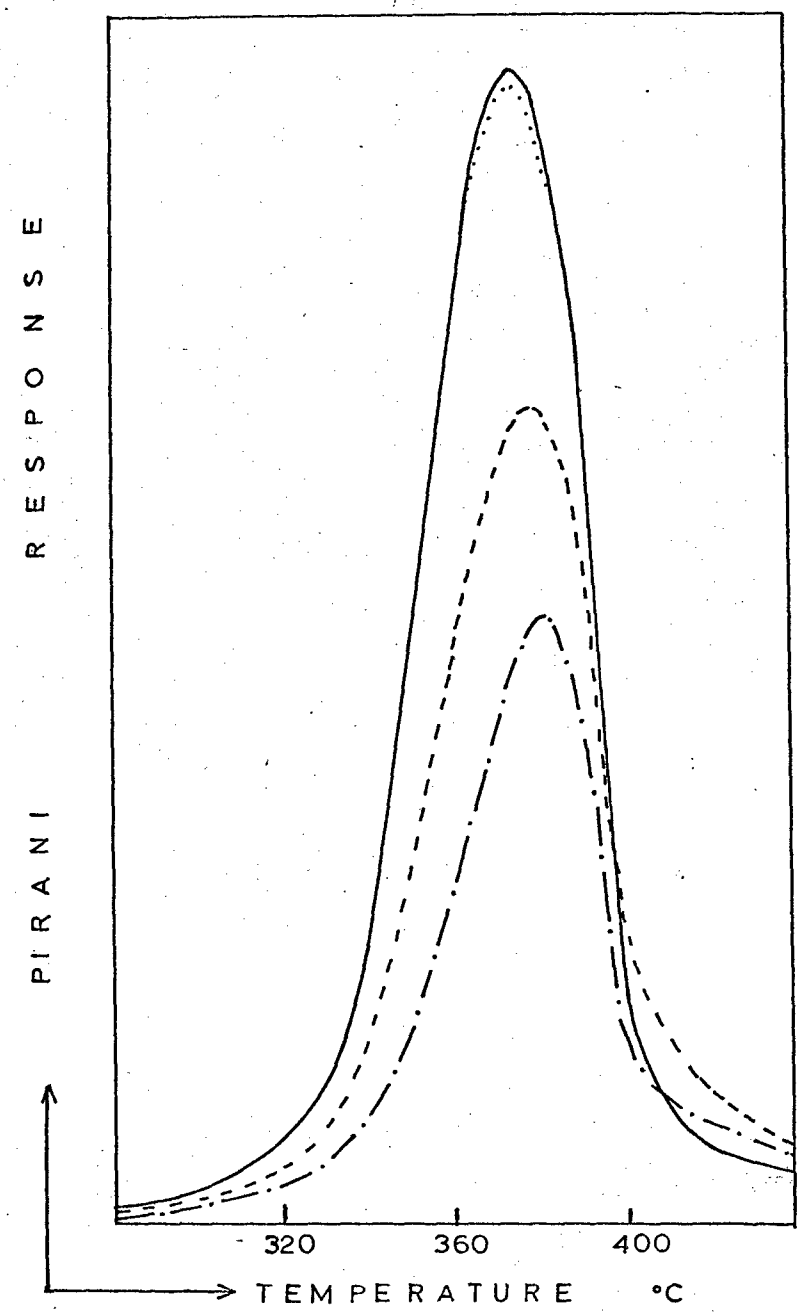
Trap Temp. (°C)

—— 0

..... -45 where not co-incident with 0°C trace.

- - - - -75 —·—· -100.

Figure 27. D.C.T.V.A. of a 50.0 mole percent n-butyl acrylate copolymer.



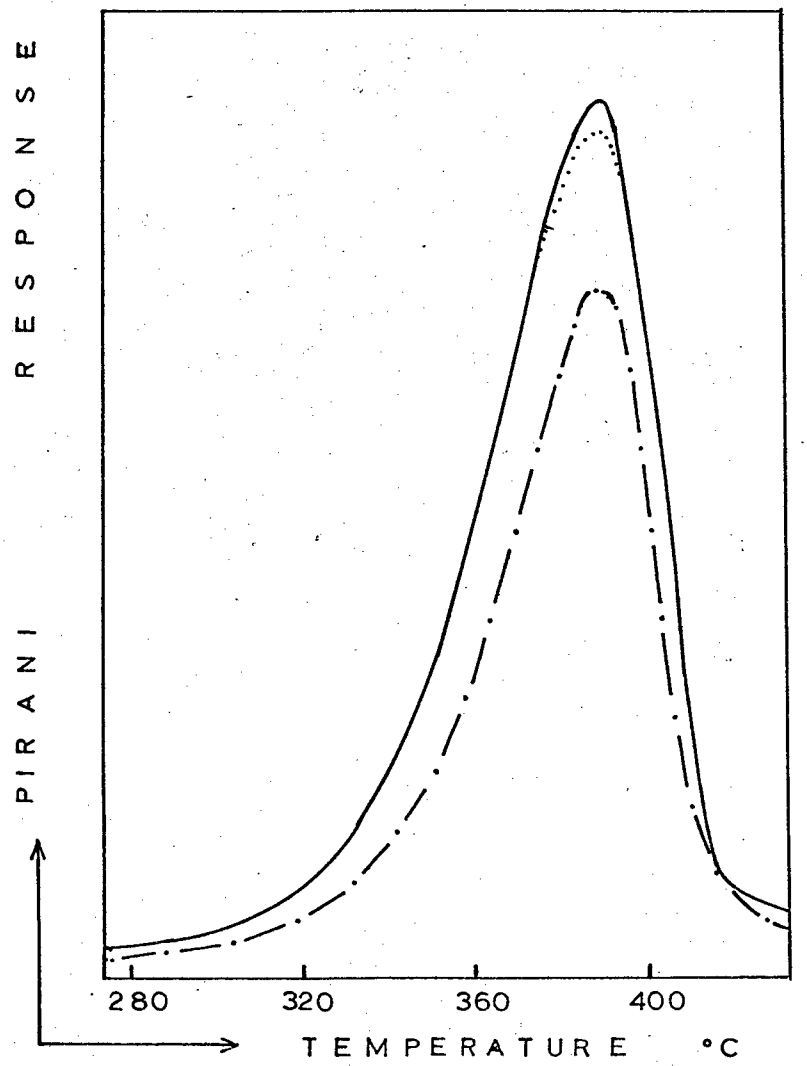
Trap Temp. (°C)

—— 0

····· -45 where not co-incident with 0°C trace.

---- -75 —·—· -100

Figure 28. D.C.T.V.A. of a 52.4 mole percent n-butyl acrylate copolymer.



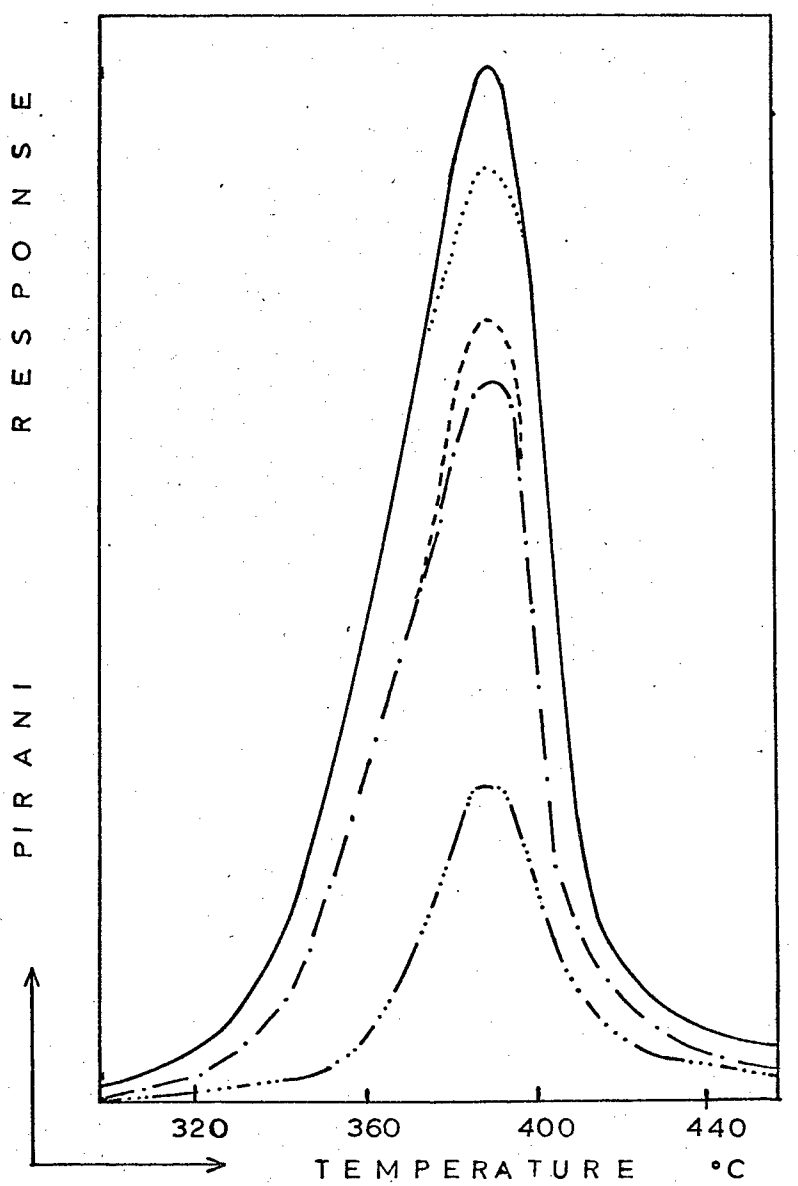
Trap Temp. (°C)

—— 0

····· -45 where not co-incident with 0°C trace.

—·—· -75 and -100

Figure 29. D.C.T.V.A. of an 82.2 mole percent n-butyl acrylate copolymer.



Trap Temp. (°C)

——— 0 —··—··— -196 —·—· -100

····· -45 where not co-incident with 0°C trace.

---- -75 where not co-incident with -100°C trace.

Figure 30. D.C.T.V.A. of a 93.4 mole percent n-butyl acrylate copolymer.

Table 16.

Polymer Composition (mole °/o n-butyl acrylate)	Temp. in °C for Rate Maxima Attributable to		
	(A) Chain End Initiated Degradation	(B) Degradation Initiated by Random Scission	(C) Products Non-Condensable at -100°C
0	292	359	385
0.4	292	360	385
3.9	292	364	385
16.3	292	367	383
50.0 $\overline{M}_n$ 100,000	-	371	381
52.4 $\overline{M}_n$ 1,330,000	-	371	381
82.2	-	388	389
93.4	-	389	389

flow system and could be attributed to gases such as carbon monoxide, methane, hydrogen and carbon dioxide. Peak (C) increases in size with increasing acrylate content. A further T.V.A. trace, shown in Figure 30, was obtained from the 93·4 mole percent n-butyl acrylate copolymer with one of the traps at liquid nitrogen temperature. Some material passes through this trap, which demonstrates that permanent gases are formed in the degradation process in addition to carbon dioxide which would be condensed at this temperature.

It is not possible to obtain quantitative information from these traces about the relative amounts of material condensable at the various trap temperatures since,

a. Pirani response is not linear with pressure, and

b. Pirani response depends upon the substance giving rise to that response.

The trace from the trap at -75°C is interesting in that for samples of high methacrylate content three peaks occur, Figure 25, the middle one of which does not correspond to any of the other peaks noted in table 16. Its presence may be explained in terms of a nucleation effect, which occurs when a considerable quantity of a material which is only partially condensed at that temperature enters the trap rather than by any explanation involving the mechanism of polymer breakdown. Thus the first surge of material passes through the trap. Later, nucleation takes place in the trap, and thereafter condensation is more efficient so less material reaches the Pirani gauge.

The results for the high and low molecular weight 50 mole percent copolymers, Figs. 27 and 28, are identical showing that in the molecular weight range 100,000 to 1,330,000 chain length has no effect on degradative behaviour at least as far as the production of volatile materials is concerned.

From these investigations it would appear that the temperature range 270-340°C should be suitable for studying the degradation reaction isothermally. The principal results may be listed as follows. With increasing acrylate content:

1. The lowest temperature peak, ascribed to chain end initiated breakdown, becomes smaller although its position remains unchanged.

2. The main peak moves to higher temperatures showing that the main polymer chain is becoming more stable to breakdown.

3. Production of chain fragments which condense immediately above the reaction zone increases with acrylate content, and they become deeper in colour (pale yellow to brown).

4. The residue becomes more abundant and darker in colour as in 3.

Interpretation of T.V.A. Data

Discussion of Results 1 and 2:

The decrease in importance of degradation initiated at unsaturated methyl methacrylate chain ends may be ascribed to a combination of effects. As the acrylate content of the copolymers increase -

i) The relative amount of methacrylate available to form susceptible chain ends decreases.

This is the most straightforward explanation of the lessening importance of peak (A) but cannot itself explain the fact that when only 16·3 mole percent of n-butyl acrylate is present, this first peak is reduced to a point of inflection.

ii) A new cross termination step in the polymerization reaction results in methacrylate radicals taking part in combination, rather than disproportionation, termination reactions.

The unsaturated methacrylate chain ends are produced in disproportionation termination reactions. Chaudhuri et al (39) found that in a methyl methacrylate - methyl acrylate copolymer containing 45·9 mole percent methacrylate crossed termination was predominant, and that 67% of the termination steps in which a methacrylate radical took part occurred by combination, thus drastically reducing the number of unsaturated chain ends. It seems reasonable to suppose that a similar mechanism could operate in the n-butyl acrylate - methyl methacrylate system.

iii) The zip length of depolymerization decreases because of the "blocking" effect of acrylate units.

This effect of acrylate content on zip length is demonstrated by molecular weight measurements reported in a later section, and has been observed in chapters 3 and 4.

In randomly initiated degradation the ease with which the initial break occurs depends upon acrylate content, since

acrylate-acrylate bonds are more difficult to rupture than methacrylate-methacrylate bonds, but in chain end initiated degradation the initial process is independent of acrylate content. Thus the temperature shift shown to occur for peak (B) in table 16 is a consequence of randomly initiated breakdown.

Discussion of Results 3 and 4:

The chain fragments may be explained by the increasing importance of transfer reactions over depolymerization with increasing acrylate content because of the reactivity of the acrylate radical and the availability of tertiary hydrogen atoms. Colouration is due to conjugated sequences of double bonds formed in the polymer backbone. This reaction is further investigated in a later chapter.

THERMOGRAVIMETRIC ANALYSIS

T.G.A. experiments were carried out in an atmosphere of nitrogen, since the Du Pont 950 Thermogravimetric Analyzer cannot be used under conditions of high vacuum. The rate of gas flow was 70 cc./min. and the sample size was about 10 mg.. Programmed work was carried out using a heating rate of 5°C/min., the sample being heated from ambient to 500°C. Typical traces obtained for the degradation of a number of copolymers are shown in Fig. 31. As the acrylate content of the copolymer examined increases, the T.G.A. trace moves to higher temperatures, showing that the copolymer is becoming more stable to weight loss. At high methacrylate content a two stage decomposition takes place, the higher temperature process accounting for the bulk of the weight loss. These observations are in agreement with the data obtained from T.V.A., although because of the different conditions used, these techniques are not strictly comparable.

Determination of Kinetic Parameters from T.G.A.

While it is difficult to determine reaction kinetics by the use of T.V.A. many methods of obtaining kinetic parameters from T.G.A. measurements have been advocated (40,41). It was considered possible that activation energies found in this way could make some contribution towards an understanding of the thermal breakdown of the copolymer system under investigation.

Dynamic T.G.A. has the advantage in theory that a single programmed weight loss curve can yield the same information as a whole set of isothermal traces, but many methods of calculating kinetic data from such programmed runs require the original

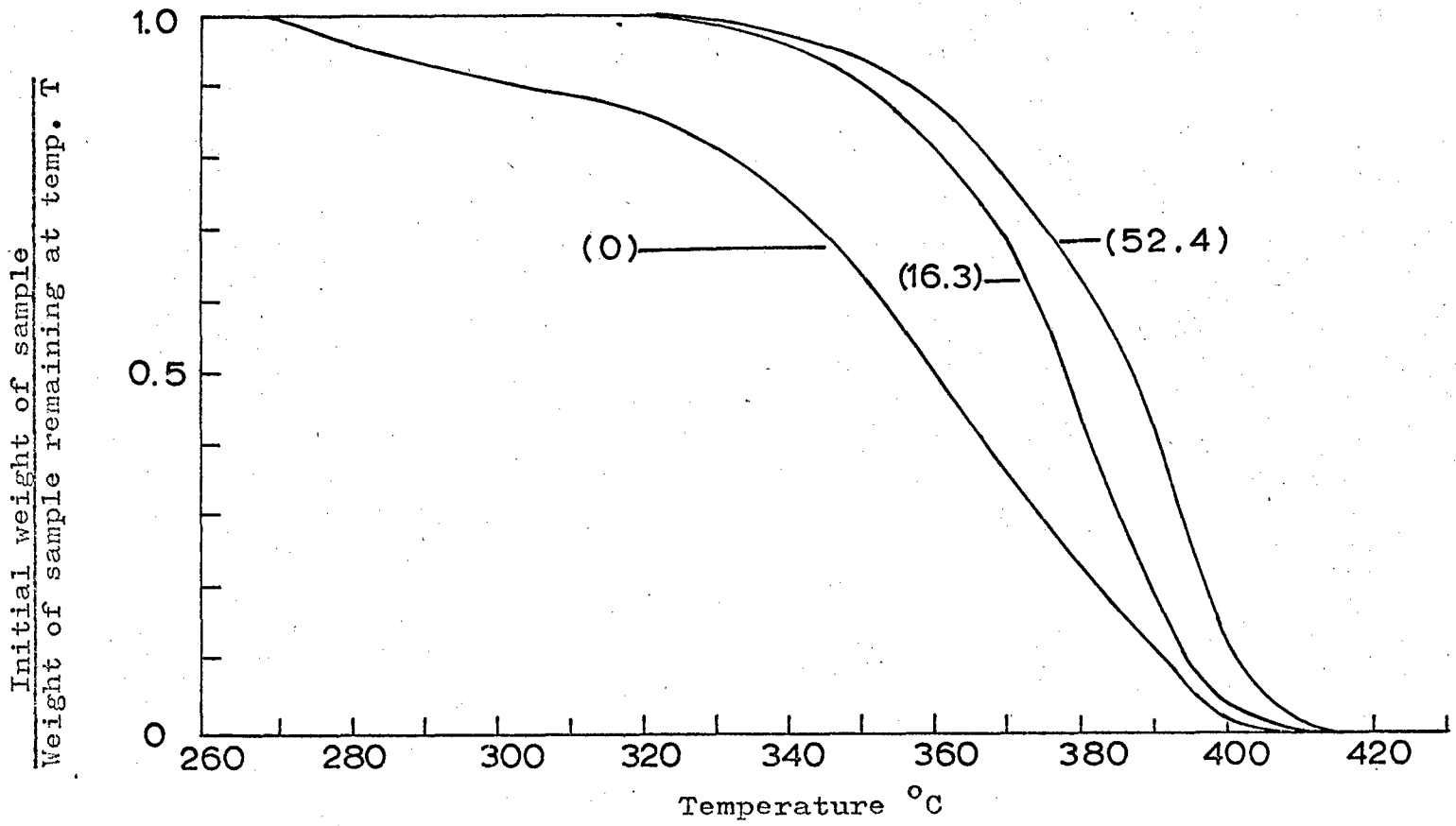


Figure 31. Programmed (5°C/min.) T.G.A. traces of a series of copolymers. The figures in brackets give copolymer composition as mole percent n-butyl acrylate.

trace to be differentiated, a process which can greatly increase experimental scatter, or require the assumption that a single set of parameters applies over the whole reaction. This assumption is not always justified since the nature of the material being degraded can change drastically in character with increasing conversion. Isothermal methods avoid such complications but in these the sample can undergo considerable reaction while being heated to the temperature of interest. In view of these considerations it was decided to carry out both dynamic and isothermal T.G.A. measurements.

Dynamic T.G.A.

In the literature many mathematical treatments of polymer degradation processes have been developed. Such treatments (42,43) show that if initiation occurs solely at chain ends or solely at random along the chain, then, in the limits of long and short depolymerization zip lengths, the overall degradation process can be described by an "order" type of equation, as in table 17.

TABLE 17

Type of Initiation	Zip Length	"Order" of Reaction
End Initiation	Long	One
	Short	Zero
Random Initiation	Long	One
	Short	Zero

The particular method used to determine activation energies was that of Coats and Redfern (44). A typical plot of log $[2{\cdot}303\log F/T^2]$ versus $1/T$, where F is the fractional weight of material remaining and T is the absolute temperature, is shown in Fig. 32. From the gradients of such plots the activation energies listed in table 18 were calculated.

TABLE 18

Copolymer Composition (mole % n-butyl acrylate)	Activation Energy of Random Initiation (kcal./mole)
0	39
0·4	41
3·9	48
16·3	50
52·4	51

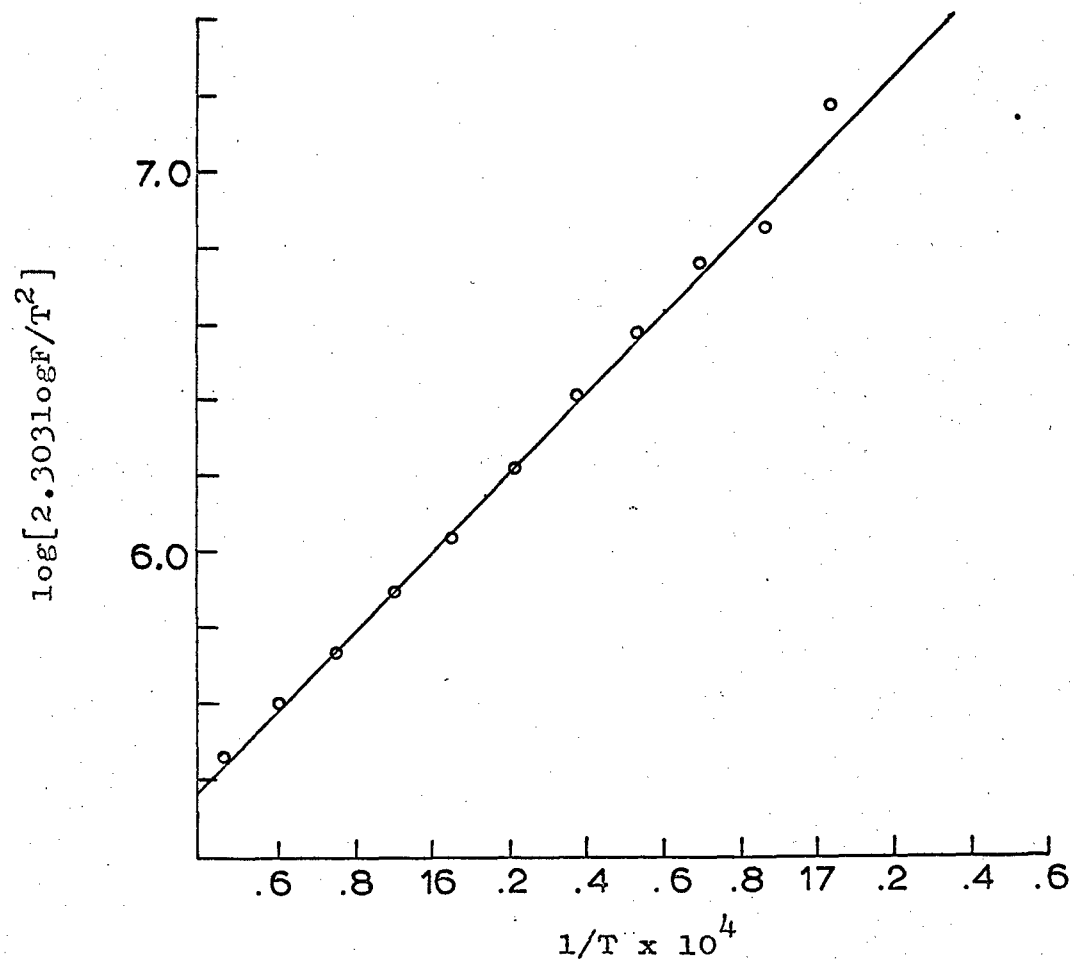


Figure 32. First order plot for a 3.9 mole percent n-butyl acrylate copolymer.

As the acrylate content of the copolymers increases, the end initiated reaction is suppressed, so that it becomes extremely difficult to separate the first decomposition from the randomly initiated one. In view of this, no activation energies are quoted here for this end initiated process. The use of a first order plot is probably less valid for the 52·4 mole percent n-butyl acrylate copolymer than for any of the others in table 18 because at this acrylate content the zip length is possibly too short for the degradation to follow first order kinetics closely. At still higher acrylate content the degradation cannot be approximated to any "order" type of process. Few published methods of obtaining kinetic parameters from programmed T.G.A. data can deal with random kinetics and those that can involve experimental measurements outwith the scope of the instrumentation available (45).

Isothermal T.G.A.

If the rate of decomposition of a sample can be found for the same extent of conversion at a number of temperatures, then an activation energy may be calculated. This value is not an average one, but refers to the particular extent of degradation at which it was calculated. It is convenient to use zero conversion as the point at which to determine activation energy, since this condition of the sample is the most reproducible. It is not possible, because of the time required for the thermobalance to attain equilibrium, to find the initial rate of decomposition directly, the technique used here being to extrapolate the rate of weight loss versus time curve back to zero time. The first 3% of degradation occurred during heat up and was neglected, the extrapolation being carried out on data obtained for up to 20% conversion. Initial rate methods are not strictly applicable where the material decomposes by random scission, since this type of breakdown leads to an initial rate of zero with respect to weight loss. In considering the copolymers in order of increasing acrylate content, as poly(n-butyl acrylate) degrades randomly there must be a point at which initial rate techniques become invalid. This point may be found simply, since "random" processes can be distinguished from "order" processes by the fact that the maximum rate of decomposition does not occur at zero conversion for random breakdown. Hence for random kinetics the T.G.A. trace i.e. weight loss versus time, will exhibit a point of inflection. For copolymers containing up to 52·4 mole percent n-butyl acrylate, no such inflection points were found. Figs. 33-37 show the log(initial rate) versus 1/T plots obtained. The activation energies calculated from the gradients of these plots are given in table 19.

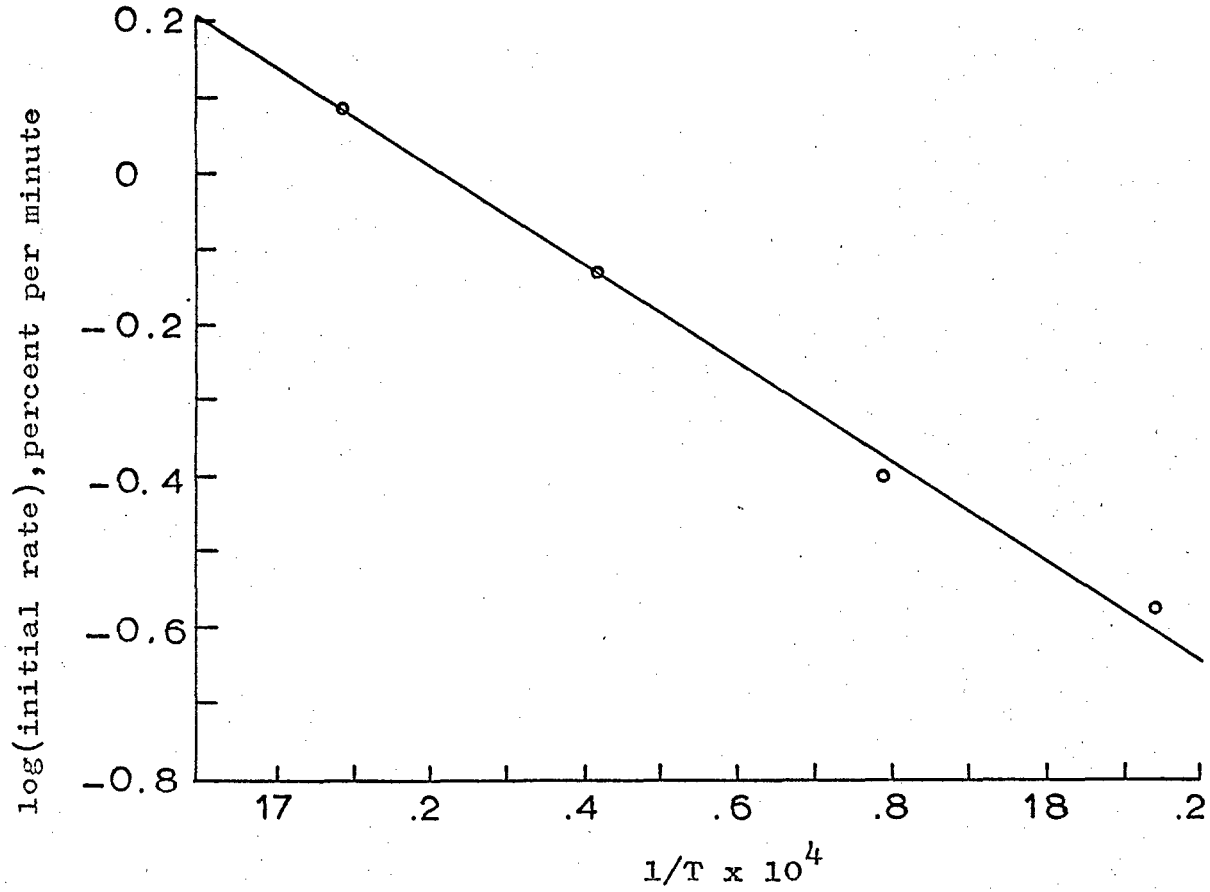


Figure 33. Activation energy plot from initial rate data for a poly(methyl methacrylate) standard.

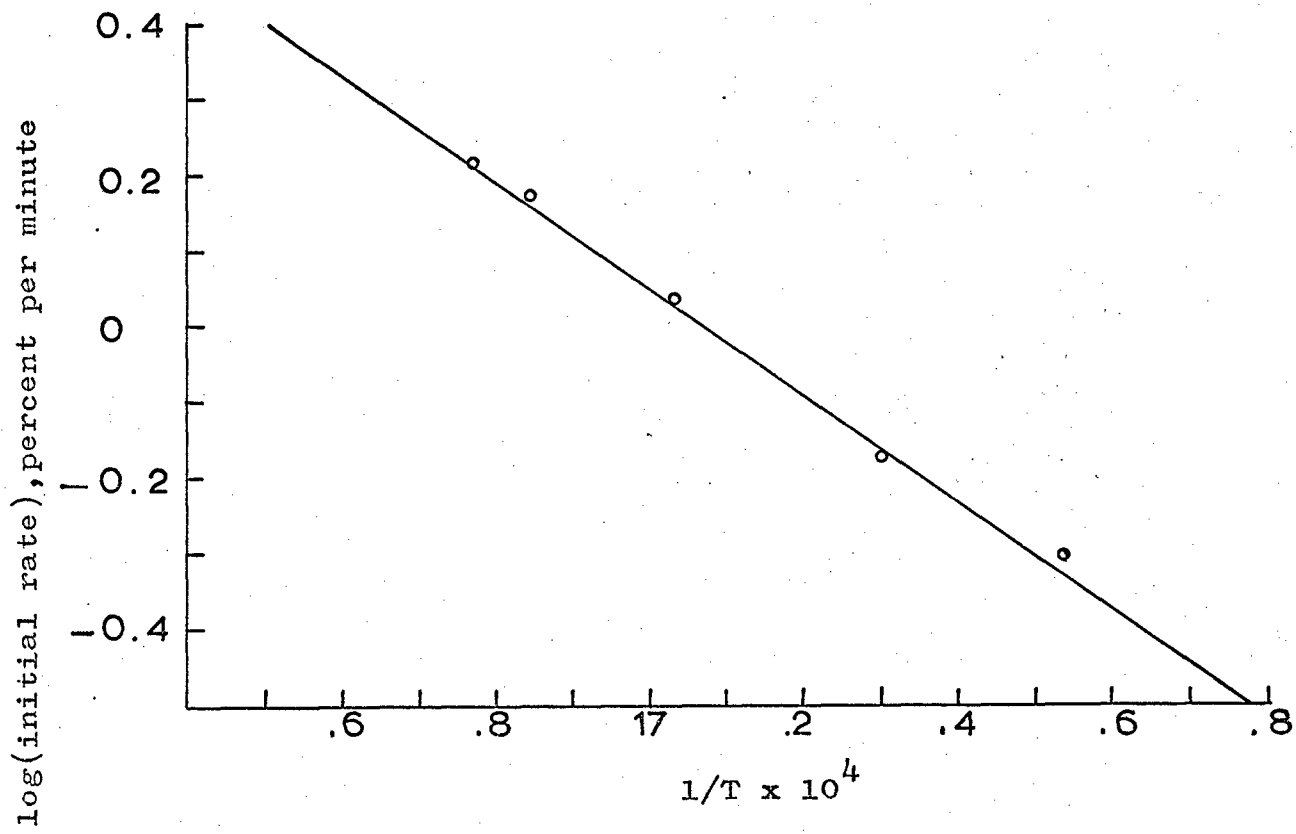


Figure 34. Activation energy plot from initial rate data for a 0.4 mole percent n-butyl acrylate copolymer.

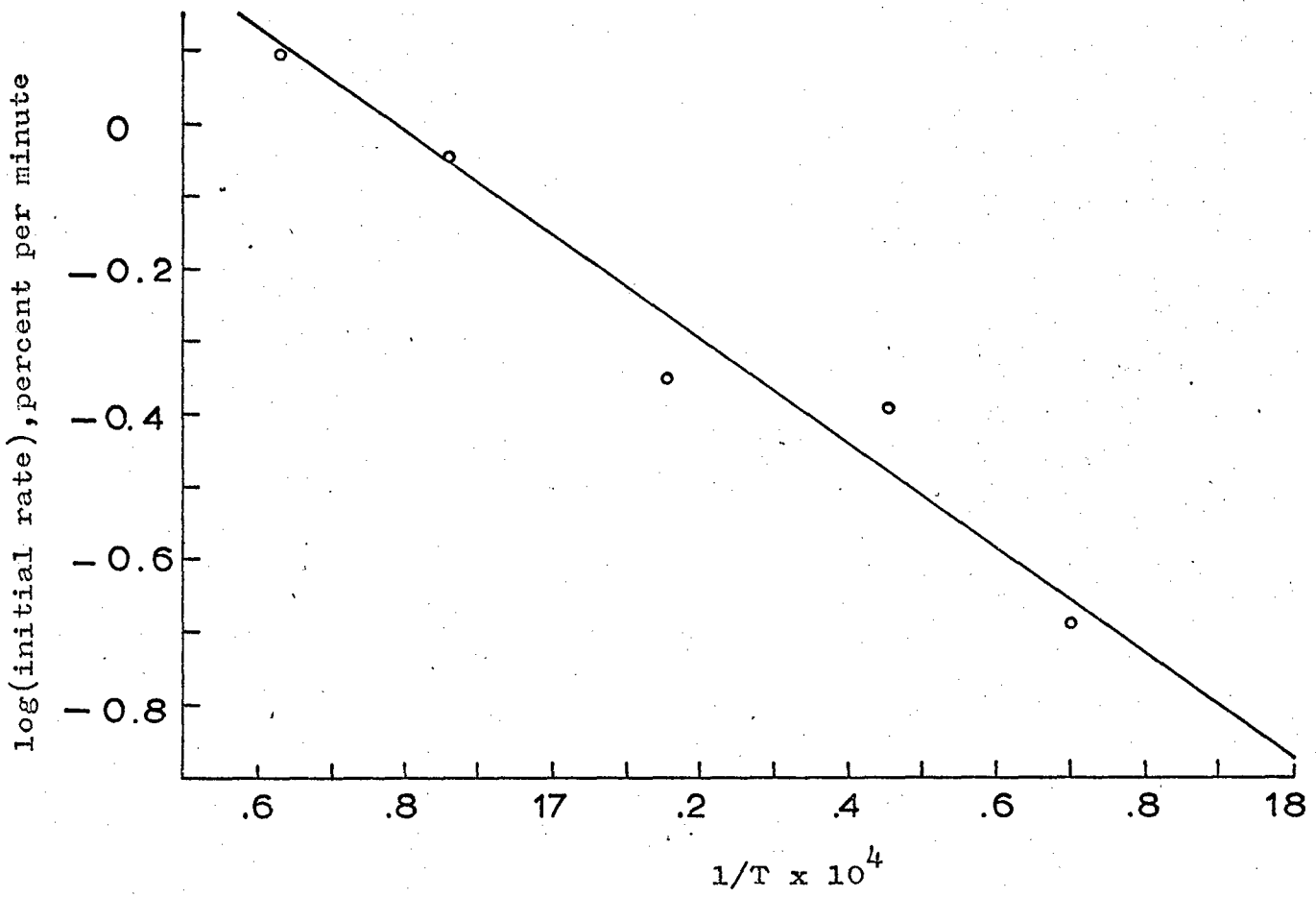


Figure 35. Activation energy plot from initial rate data for a 3.9 mole percent n-butyl acrylate copolymer.

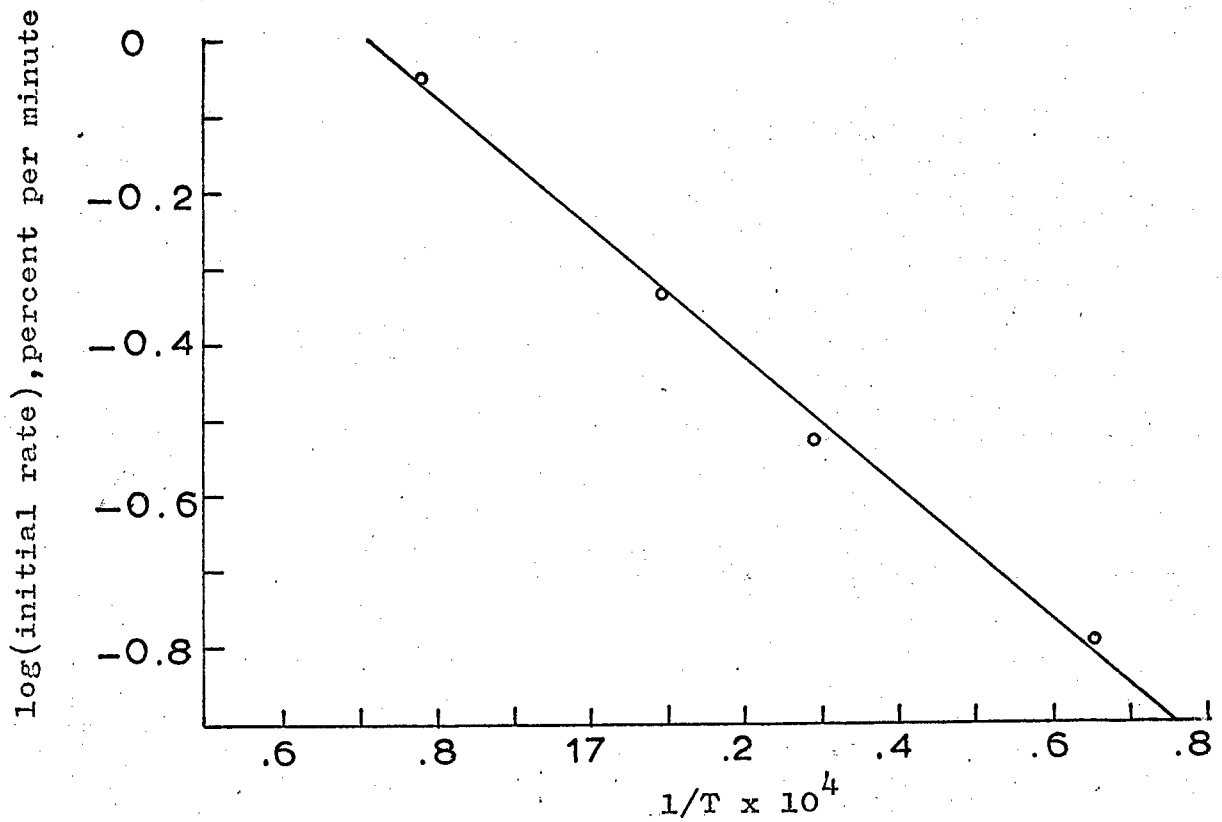


Figure 36. Activation energy plot from initial rate data for a 16.3 mole percent n-butyl acrylate copolymer.

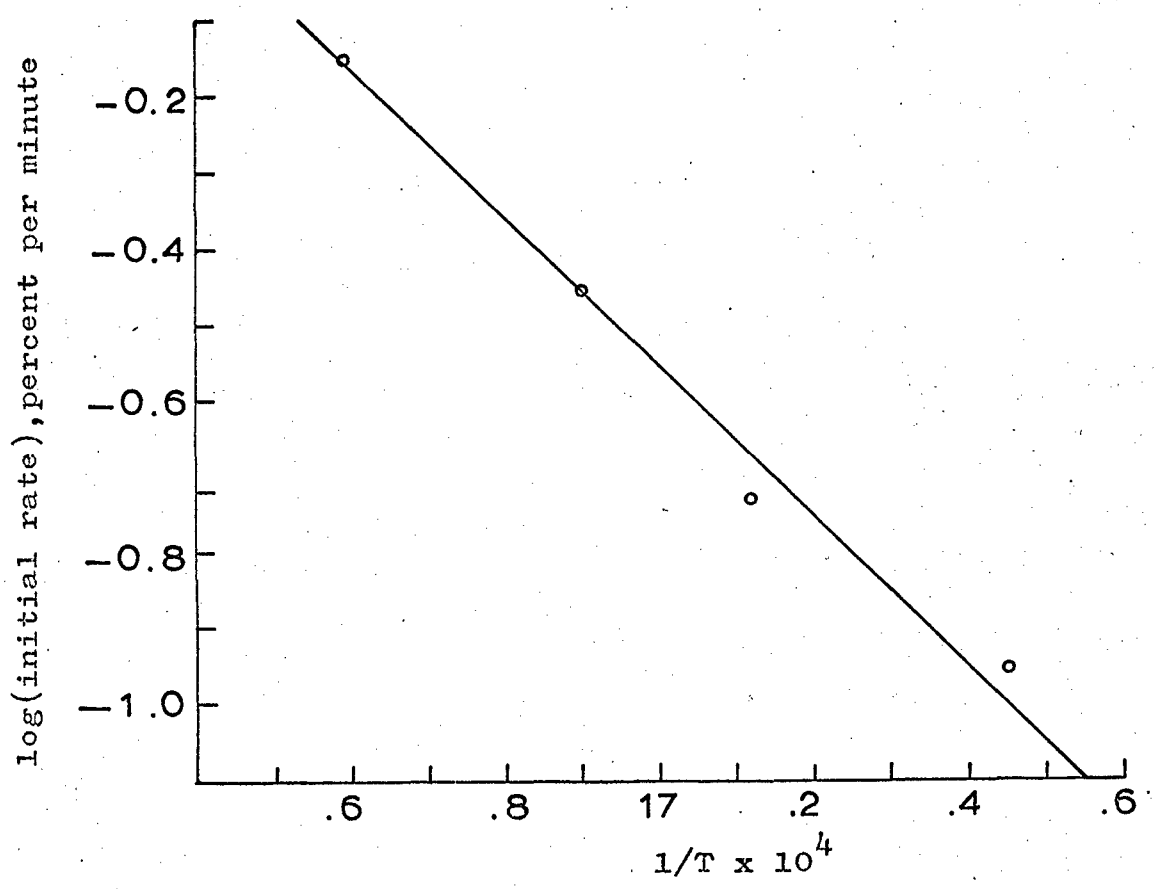


Figure 37. Activation energy plot from initial rate data for a 52.4 mole percent n-butyl acrylate copolymer.

TABLE 19. Activation Energy From Initial Rate Measurements

Copolymer Composition (mole % n-butyl acrylate)	Activation Energy (kcal./mole)
0	30
0·4	32
3·9	34
16·3	39
52·4	46

In the literature there are many examples of initial rate measurements being made on randomly degrading polymers (46). This type of measurement not only involves a very inaccurate plot, but attempts to fit the degradation to an erroneous set of parameters, and should be avoided.

DISCUSSION OF RESULTS

For copolymers of high methyl methacrylate content, the activation energies quoted in table 19 are considerably lower than those listed in table 18 for the randomly initiated reaction. This may be explained by noting that the values found by the initial rate method will, in this copolymer composition region, refer to the end initiated degradation. In the literature many determinations of the energy of activation for poly(methyl methacrylate) decomposition have been reported (47-51). Typical values obtained for the chain end initiated reactions are 31 and 49 kcal./mole respectively.

The activation energy for poly(methyl methacrylate) degradation is a composite quantity involving contributions from the energies involved in the elementary steps of initiation, depropagation and termination (52,53). If copolymers of very low acrylate content are considered, it is likely that the initial step in their breakdown will be the same as that in pure poly(methyl methacrylate) and that the energy involved in the termination step, being diffusion controlled because of the high viscosity of the degrading polymer, will not change markedly. This would imply that the increase in activation energy found at this range of copolymer composition with increasing n-butyl acrylate content is due to an increase in the activation energy of depropagation, E_d. Since $E_d = E_p - \Delta H_p$, where E_p is the energy of propagation in polymerization

and $-\Delta H_p$ the heat of polymerization, and the value of E_p is about 5 kcal./mole for a large variety of polymers (53), any increase in E_d with increasing acrylate content would be reflected by an increase in $-\Delta H_p$. In the limiting case this means that $-\Delta H_p$ for n-butyl acrylate must be greater than that for methyl methacrylate. The experimental values of this quantity for n-butyl acrylate and methyl methacrylate were found to be 18·6 and 13·3 kcal./mole respectively, lending support to the above theory (54).

At higher acrylate content, new initiation steps involving n-butyl acrylate units become likely, as well as the possibility of transfer reactions and the modification of the termination step. It is the interplay of all these contributions which determines the overall activation energy as found by methods such as T.G.A..

CHAPTER 8

THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. C. IDENTIFICATION OF THE PRODUCTS OF REACTION

INTRODUCTION

Before any quantitative measurements can be undertaken, a knowledge of the nature of the degradation products is necessary so that techniques may be devised to estimate these materials. Preliminary degradations were carried out for times up to twenty four hours at 313°C using the sealed tube technique, samples of the product gases and liquid volatiles being obtained as described in chapter 6. Where possible, more than one technique was used to establish the structure of these compounds.

ANALYSIS OF PRODUCT GASES

Gas Chromatography

Experiments were carried out on these gases as described in chapter 6. The resulting traces, using the columns listed in table 15 under the conditions specified, are shown in Figs. 38-40. The retention time for each peak was obtained, and standard samples of the pure gases were introduced into the column under the same conditions. Tables 20-22 list the gases with the same retention times as those shown in Figs. 38-40.

Mass Spectrometry

Mass spectrometric data on the product gases were obtained as in chapter 6 using an electron beam energy of 20ev. Fig. 41 compares the cracking patterns obtained from a standard sample of but-1-ene (Mathieson Inc.) and from the gases evolved when a 16·3 mole percent n-butyl acrylate copolymer was degraded. Table 23 lists the fragment masses in order of abundance and gives the possible structures corresponding to each.

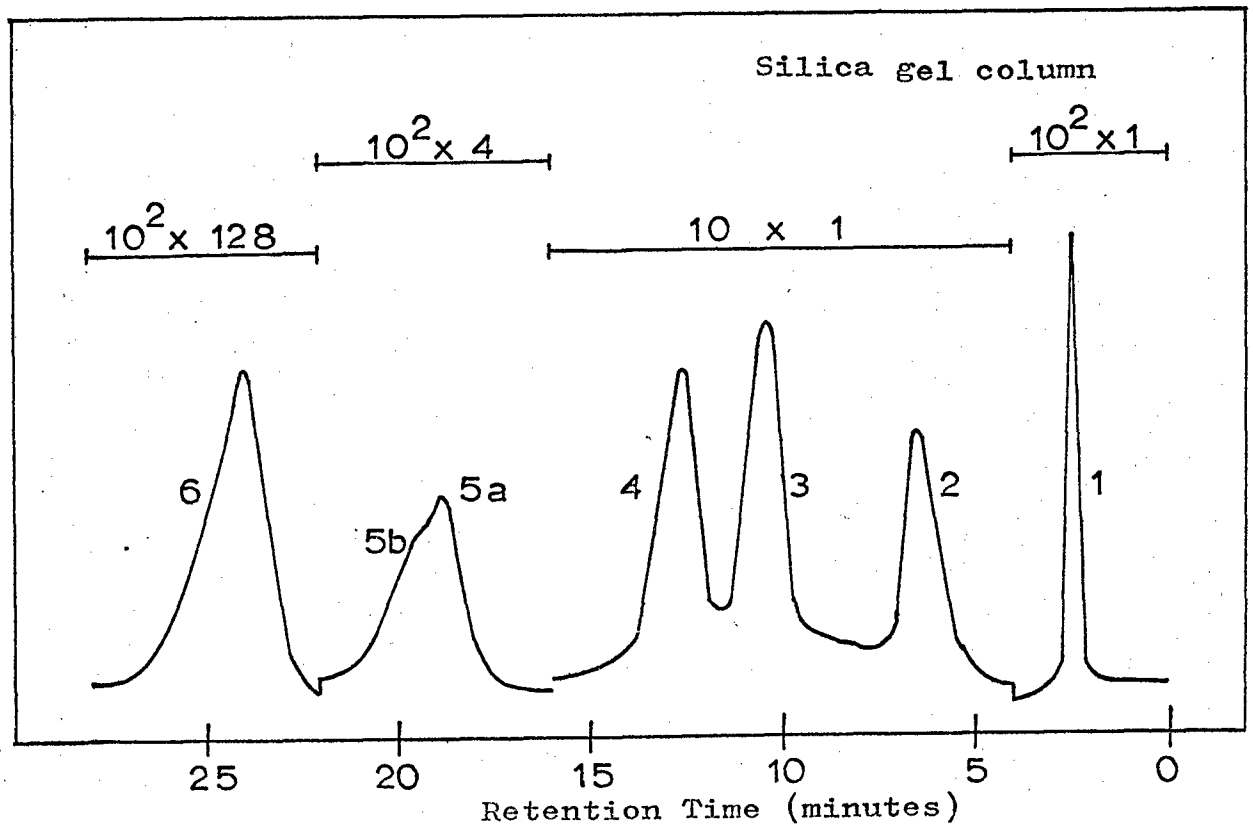


Figure 38. G.L.C. trace for a 50.0 mole percent n-butyl acrylate copolymer degraded at 313°C for 11 hours. Column run isothermally at 40°C for 3min. then programmed at 5°C/min.

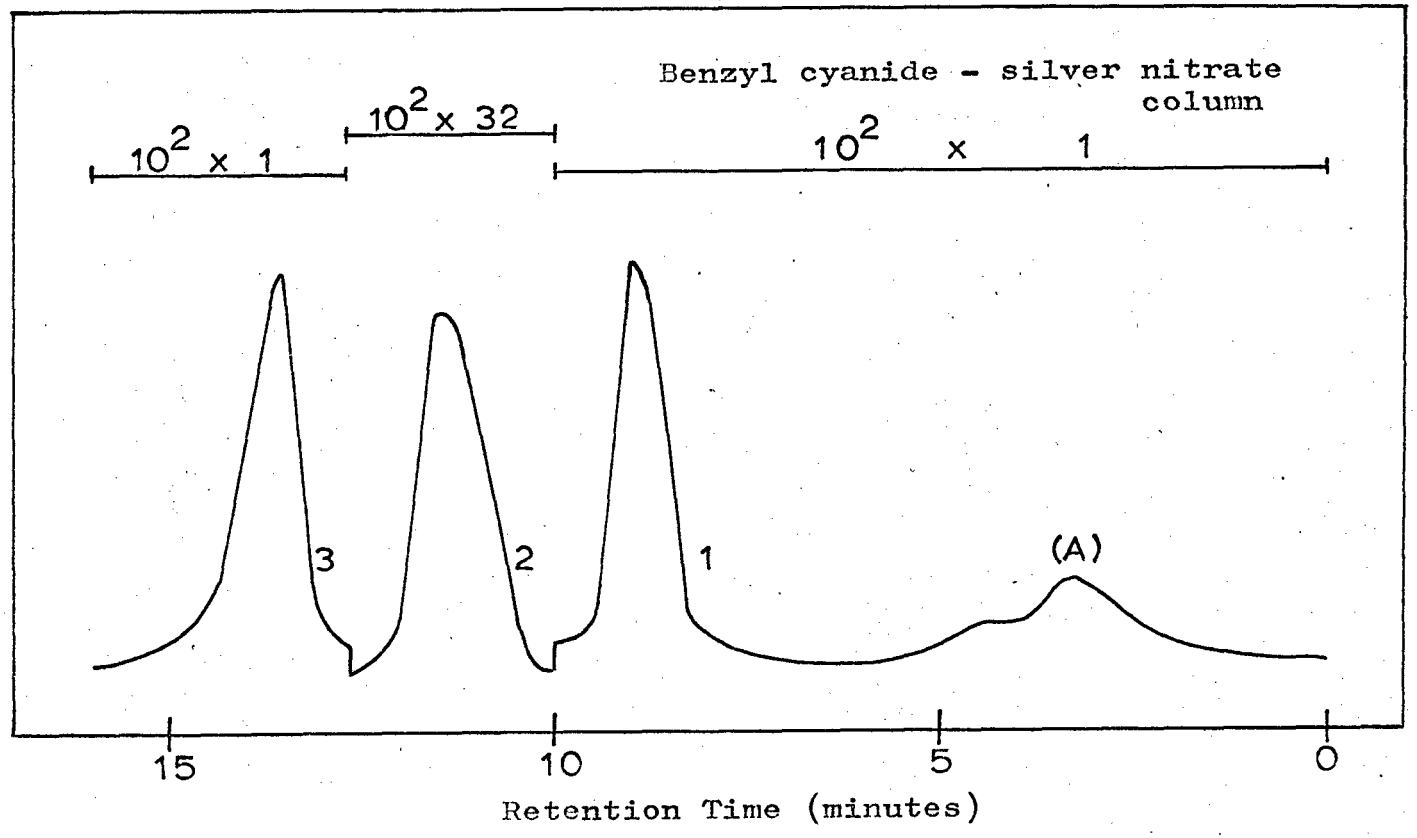


Figure 39. Room temperature g.l.c. of a 16.3 mole percent n-butyl acrylate copolymer degraded at 313°C for 16 hours.

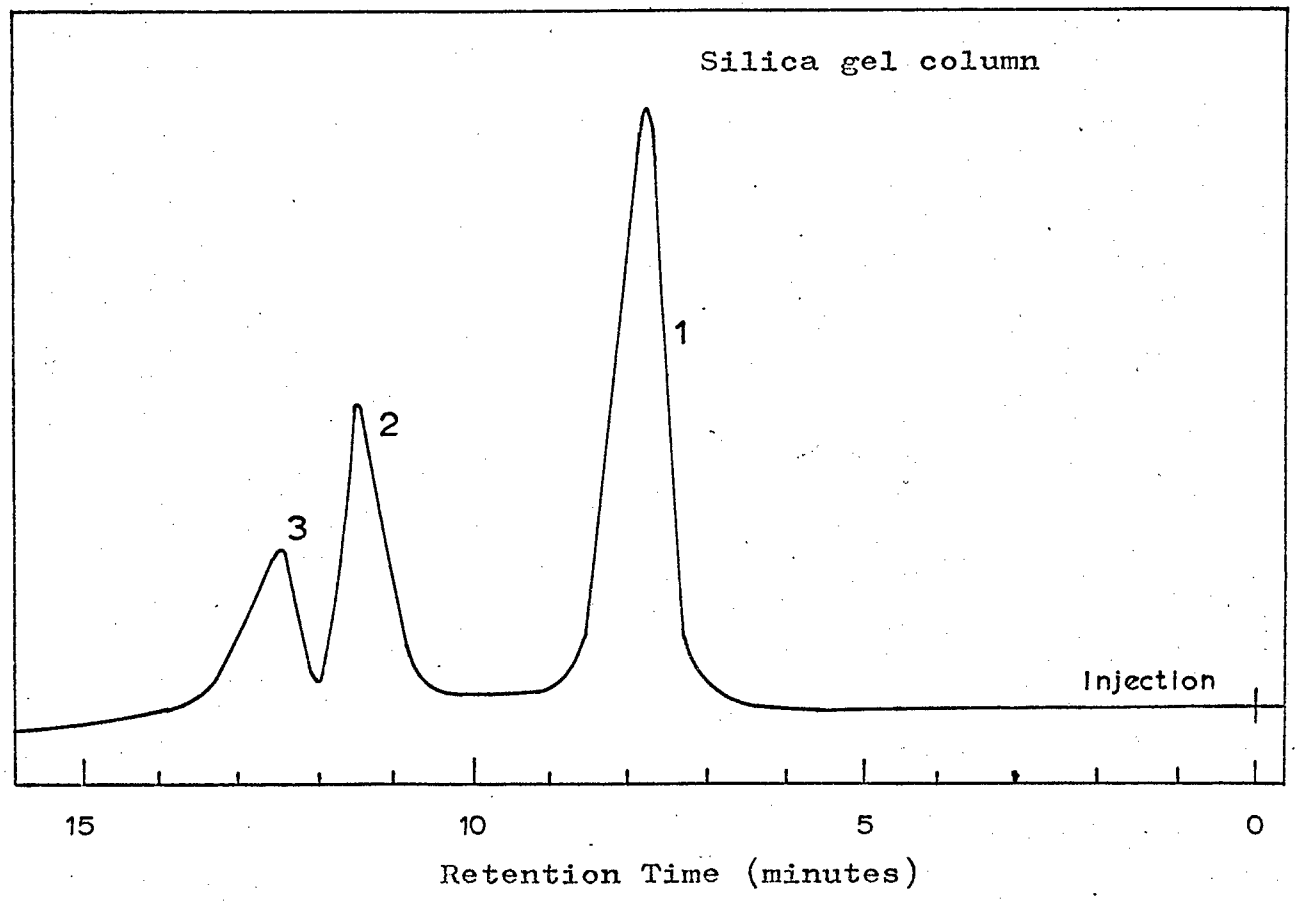


Figure 40. Room temperature g.l.c. of the permanent gas fraction from the degradation of a 52.4 mole percent n-butyl acrylate copolymer pyrolyzed at 313°C for 24 hours.

Table 20.

Peak no. in Fig.4.1	Gas	Retention Time (minutes)	Temperature (°C)
1	Methane	2.5	40
2	Ethane	6.5	58
3	Ethylene	10.5	78
4	Propane	12.5	88
5a	Propylene	19.0	120
5b	Butane	19.5	123
6	Butene	24.0	145

Table 21.

Peak no. in Fig.4.2	Gas	Retention Time (minutes)
1	Trans But-2-ene	9.0
2	But-1-ene	11.5
3	Cis But-2-ene	13.5

Table 22.

Peak no. in Fig.4.3	Gas	Retention Time (minutes)
1	Hydrogen	8.0
2	Carbon Monoxide	11.5
3	Methane	12.5

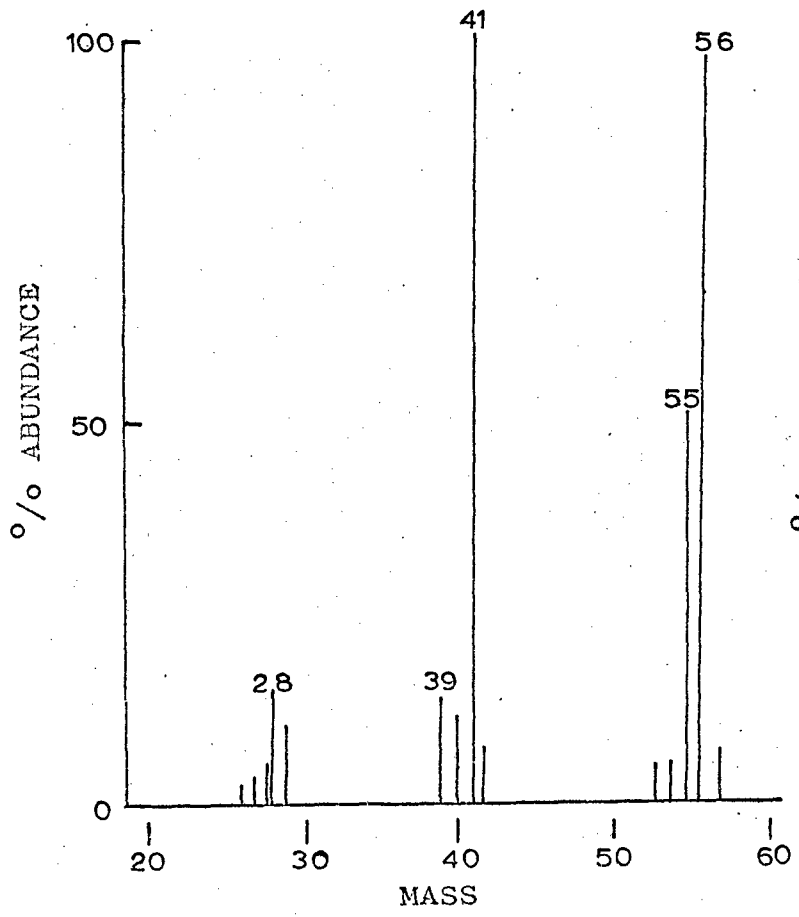
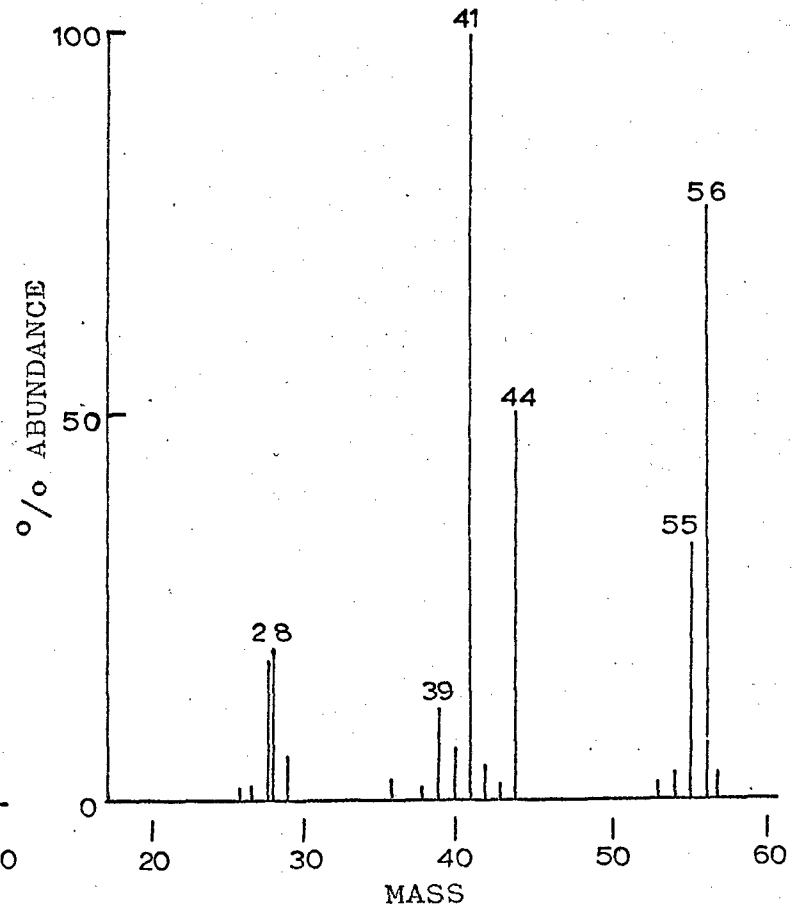


Figure 41. (a) But-1-ene standard.



(b) Product gases from a 16.3 mole % n-butyl acrylate copolymer degraded for 12 hours at 313°C.

TABLE 23

Mass in Order of Abundance	Structure
41	$CH_2=\overset{+}{C}-CH_3$
56	$[CH_3-CH_2-CH=CH_2]^{+\cdot}$
44	$[O=C=O]^{+\cdot}$
55	$CH_3-\overset{+}{C}H-CH=CH_2$
28	$\dot{C}H_2-\overset{+}{C}H_2$

A significant difference between Figs. 41a and 41b is that the peak in 41b at mass 44, attributed to CO_2, is absent from Fig. 41a. This shows that the product gases contain carbon dioxide in addition to the gases already listed in tables 20-22. There are not sufficient differences in the mass spectra of the isomeric butenes to allow them to be readily distinguished, since double bonds appear to be able to migrate easily in the molecular ion. It may also be noted that in Fig. 41 there is a doublet at mass 28 and that, comparing the spectra of but-1-ene and the evolved gases, the peak of lower mass has increased in size in the latter relative to the peak of higher mass. Mass 28 may be ascribed to carbon monoxide, nitrogen, or ethylene, in order of increasing mass. This makes it likely that the enhancement of the lower mass 28 peak is due to carbon monoxide.

Infra-red

A typical infra-red spectrum for the gaseous degradation products from a 93·4 mole percent n-butyl acrylate copolymer, obtained as in chapter 6, is shown in Fig. 42. The assignments of the various absorptions are listed in table 24. These are consistent with the presence of a vinyl double bond $RCH=CH_2$ which is found in only one of the butenes, but-1-ene. The presence of carbon dioxide is confirmed by the absorptions at 2350 cm.$^{-1}$ and 677 cm.$^{-1}$, while the characteristic absorption at 2140 cm.$^{-1}$ can be attributed to carbon monoxide.

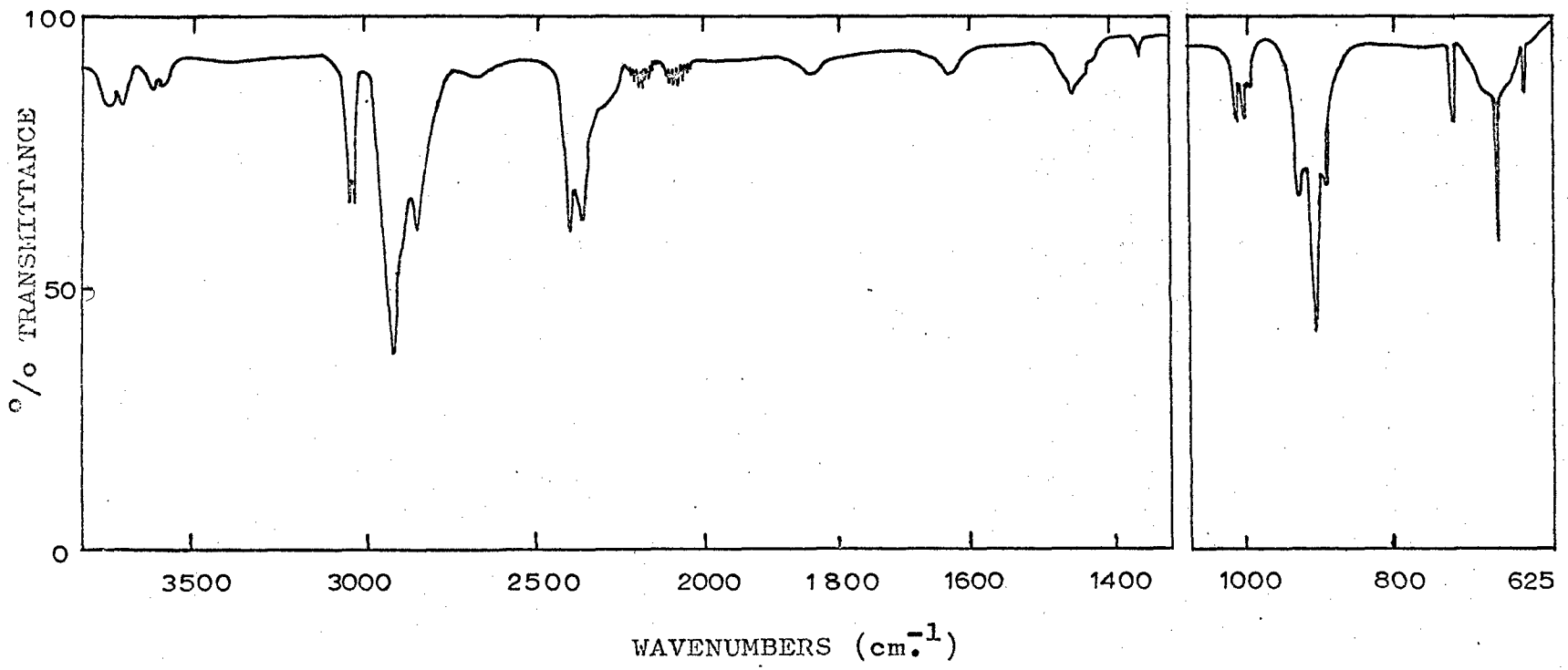


Figure 42. Infra-red spectrum of a 93.4 mole percent n-butyl acrylate copolymer degraded for 12.5 hours at 313°C.

Table 24.

Assignments of the Infra-red Absorptions Shown in Fig. 42.

Wavenumber, $cm.^{-1}$	Intensity	Assignment
3090	m	C—H stretch in =C—H
2970 2940 2898 2878	s	C—H stretch in $-CH_3$ and $-CH_2-$
2350	s	CO_2 antisymmetric stretch
2140	w	C≡O stretch
1835	w	overtone of peak at $912 cm.^{-1}$
1650	m	C=C stretch
1470	m	C—H deformation in $-CH_2-$ and $-C-CH_3$
1309	vw	C—H deformation in $-CH=C-$
998	m	C—H deformation in $-CH=C-$
912	s	CH_2 deformation in $=CH_2$
677	s	CO_2 bend

s = strong m = medium w = weak vw = very weak

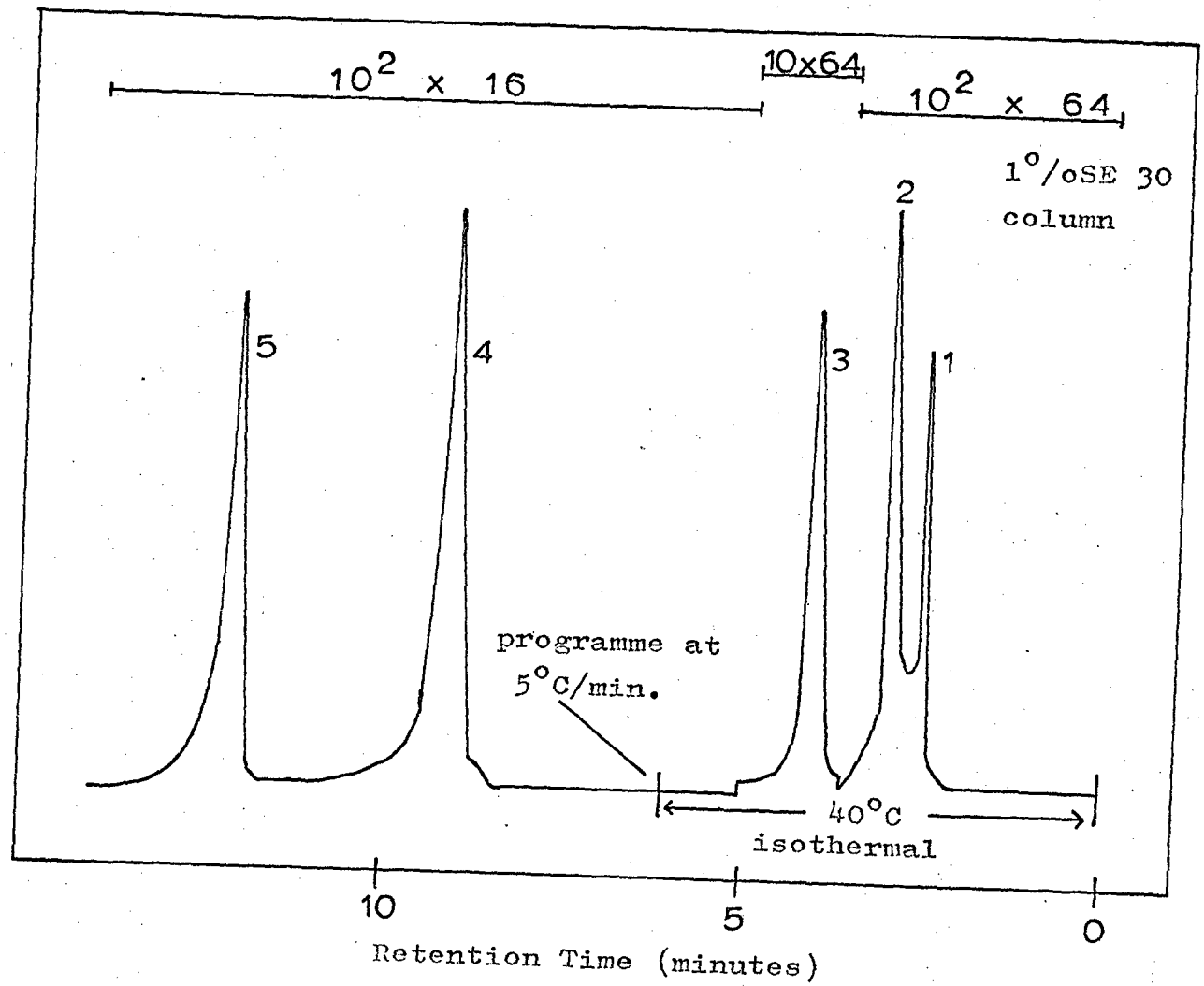


Figure 43. G.L.C. trace of the liquid degradation products from the breakdown of a 50.0 mole percent n-butyl acrylate copolymer heated at 313°C for 4 hours.

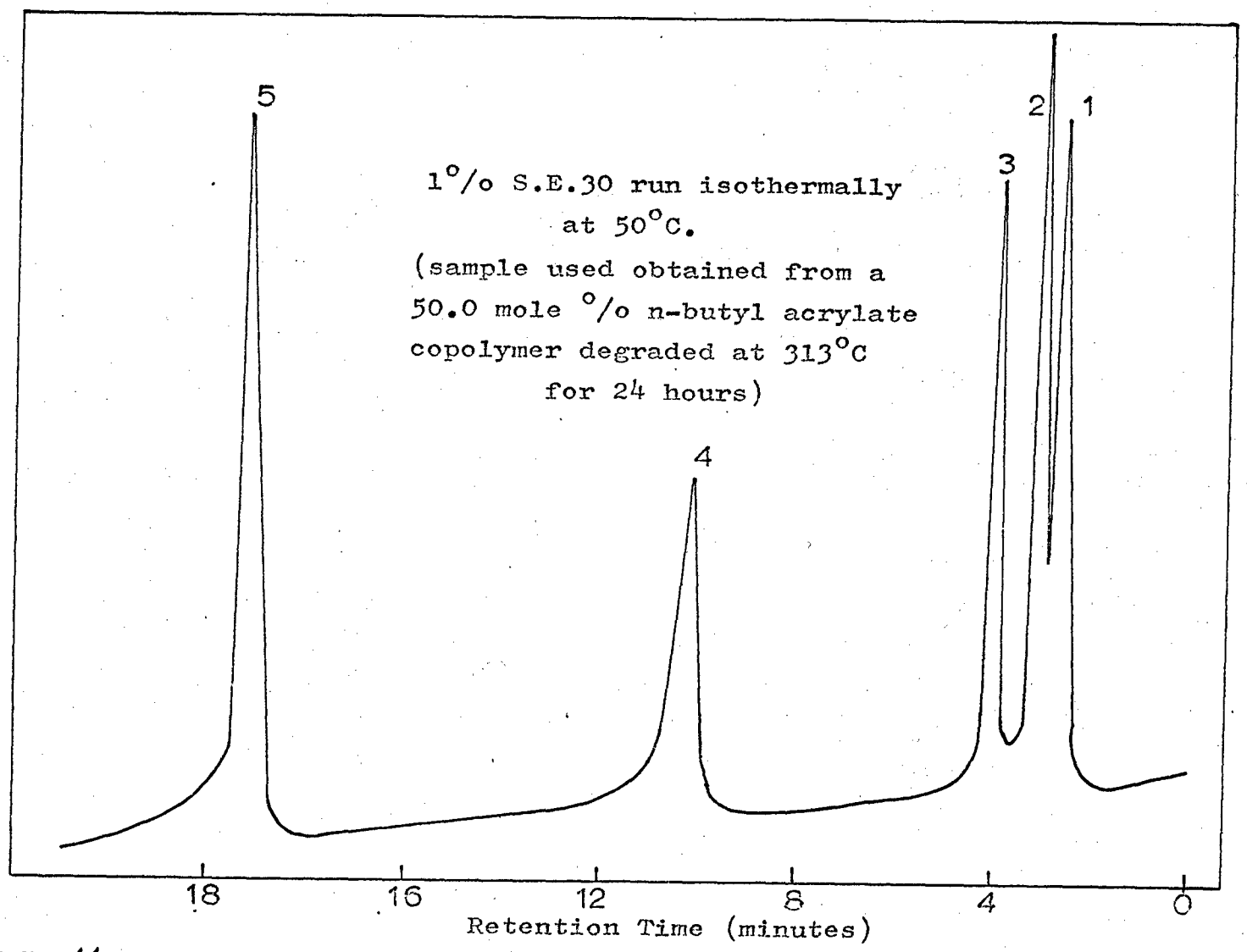


Figure 44. G.L.C. trace from G.C.M.S. of liquid degradation products.

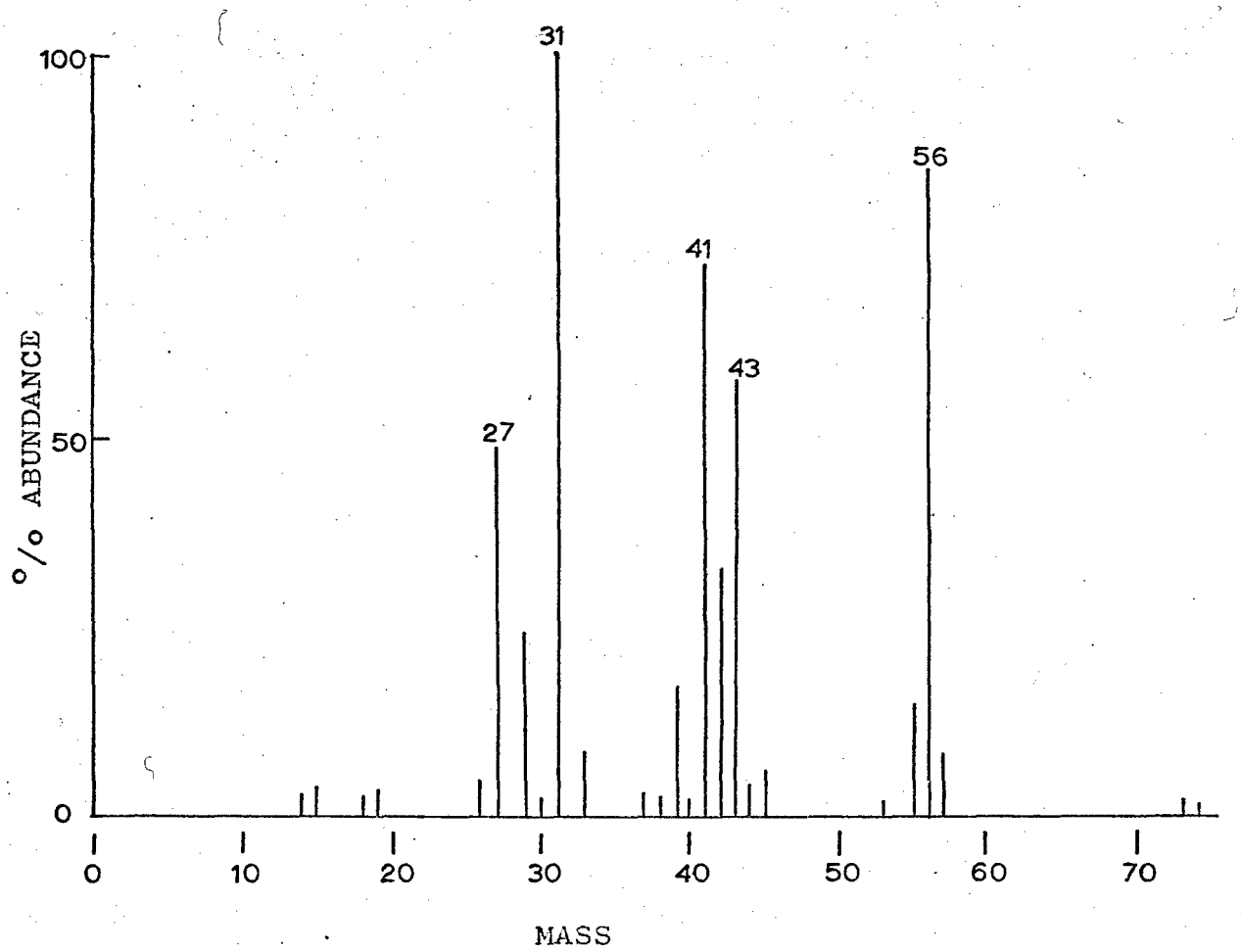


Figure 45. Mass spectrum of component 1 in Fig. 44 (n-butanol)

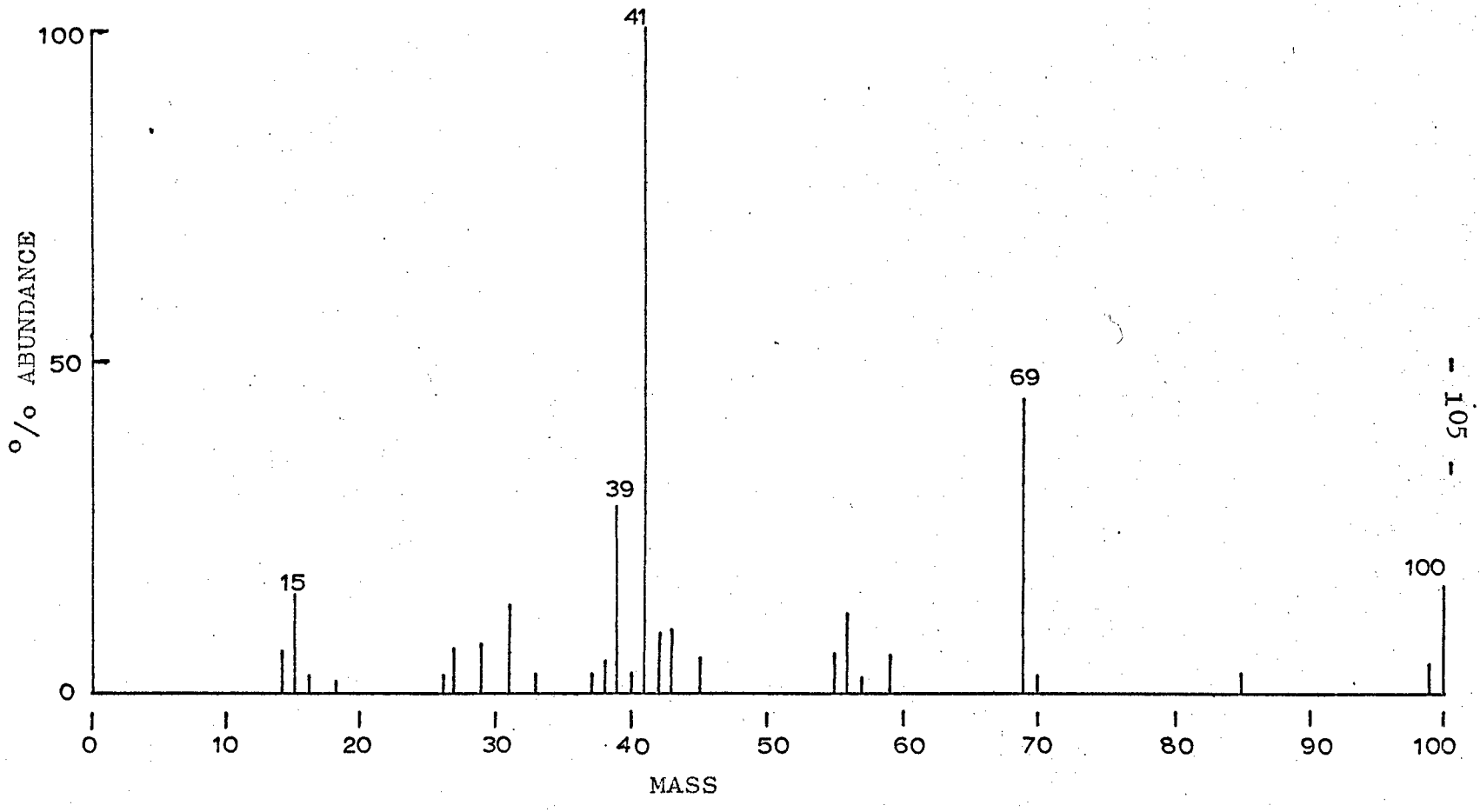


Figure 46. Mass spectrum of component 2 in Fig. 44 (methyl methacrylate)

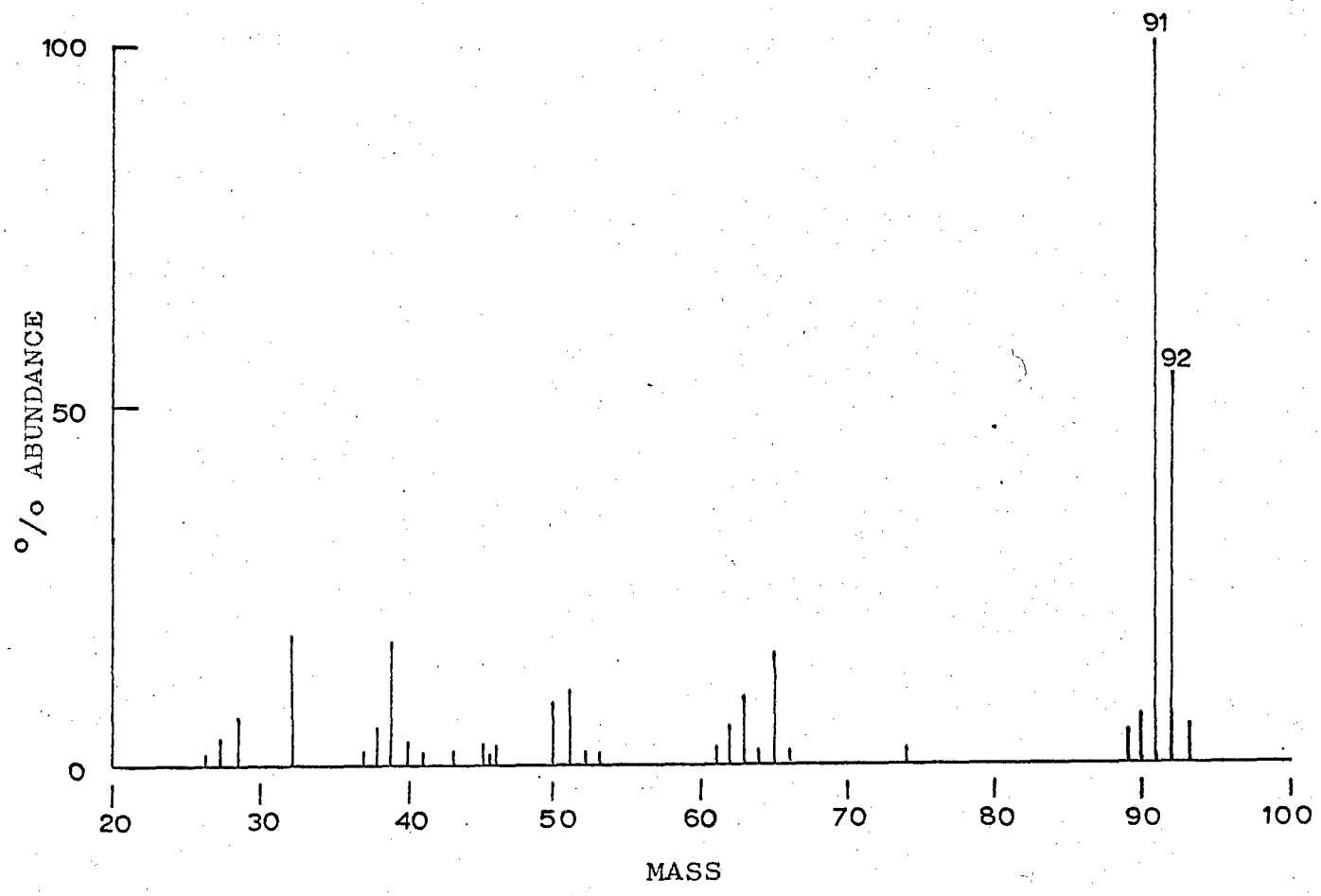


Figure 47. Mass spectrum of component 3 in Fig. 44 (toluene)

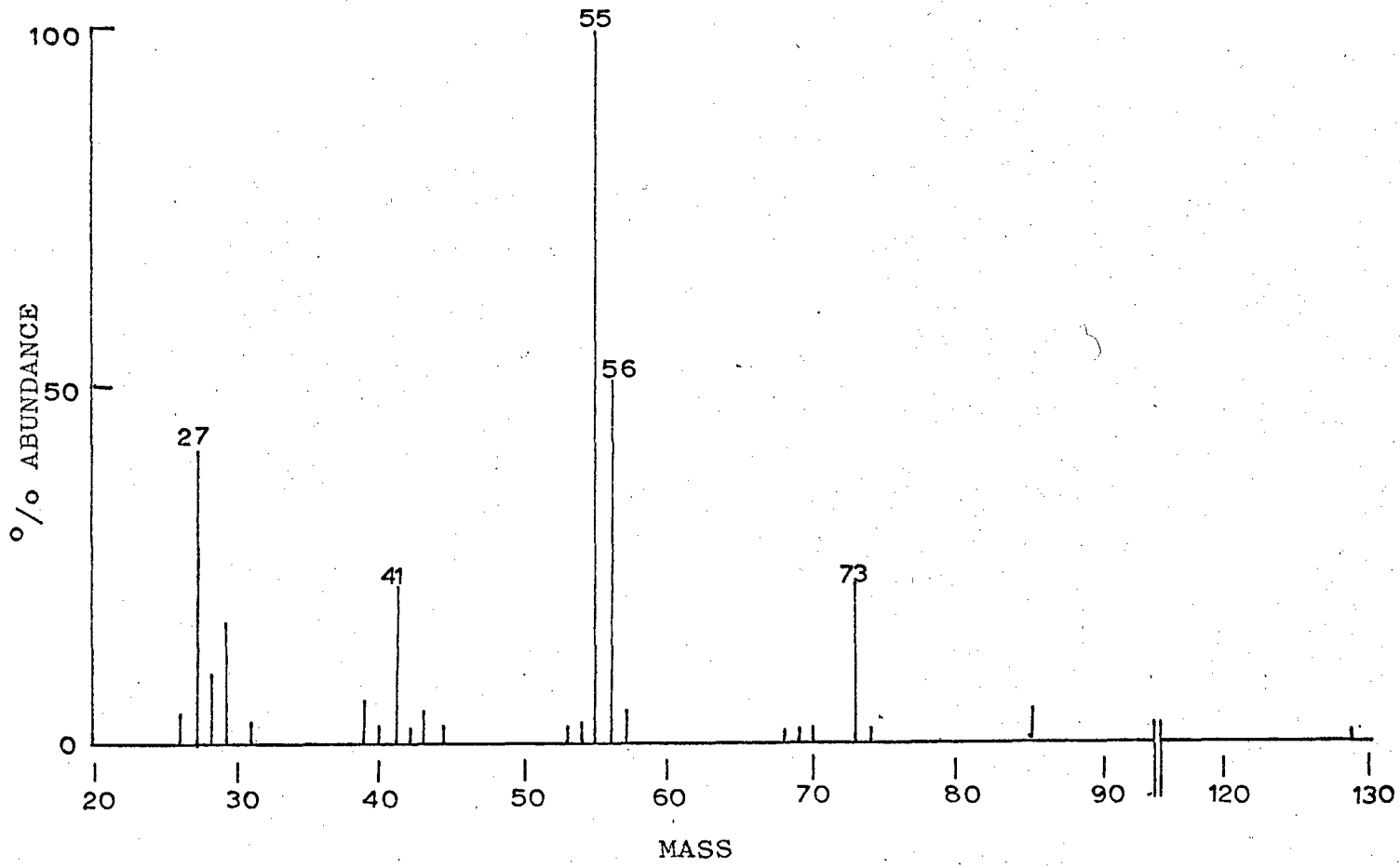


Figure 48. Mass spectrum of component 4 in Fig. 44 (n-butyl acrylate)

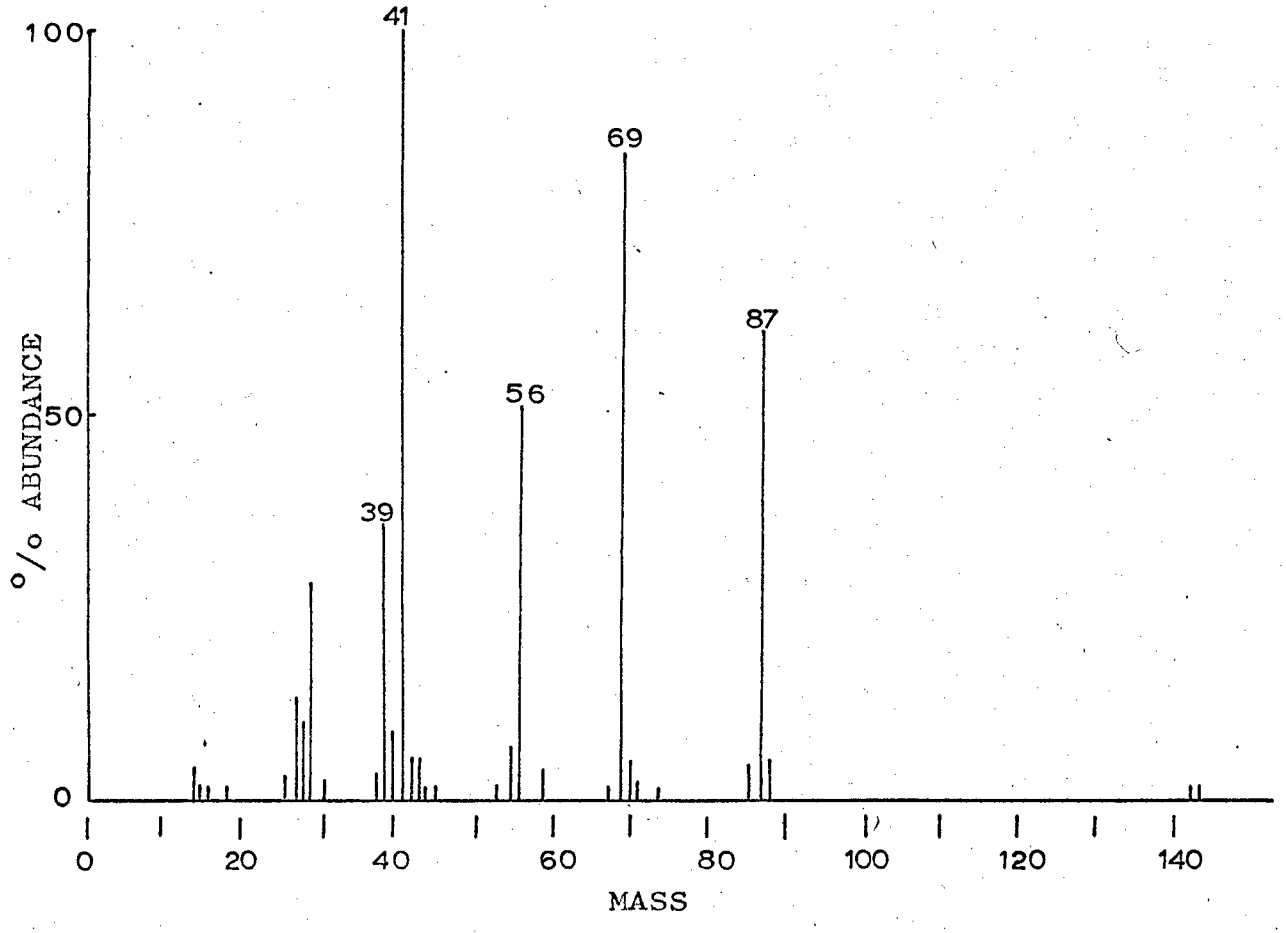


Figure 49. Mass spectrum of component 5 in Fig. 44 (n-butyl methacrylate)

molecular ion due to the abstraction of a proton from a neutral molecule. Since the percentage abundance of the molecular ion depends upon its stability to further decomposition, aromatic compounds give rise to very abundant molecular ion peaks because of the presence of the π electron system (Fig. 47). The most abundant masses in each spectrum are listed in the order of their relative abundance in table 26.

TABLE 26

Suspected Compound	Mass
n-butanol	31,56,41,43,27.
Methyl Methacrylate	41,69,39,100,15.
Toluene (solvent)	91,92.
n-Butyl Acrylate	55,56,27,73,41.
n-Butyl Methacrylate	41,69,87,56,39.

Assignment of these major fragments is most conveniently done by looking in some detail at one compound, and seeing how similar mechanisms might be extended to other structures. The first compound to be examined was n-butyl methacrylate.

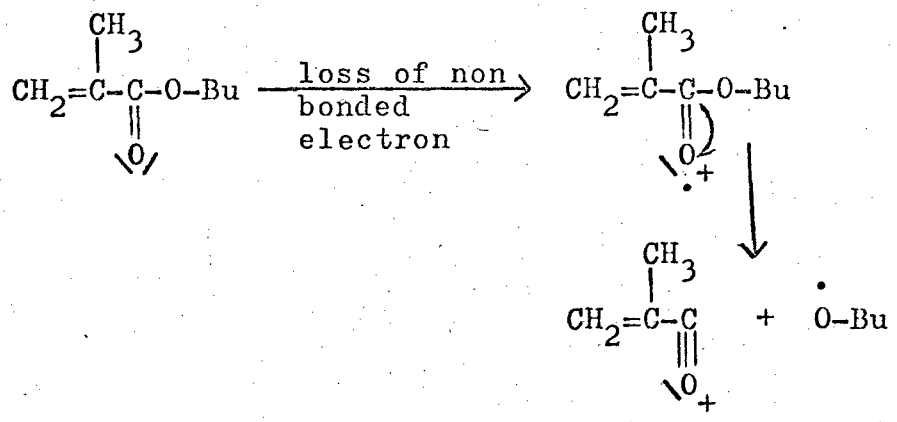
Some common fragmentation processes are (55),

i. Simple fission in which a neutral fragment is lost by the breaking of one bond.

ii. Rearrangement processes in which more than one bond fission occurs accompanied by transfer of one hydrogen atom from one atom to another within the decomposing ion.

iii. Double rearrangement processes in which two hydrogen atoms are transferred simultaneously from the neutral fragment being lost to the fragment ion being formed.

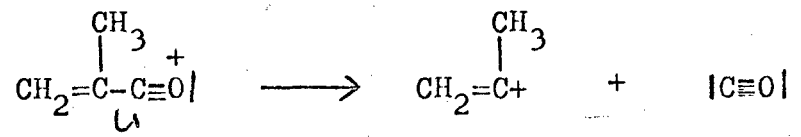
Considering the mass spectrum of n-butyl methacrylate, the fragments of masses 41 and 69 may be accounted for by simple fission. Where such fission occurs a neutral radical is eliminated from the molecular ion. Firstly, a non-bonded electron is lost from the ester carbonyl oxygen atom followed by transfer of an electron to the positively charged site from the α bond. This process is therefore called α fission.



69

(A double headed arrow is used here to mean the transfer of two electrons, while a single headed arrow means the transfer of one electron. The symbol Bu denotes an n-butyl group).

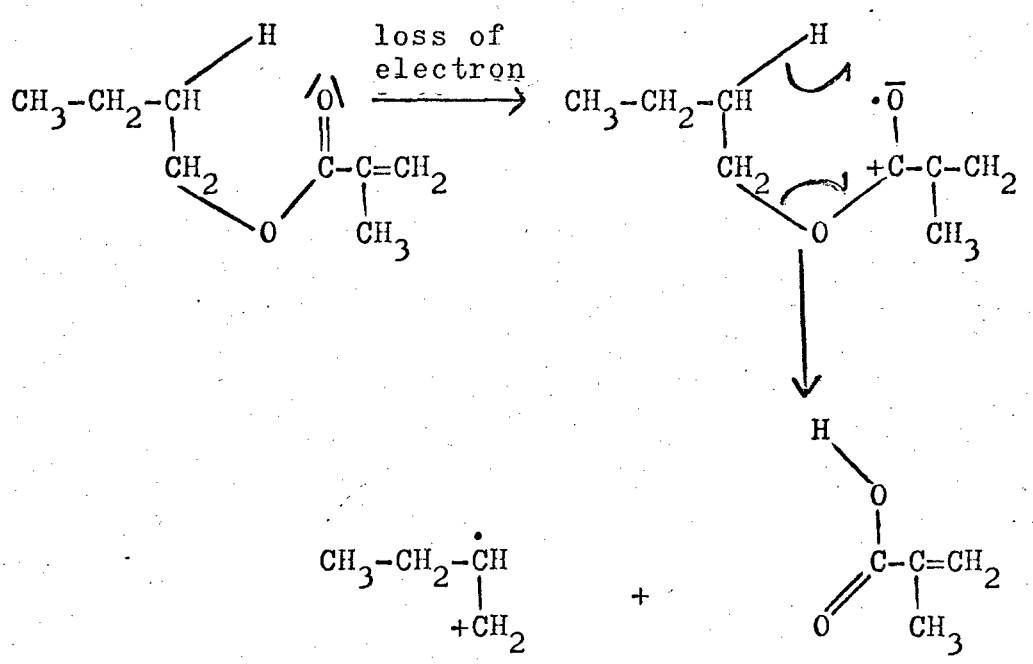
A neutral molecule may then be eliminated from the fragment ion by cleavage of a single bond, the mechanism involving a two electron shift.



41

This process is known as fragment ion fission.

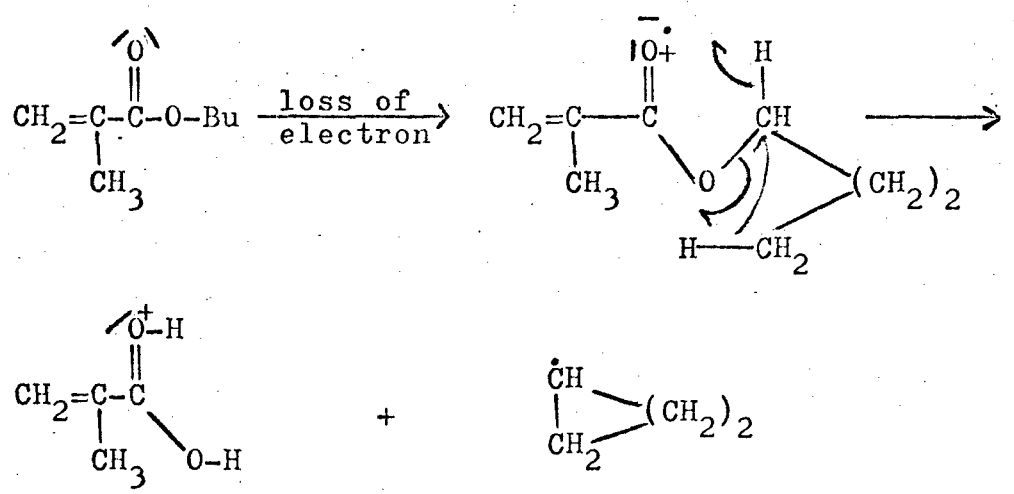
A rearrangement process can be used to explain the fragment of mass 56. The most generally applicable specific rearrangement process is called the McLafferty rearrangement. The essentials are a double bond which has a γ hydrogen available for migration.



56

After the loss of an electron from the carbonyl bond the rearrangement proceeds with a proton transfer from the γ carbon and a transfer of two electrons as shown above completes the reaction.

Double rearrangement processes are important in the breakdown of almost every ester greater than methyl. The process, involving the simultaneous rearrangement of two hydrogen atoms, may be represented as follows.



87

In the saturated hydrocarbon fission processes occur as shown below

$$(R_3C\text{-}CR_3)^{+\cdot} \longrightarrow R_3C^+ + \dot{C}R_3$$

Such fissions can occur in the n-butyl side chain of the ester. The spectrum will show a series of peaks at odd masses corresponding to the above fission, appearing at masses corresponding to C_nH_{2n+1}. Random processes may also take place whereby a molecule of hydrogen is lost from the fragment ion. Such reactions can explain the peak at mass 39 so far not accounted for in table 26 for n-butyl methacrylate.

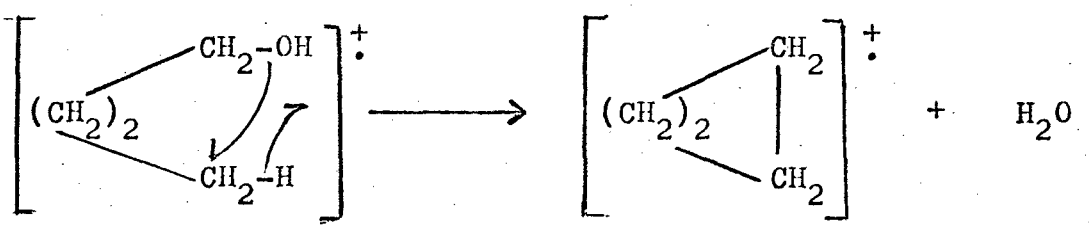
It should be noted that several mechanisms may be invoked to account for a given mass number. Mass 41 for example may be ascribed to the fragment $[CH_2{=}C\text{-}CH_3]^+$ from the fission of the fragment ion $R\text{-}C{\equiv}O^+$ or by scission of the n-butyl side chain followed by hydrogen elimination from the fragment $CH_3\text{-}CH_2\text{-}\overset{+}{C}H_2$.

The reaction schemes detailed above may be used to explain the presence of all of the fragments listed for the esters in table 26. Only two spectra, those of n-butanol and toluene, require further investigation.

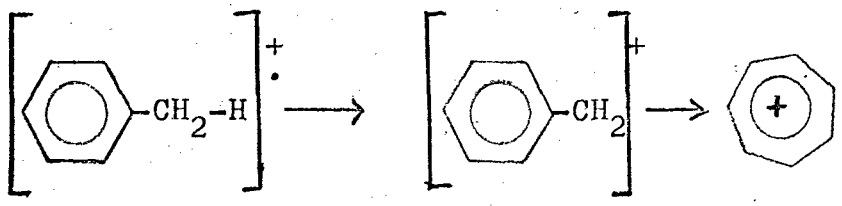
Fission of the bond α to the hydroxyl group of n-butanol leads to a fragment of mass 31.

$$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}\overset{+\cdot}{O}H \longrightarrow CH_3\text{-}CH_2\text{-}\dot{C}H_2 + \underset{31}{CH_2\text{-}\overset{+}{O}H}$$

Random rearrangement of the molecular ion leads to loss of water giving a peak at M-18 = 56



The solvent, toluene, gives two major peaks. 92 is the mass of the parent ion, while β fission yields a peak at mass 91.



Tropylium Ion, mass 91.

The driving force is the high stability of the resulting aromatic ion. A summary of the mechanisms discussed above applied to all the mass spectra considered is given in table 27, while, for each compound, a list of possible structures corresponding to the masses noted in table 26 is shown in table 28.

It has been shown that the degradation products suggested on the basis of retention times can be used to give a reasonable account of the main features of the observed mass spectra. Pure samples of each of the compounds listed in table 25 were injected separately into the L.K.B. mass spectrometer. The mass spectra obtained were identical to those shown in Figs. 45-49.

TABLE 27

Component	Parent Ion	Fragmentation Process		
		Simple Fission	Rearrangement	Double Rearrangement
n-Butanol	74	43,41,31, 27	56	-
Methyl Methacrylate	100	69,41,39, 15	-	-
Toluene	92	91	-	-
n-Butyl Acrylate	128	55,41,27	56	73
n-Butyl Methacrylate	142	69,41,39	56	87

TABLE 28

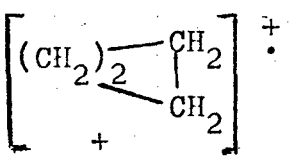
n-Butyl Acrylate

Mass	Structure
55	$CH_2{=}CH{-}C{\equiv}O^+$
56	$[CH_3{-}CH_2{-}CH{=}CH_2]^{+\cdot}$
27	$CH_2{=}CH^+$
73	$CH_2{=}CH{-}C(OH){=}\overset{+}{O}H$
41	$CH_2{=}\overset{+}{C}{-}CH_3$

n-Butyl Methacrylate

Mass	Structure
41	$CH_2{=}\overset{+}{C}{-}CH_3$
69	$CH_2{=}C(CH_3){-}C{\equiv}O^+$
87	$CH_2{=}C(CH_3){-}C(OH){=}\overset{+}{O}H$
56	$[CH_3{-}CH_2{-}CH{-}CH_2]^{+\cdot}$
39	$CH_2{=}C{=}\overset{+}{C}H$

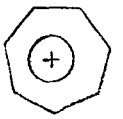
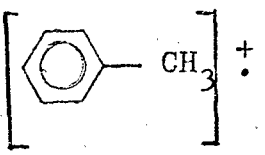
n-Butanol

Mass	Structure
31	$CH_2{=}\overset{+}{O}H$
56	
41	$CH_2{=}\overset{+}{C}{-}CH_3$
43	$CH_3{-}\overset{+}{C}H{-}CH_3$
27	$CH_2{=}\overset{+}{C}H$

Methyl Methacrylate

Mass	Structure
41	$CH_2{=}\overset{+}{C}{-}CH_3$
69	$CH_2{=}C(CH_3){-}C{\equiv}O^+$
39	$CH_2{=}C{=}\overset{+}{C}H$
100	$[CH_2{=}C(CH_3){-}C(=O){-}OCH_3]^{+\cdot}$
15	CH_3^+

Toluene

Mass	Structure
91	 Tropylium Ion
92	

CHAPTER 9

THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. D. QUANTITATIVE ANALYSIS OF LIQUID AND GASEOUS PRODUCTS.

INTRODUCTION

In the previous chapter the identification of the degradation products was described. It was appropriate to follow this up by quantitative measurements.

The degradations studied were all carried out by the sealed tube technique (chapter 6) at two temperatures, 313°C and 332°C, so that the effect of both composition and temperature of degradation on the pattern of breakdown could be observed. A detailed analysis of the gaseous and liquid decomposition products is given, the investigation of the residue and chain fragments being described in the following chapter.

ANALYSIS OF THE GASEOUS DEGRADATION PRODUCTS

Analytical Techniques

Gas Chromatography

The trace obtained using a silica gel column to analyze the gases evolved on the breakdown of a 50 mole percent n-butyl acrylate copolymer heated for eleven hours at 313°C was shown in Fig. 38. From the trace it would appear that the major product is butene, provided that the sensitivity of the detector to each of the gases examined is of the same order of magnitude. A determination of these sensitivity factors was made by analyzing mixtures of the pure gases containing known amounts of each of the components. The sensitivity factor for a particular gas, k, relative to some standard, in this case but-1-ene, was defined as the ratio of the areas of the gas and but-1-ene peaks when equal pressures of gas and but-1-ene are considered.

$$k = \left(\frac{\text{area of gas peak}}{\text{area of but-1-ene peak}}\right)\left(\frac{\text{pressure of but-1-ene}}{\text{pressure of gas}}\right)$$

Sensitivity factors are listed in table 29 and used in this context to calculate the relative pressures of the various gases present, taking the pressure of butene as 100. Since propylene and n-butane are not separated, an average value of the appropriate sensitivity factors was used. It was not necessary to carry out systematically such a detailed analysis on the other copolymers, as it is sufficient to show that the but-1-ene peak is by far the largest, so that its exact relationship to the other gases determined by this method is of little consequence. The value quoted in table 29 for methane is of necessity lower than that actually present in the evolved gases, since distillation under liquid nitrogen was involved in preparing these product gases for g.l.c. analysis. Remembering that to examine the permanent gases at all, large sample sizes were required, it may be concluded that methane is a minor degradation product in comparison to butene.

TABLE 29. G.L.C. Data for a 50·0 Mole Percent n-Butyl Acrylate Copolymer Degraded at 313°C for 11 Hours.

Gas	Area of Gas Peak / Area of Butene Peak	Sensitivity Factor, k, Relative to But-1-ene	Pressure Relative to Butene
Methane	0·23	0·60	0·38
Ethane	0·03	0·96	0·03
Ethylene	0·05	0·70	0·07
Propane	0·04	1·54	0·03
Propylene n-Butane	1·12	0·98) 1·80) 1·39	1·01
Butene	100·00	1·00	100·00

The isomeric butenes were separated using a benzyl cyanide - silver nitrate column, (table 15) and the trace obtained for the degradation products from a 16·3 mole percent n-butyl acrylate copolymer at 313°C was shown in Fig. 39. It is to be expected that the sensitivities of the detector to the butenes would be about the same, and this was confirmed by once again making up standard mixtures of pure gases. The results are quoted in table 30 which also lists the relative pressures of gases found from the trace of Fig. 39, assuming the pressure of but-1-ene to be 100. Once more no detailed

experiments were carried out routinely on the other copolymers, it being sufficient to show that but-1-ene is the predominant isomer present.

TABLE 30. G.L.C. Data for a 16·3 Mole Percent n-Butyl Acrylate Copolymer Degraded at 313°C for 16 hours.

Gas	Area of Gas Peak / Area of But-1-ene Peak	Sensitivity Factor, k, Relative to But-1-ene	Pressure Relative to But-1-ene
Trans But-2-ene	4·42	0·91	4·86
But-1-ene	100·00	1·00	100·00
Cis But-2-ene	4·08	1·01	4·04

Although the permanent gases make only a very small contribution to the measured total gas pressure, it was considered of interest to examine in a semi-quantitative fashion the relative amounts of carbon monoxide, methane, and hydrogen present. The column employed was silica gel used as specified in table 15. Taking the height of the peak due to carbon monoxide as unity, the results are shown in table 31. This table also lists the relative height of the peaks shown in Fig. 22, obtained from the degradation of 1·5 g. of a 52·4 mole percent n-butyl acrylate copolymer degraded at 313°C for twenty-four hours, and gives the pressure of each gas relative to carbon monoxide as 100. No further investigation of the permanent gases was undertaken.

TABLE 31. Data for a 52·4 Mole Percent n-Butyl Acrylate Copolymer Degraded at 313°C for 24 hours.

Gas	Height of Gas Peak / Height of CO Peak	Peak Height for One Atmosphere of Gas Relative to CO	Pressure Relative to CO
Hydrogen	200	10·6	18·9
Carbon Monoxide	100	1·0	100·0
Methane	80	1·3	61·6

Infra-Red Spectroscopy

Plots of optical density versus pressure were made for pure samples of but-1-ene and carbon dioxide and these are shown in Fig. 50. The use of these plots establishes that these gases constitute the major part of the gaseous degradation products, since such analyses show that the total pressure of evolved gases may be accounted for by carbon dioxide and butene alone. This greatly simplifies the quantitative analysis of the gaseous breakdown products since, routinely, infra-red measurements are all that are required.

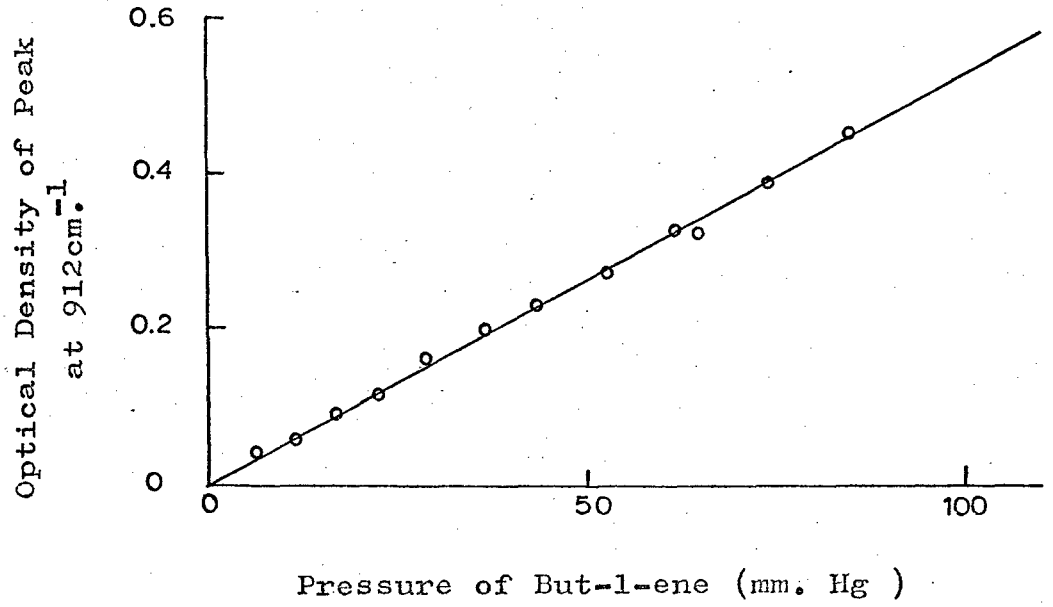
Treatment of Results

The method of examining the gases mentioned in chapter 6 involves a pressure measurement of total gas on the constant volume manometer, P_{total}. The pressures attributed to carbon dioxide and but-1-ene read from the calibration curves of Fig. 50, were found generally to come to about 5-15% more than the total gas pressure as found using the manometer. This same effect has been reported in connection with measurements of the gaseous products of decomposition of polyacrylates (2). Thus infra-red data were used to find the ratio of the pressures of carbon dioxide, (P_{CO_2}), to but-1-ene, ($P_{but-1-ene}$). Corrected pressures, CP_{CO_2} and $CP_{but-1-ene}$, were found for each of these gases such that,

$$\frac{CP_{CO_2}}{CP_{but-1-ene}} = \frac{P_{CO_2}}{P_{but-1-ene}} \quad \ldots\ldots\ldots\ldots [11]$$

and $$P_{total} = CP_{CO_2} + CP_{but-1-ene} \quad \ldots\ldots\ldots\ldots [12]$$

A typical calculation for a 16·3 mole percent n-butyl acrylate copolymer degraded at 313°C involves plotting total gas pressure, P_{total}, against time of degradation, then reading off values, P'_{total}, from this curve at suitable intervals, in this case two hour periods. Graphs of P_{CO_2} and $P_{but-1-ene}$ are then plotted from the infra-red data, and values, P'_{CO_2} and $P'_{but-1-ene}$, read off from these curves every two hours. From these measurements, values of CP_{CO_2} and $CP'_{but-1-ene}$ are calculated throughout the degradation from equations [11] and [12]. These plots are shown in Fig. 51 and the data presented in table 32. A similar treatment was used for all the other copolymers examined. Plots of total gas pressure, carbon dioxide pressure and but-1-ene pressure are given in Figs. 52-57, and the data shown in tables 33-38.



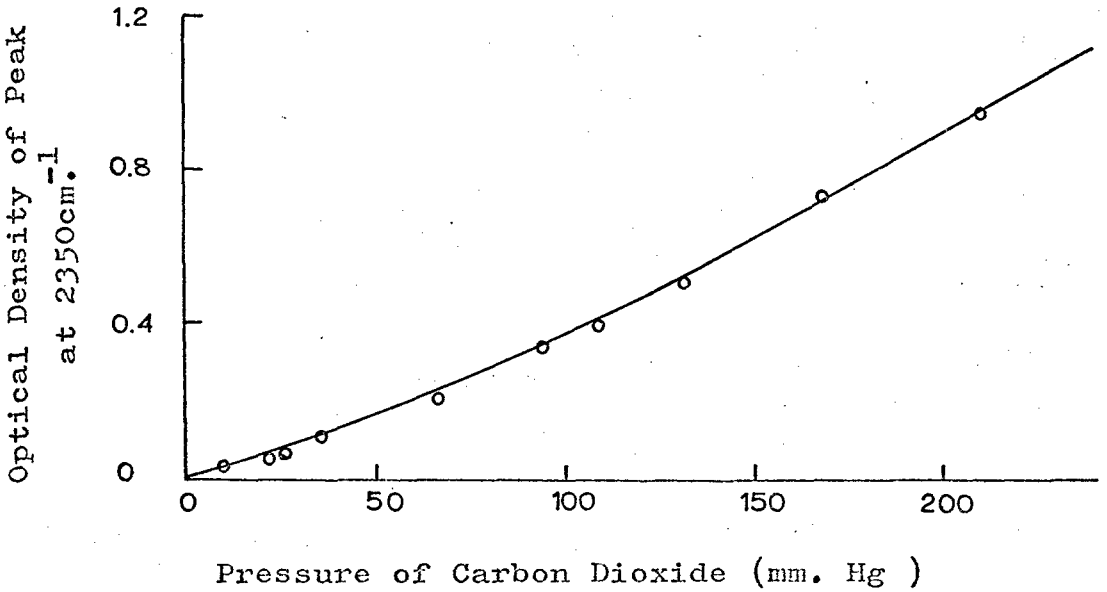
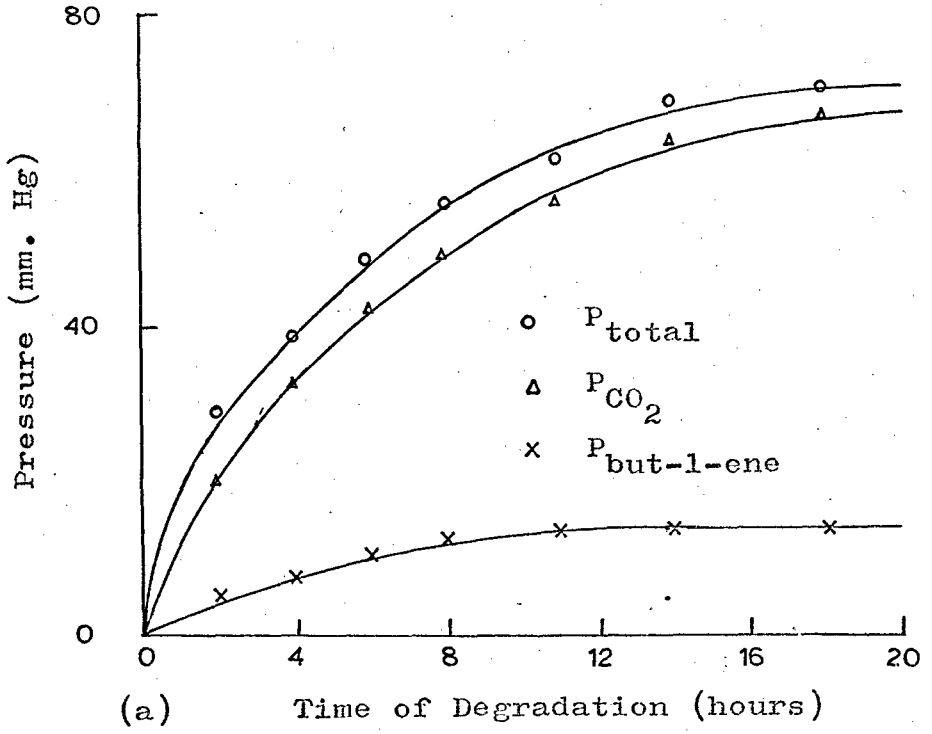


Figure 50. Infra-red Calibration Curves for But-1-ene and Carbon Dioxide.



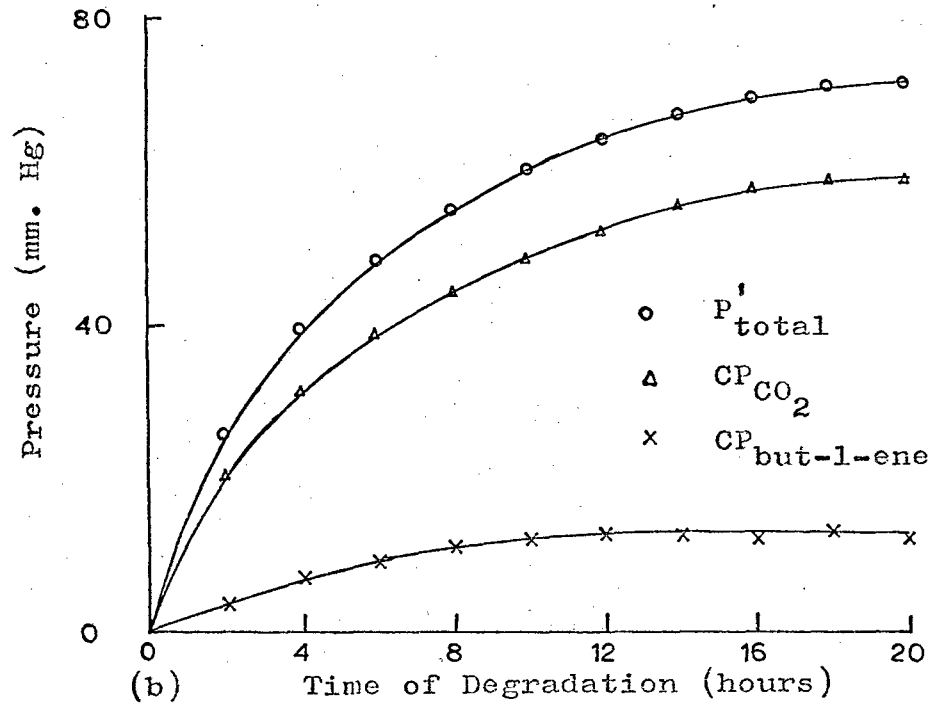


Figure 51. Gas pressure plots for a 16.3 mole percent n-butyl acrylate copolymer degraded at 313°C.

Table 32.

Gas Evolution Data for a 16.3 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	2	4	6	8	11	14	18	
P_{total}	28.8	38.8	48.8	56.0	61.8	69.2	70.5	Initial Polymer Weight = 0.331g.
P_{CO_2}	20.0	32.2	42.6	49.2	56.0	64.0	67.3	
$P_{but-1-ene}$	5.1	7.6	10.8	12.9	13.4	13.7	14.2	

Time of Degradation, hours	2	4	6	8	10	12	14	16	18	∞
P'_{total} (Fig.51)	25.5	39.0	48.0	55.0	60.0	64.0	67.3	69.8	71.0	71.0
P'_{CO_2} (Fig.51)	20.0	33.0	42.0	49.6	55.3	59.5	63.0	65.5	67.0	68.0
$P'_{but-1-ene}$ (Fig.51)	4.6	8.0	10.4	12.1	13.2	13.8	14.0	14.0	14.0	14.0
CP_{CO_2}	20.7	31.4	38.5	44.2	48.4	52.0	55.1	57.5	58.7	58.9
$CP_{but-1-ene}$	4.8	7.6	9.5	10.8	11.6	12.0	12.2	12.3	12.3	12.1
m.moles CO_2 per g. polymer	.184	.278	.341	.393	.429	.459	.486	.511	.520	.523
m.moles but-1-ene per g. polymer	.042	.067	.085	.097	.103	.106	.109	.109	.109	.109
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	1.0	1.6	2.0	2.3	2.5	2.6	2.8	2.9	2.9	2.9

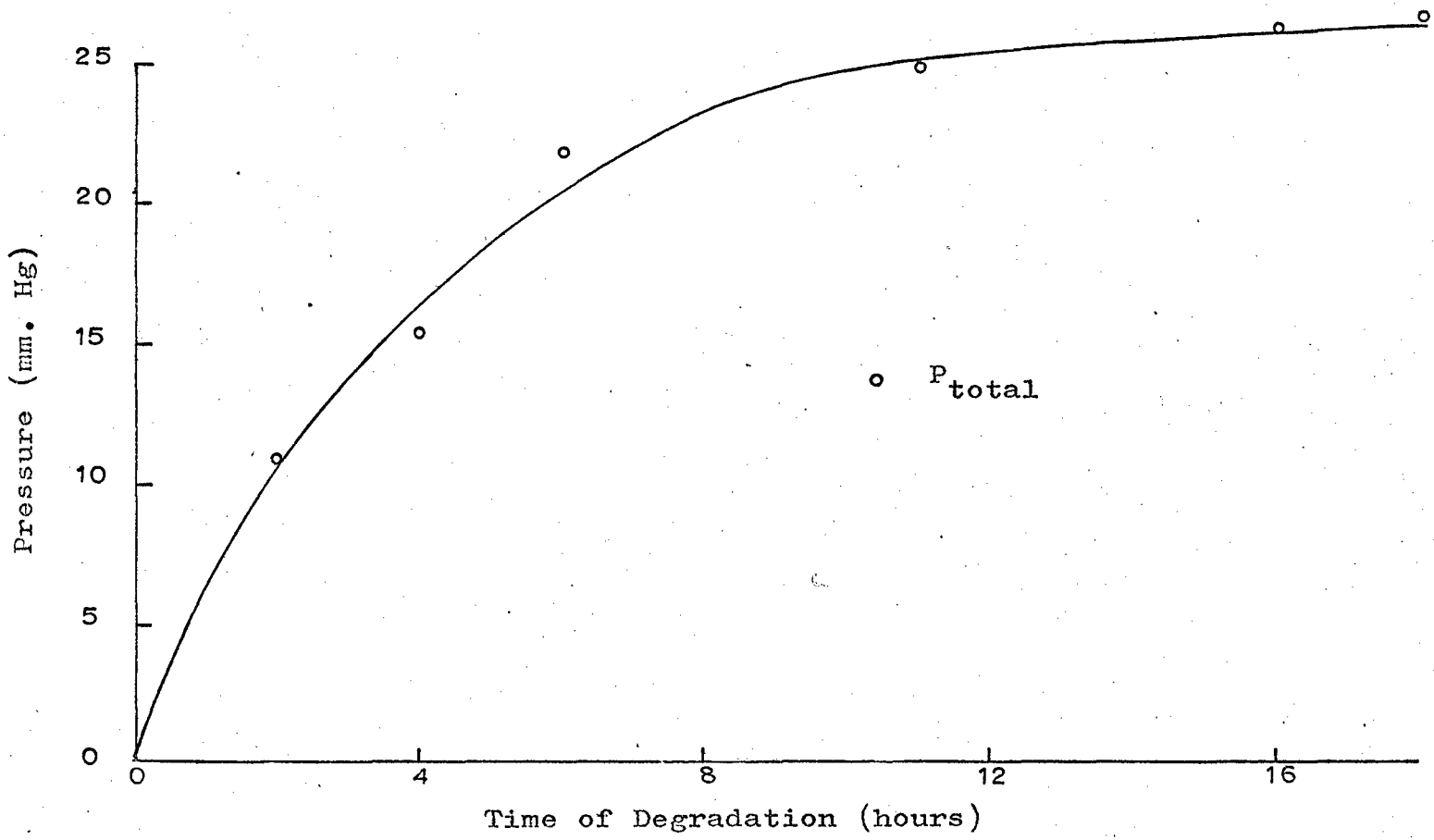


Figure 52. Gas pressure plot for a 3.9 mole percent n-butyl acrylate copolymer degraded at 313°C.

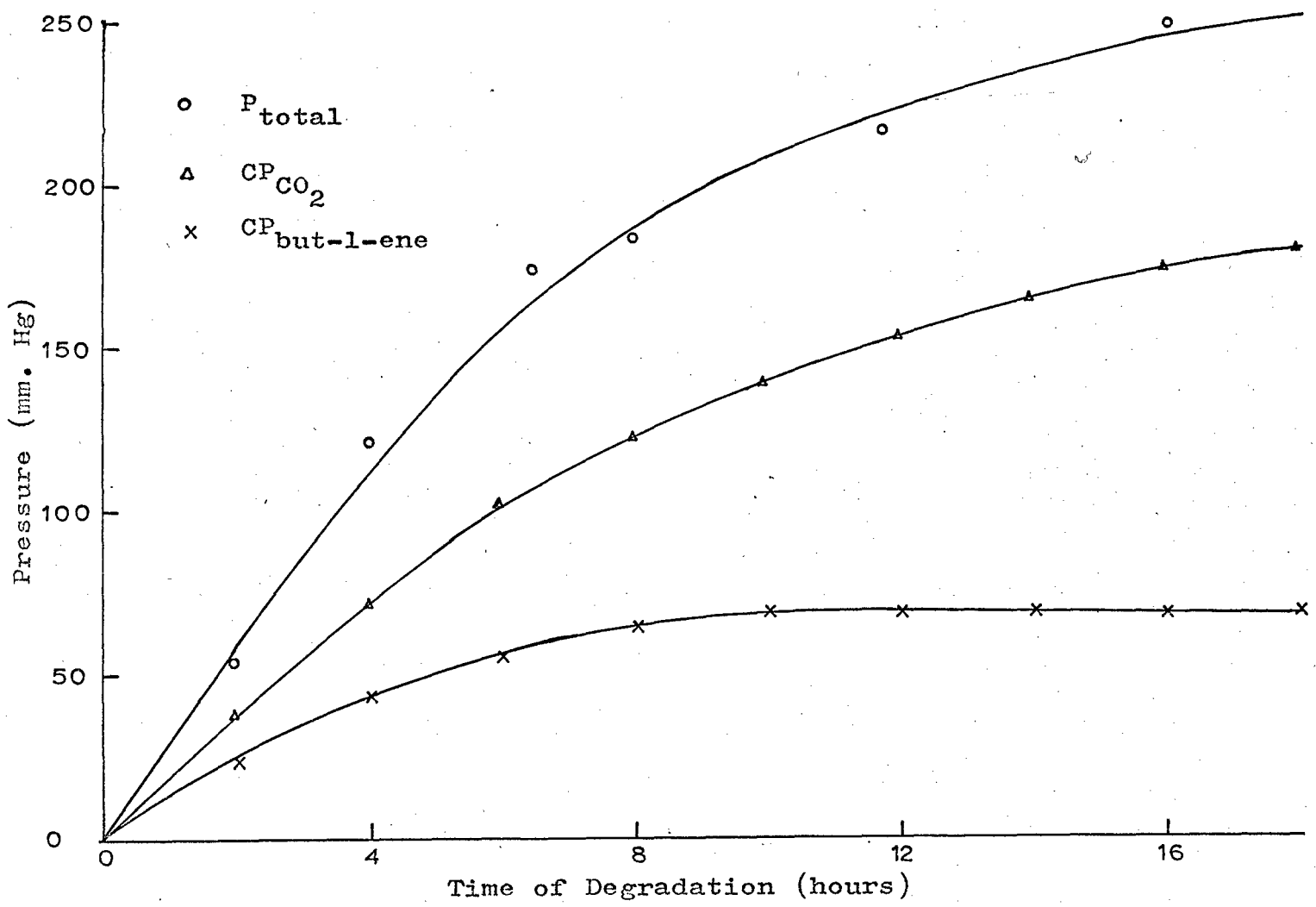


Figure 53. Gas pressure plots for a 50.0 mole percent n-butyl acrylate copolymer degraded at 313°C.

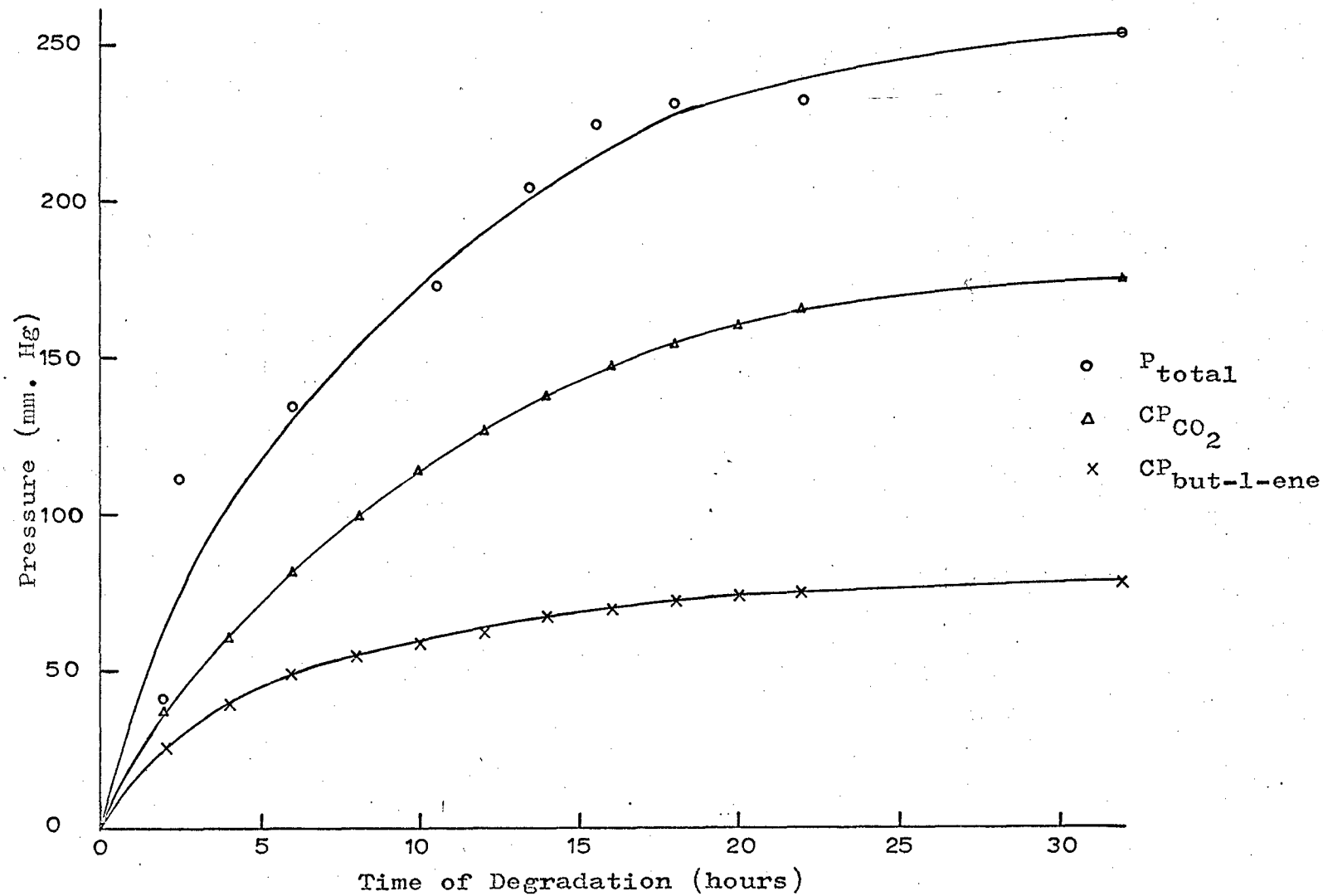


Figure 54. Gas pressure plots for an 82.2 mole percent n-butyl acrylate copolymer degraded at 313°C.

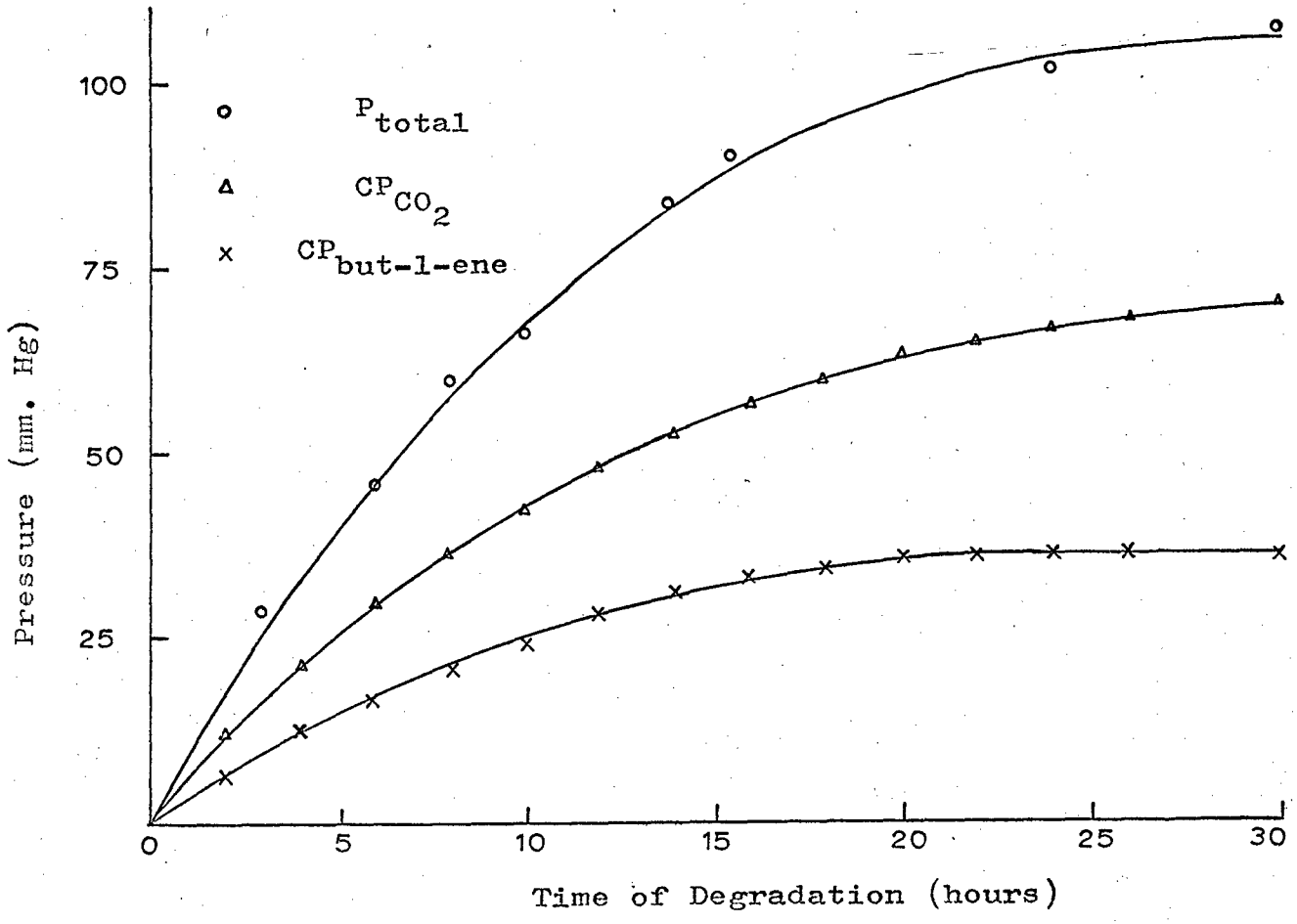


Figure 55. Gas pressure plots for a 93.4 mole percent n-butyl acrylate copolymer degraded at 313°C.

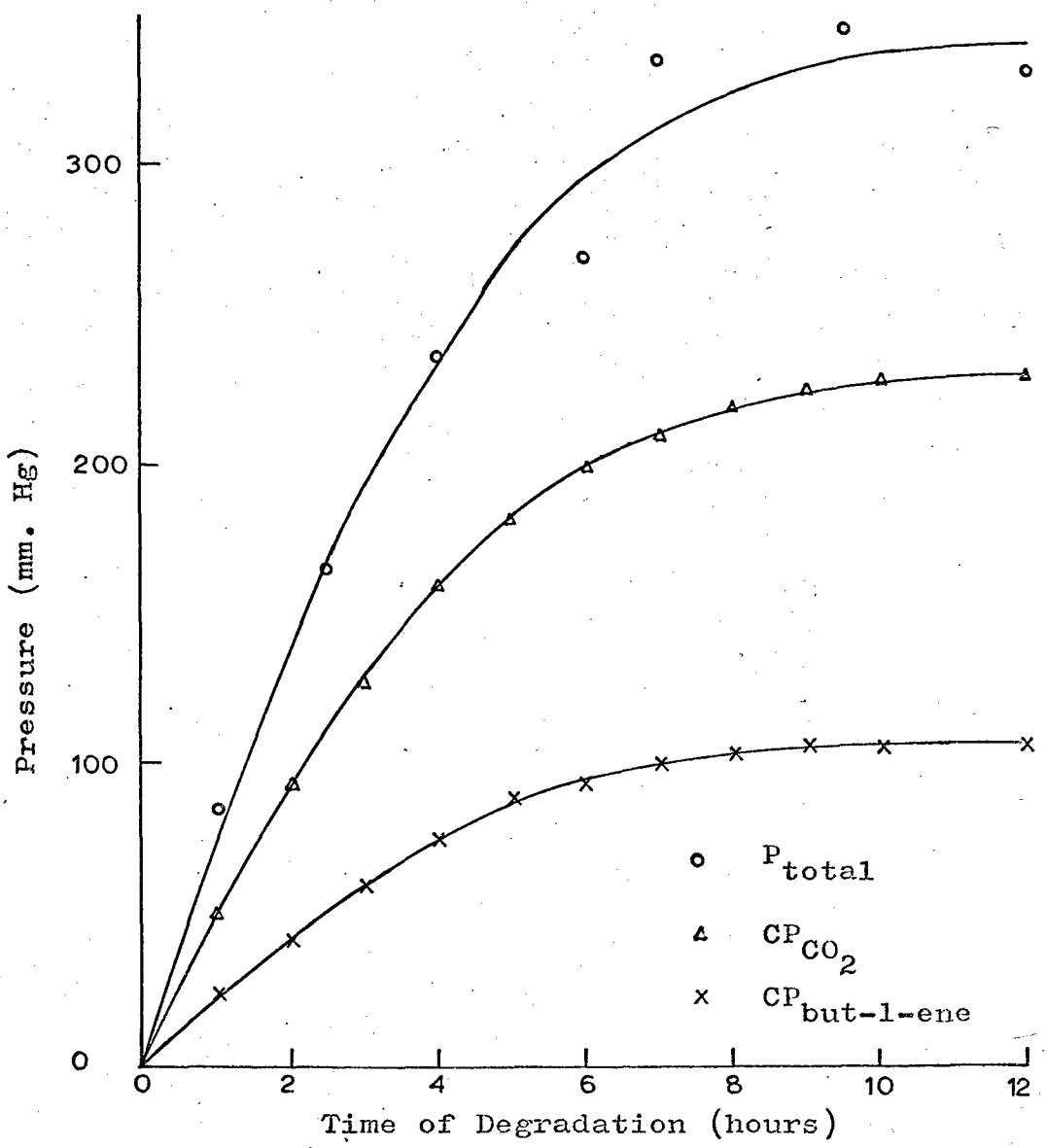


Figure 56. Gas pressure plots for a 50.0 mole percent n-butyl acrylate copolymer degraded at 332°C.

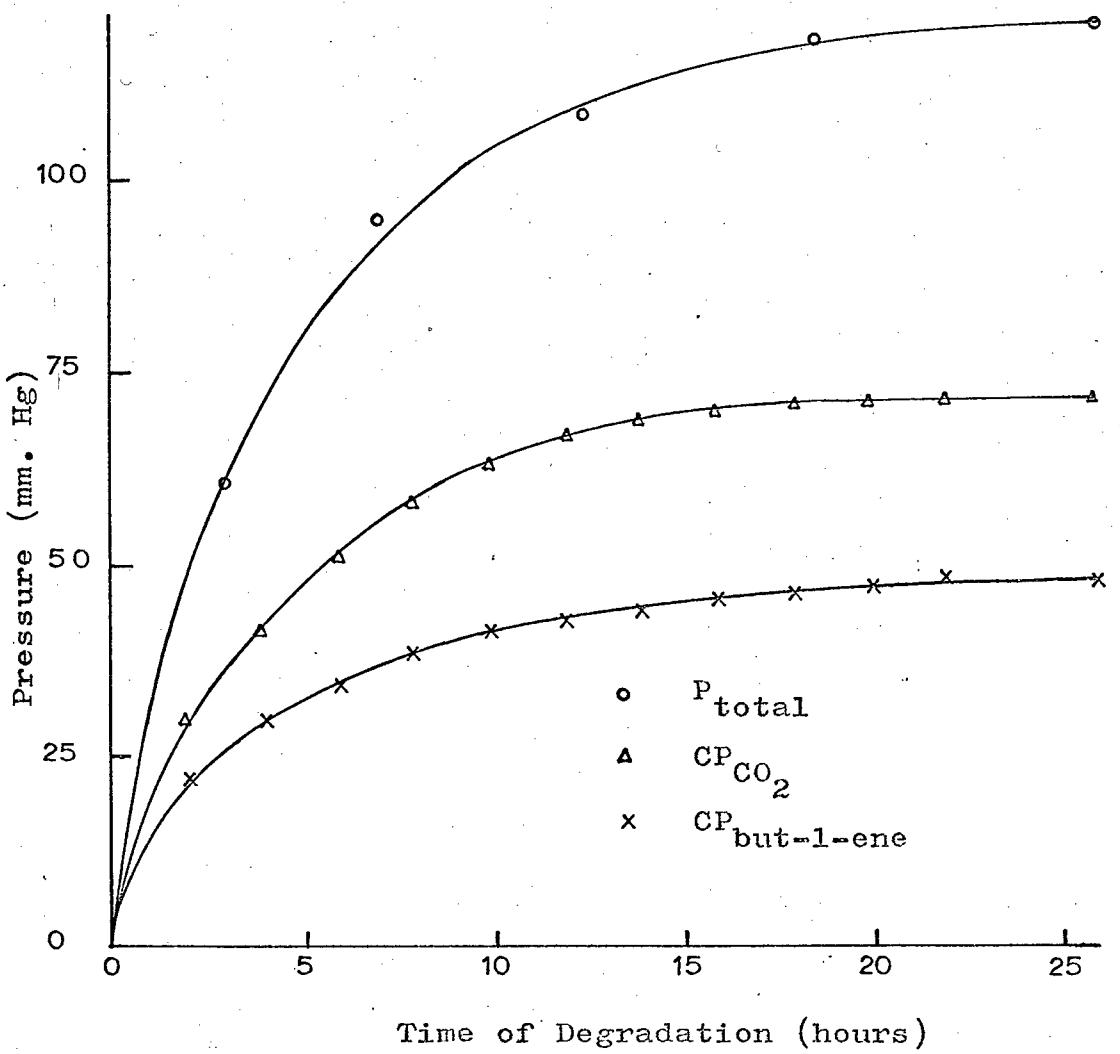


Figure 57. Gas pressure plots for a 93.4 mole percent n-butyl acrylate copolymer degraded at 332°C.

Table 33.

Gas Evolution Data for a 3.9 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	2	4	6.5	11	16	18	Initial Polymer Weight = 0.345g.
P_{total}	10.6	15.4	21.6	24.6	26.0	26.5	

Time of Degradation, hours	2	4	6	8	10	12	14	16	18	∞
P'_{total} (Fig.5.3)	10.6	16.2	20.2	23.0	24.4	24.9	25.5	26.0	26.5	26.5
m.moles CO_2 per g. polymer	.090	.139	.171	.194	.209	.212	.217	.220	.226	.226
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	0.4	0.6	0.8	0.9	0.9	0.9	1.0	1.0	1.0	1.0

Table 34.

Gas Evolution Data for a 50.0 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	2	4	6.5	8	11.5	16	Initial Polymer Weight = 0.430g.
P_{total}	52.8	120.2	172.5	183.8	216.0	248.2	

Time of Degradation, hours	2	4	6	8	10	12	14	16	∞
P'_{total} (Fig.5.4)	60.0	113.0	156.0	188.0	207.9	222.2	234.0	245.0	250.0
CP_{CO_2}	37.2	71.1	100.5	123.5	139.6	152.7	164.1	175.1	180.1
$CP_{but\text{-}1\text{-}ene}$	22.8	41.9	55.5	64.5	68.3	69.5	69.9	69.9	69.9
m.moles CO_2 per g. polymer	.253	.486	.686	.842	.951	1.04	1.12	1.19	1.23
m.moles but-1-ene per g. polymer	.156	.286	.379	.440	.465	.474	.477	.477	.477
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	2.0	3.7	5.1	6.2	6.8	7.2	7.6	7.9	8.1

Table 35.

Gas Evolution Data for an 82.2 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	2	3	6	10.5	13.5	15.5	18	22	32
P_{total}	40.0	111.8	133.9	172.0	203.5	223.2	229.9	230.0	253.0

PART A Data Calculated for Degradation Times up to 12 Hours.

Time of Degradation, hours	2	4	6	8	10	12	
P'_{total} (Fig.5.5)	65.0	102.0	129.5	153.0	172.0	189.0	Initial Polymer Weight = 0.270g.
CP_{CO_2}	38.2	62.5	81.1	98.9	113.5	126.3	
$CP_{but-1-ene}$	26.8	39.5	48.4	54.1	58.5	62.7	
m.moles CO_2 per g. polymer	.415	.678	.881	1.07	1.23	1.37	
m. moles but-1-ene per g. polymer	.293	.430	.526	.589	.637	.681	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	3.5	5.4	6.8	8.o	9.0	9.9	

Table 35 (contd.)

Gas Evolution Data for an 82.2 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

PART B Data Calculated for Degradation Times Greater Than 12 Hours.

Time of Degradation, hours	14	16	18	20	22	∞	
P'_{total} (Fig.5.5)	204.0	216.2	226.0	233.9	239.5	253.0	Initial Polymer Weight = 0.270g.
CP_{CO_2}	137.7	146.4	153.6	159.7	164.9	174.7	
$CP_{but-1-ene}$	66.3	69.8	72.4	74.2	74.6	78.3	
m.moles CO_2 per g. polymer	1.50	1.59	1.67	1.73	1.79	1.90	
m.moles but-1-ene per g. polymer	.719	.759	.785	.807	.811	.852	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	10.6	11.3	11.8	12.2	12.4	13.1	

Table 36.

Gas Evolution Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

Time of Degradation, hours	3	6	8	10	13.75	15.5	24	30
P_{total}	29.0	45.9	59.9	66.2	83.8	89.8	101.8	107.0

PART A Data Calculated for Degradation Times up to 14 Hours.

Time of Degradation, hours	2	4	6	8	10	12	14	
P'_{total} (Fig.5.6)	19.0	34.0	46.5	57.5	67.0	76.0	83.5	Initial Polymer Weight = 0.085g.
CP_{CO_2}	12.5	21.7	29.8	36.5	42.6	48.3	52.9	
$CP_{but\text{-}1\text{-}ene}$	6.5	12.3	16.7	21.0	24.4	27.7	30.6	
m.moles CO_2 per g. polymer	.435	.753	1.02	1.26	1.47	1.67	1.82	
m.moles but-1-ene per g. polymer	.224	.424	.576	.729	.847	.953	1.06	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	3.1	5.7	7.8	9.6	11.2	12.7	14.0	

Table 36 (contd.)

Gas Evolution Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer Degraded at 313°C.

PART B Data Calculated for Degradation Times Greater Than 14 Hours.

Time of Degradation, hours	16	18	20	22	24	26	∞	
P'_{total} (Fig.5.6)	90.0	94.5	98.5	101.0	103.0	104.5	106.0	Initial Polymer Weight = 0.085g.
CP_{CO_2}	56.9	60.1	63.1	65.1	67.1	68.6	70.1	
$CP_{but\text{-}1\text{-}ene}$	33.1	34.4	35.4	35.9	35.9	35.9	35.9	
m.moles CO_2 per g. polymer	1.96	2.07	2.18	2.25	2.32	2.36	2.42	
m.moles but-1-ene per g. polymer	1.14	1.19	1.22	1.24	1.24	1.24	1.24	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	15.1	15.8	16.5	16.9	17.2	17.4	17.7	

Table 37.

Gas Evolution Data for a 50.0 Mole °/o n-Butyl Acrylate Copolymer Degraded at 332°C.

Time of Degradation, hours	1.25	2.5	4	6	7	9.5	12
P_{total}	86.1	167.3	237.0	270.3	331.7	345.8	334.0

PART A Data Calculated for Degradation Times up to 6 Hours.

Time of Degradation, hours	1	2	3	4	5	6	
P'_{total} (Fig.5.7)	77.8	139.2	190.4	237.4	275.2	298.8	Initial Polymer Weight = 0.346g.
CP_{CO_2}	53.5	96.3	129.7	160.9	186.0	202.0	
$CP_{but\text{-}1\text{-}ene}$	24.3	42.9	60.7	76.5	89.2	96.8	
m.moles CO_2 per g. polymer	.454	.815	1.10	1.36	1.58	1.71	
m.moles but-1-ene per g. polymer	.205	.364	.514	.647	.757	.821	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	3.2	5.6	7.7	9.6	11.2	12.1	

Table 37 (contd.)

Gas Evolution Data for a 50.0 Mole °/o n-Butyl Acrylate Copolymer Degraded at 332°C.

PART B Data Calculated for Degradation Times Greater Than 6 Hours.

Time of Degradation, hours	7	8	9	10	∞	
P'_{total} (Fig.5.7)	316.1	327.5	337.5	339.8	340.1	Initial Polymer Weight = 0.346g.
CP_{CO_2}	213.8	221.6	228.6	230.9	231.2	
$CP_{but\text{-}1\text{-}ene}$	102.3	105.9	108.9	108.9	108.9	
m.moles CO_2 per g. polymer	1.81	1.88	1.94	1.96	1.96	
m.moles but-1-ene per g. polymer	.867	.899	.922	.922	.922	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	12.8	13.3	13.7	13.8	13.8	

Table 38.

Gas Evolution Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer Degraded at 332°C.

Time of Degradation, hours	3	7	10.5	18.5	24
P_{total}	60.2	94.2	108.0	117.0	120.0

PART A Data Calculated for Degradation Times up to 12 Hours.

Time of Degradation, hours	2	4	6	8	10	12	
P'_{total} (Fig.5.8)	50.0	70.0	85.0	95.5	103.0	108.0	Initial Polymer Weight = 0.079g.
CP_{CO_2}	29.0	40.7	51.2	57.7	62.7	66.0	
$CP_{but\text{-}1\text{-}ene}$	21.0	29.3	33.8	37.8	40.3	42.0	
m.moles CO_2 per g. polymer	1.08	1.51	1.90	2.14	2.33	2.46	
m.moles but-1-ene per g. polymer	.785	1.09	1.25	1.41	1.49	1.56	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	9.1	12.7	15.4	17.3	18.6	19.5	

Table 38 (contd.)

Gas Evolution Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer Degraded at 332°C.

PART B Data Calculated for Degradation Times Greater Than 12 Hours.

Time of Degradation, hours	14	16	18	20	22	∞	
P'_{total} (Fig.5.8)	112.0	115.0	117.0	118.0	119.2	120.0	Initial Polymer Weight = 0.079g.
CP_{CO_2}	68.2	69.7	70.4	70.8	71.3	71.8	
$CP_{but\text{-}1\text{-}ene}$	43.8	45.3	46.6	47.2	47.9	48.2	
m.moles CO_2 per g. polymer	2.53	2.58	2.62	2.63	2.65	2.67	
m.moles but-1-ene per g. polymer	1.62	1.68	1.73	1.75	1.78	1.78	
$\frac{\text{Weight of gas}}{\text{Initial polymer wt.}} \times 100$	20.2	20.8	21.2	21.4	21.6	21.7	

Measurable amounts of gases were not evolved from the 0·4 mole percent n-butyl acrylate copolymer examined, while only carbon dioxide was detected from the decomposition of a 3·9 mole percent n-butyl acrylate copolymer at 313°C. In the latter case $P_{total} = CH_{CO_2}$ so that infra-red measurements were not required.

In order that a comparison of the amount of gases evolved from the copolymers examined can be made, plots of the number of millimoles of gas per gram of initial polymer are shown in Figs. 58-62 and the data listed in tables 32-38.

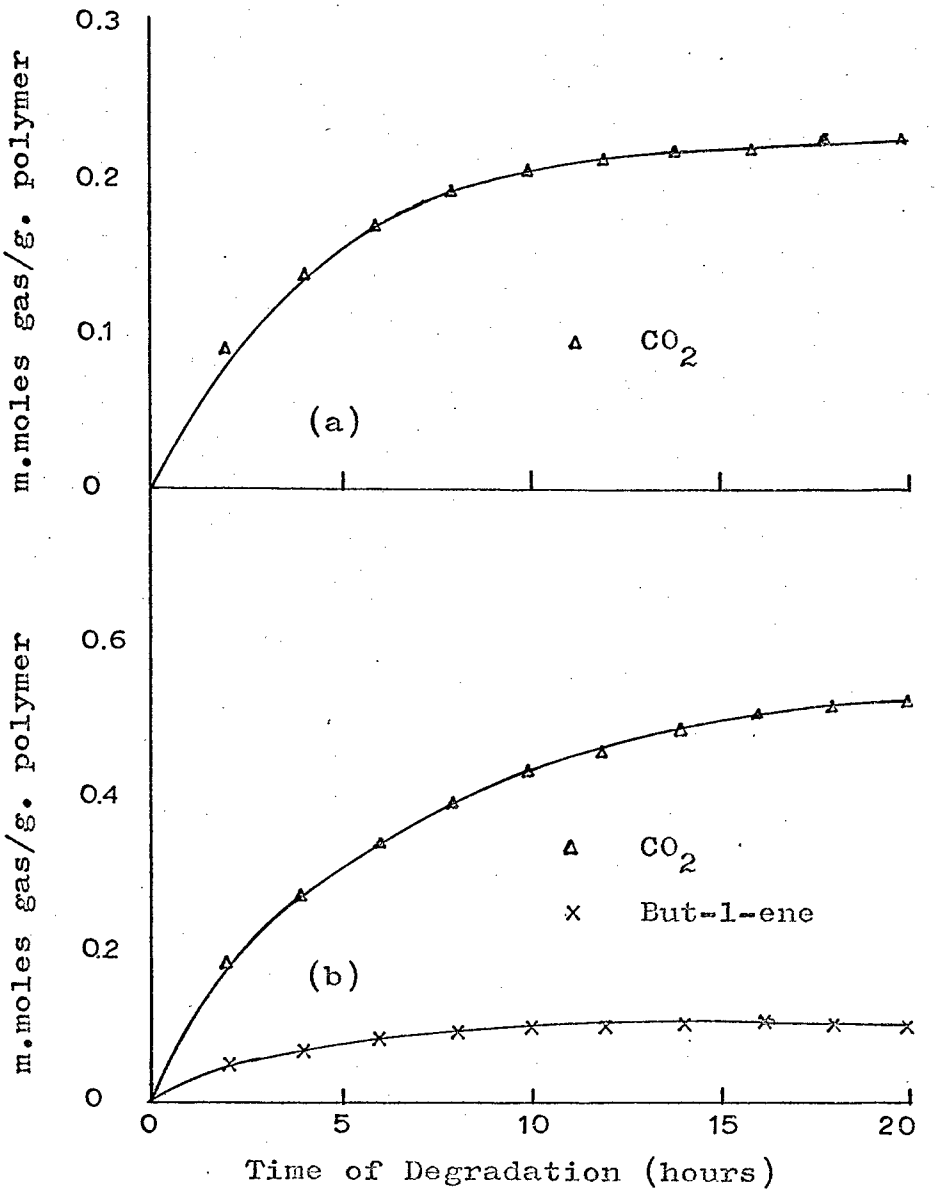
In order to obtain a mass balance, the percentage by weight of the gaseous products was calculated. These values are given in tables 32-38.

DISCUSSION OF RESULTS

It is clear from Figs. 58-62 that, as expected, the amount of both carbon dioxide and but-1-ene per gram of initial polymer increases with increasing acrylate content for a fixed temperature of degradation, and that it also increases with increasing temperature when copolymers of a given composition are considered.

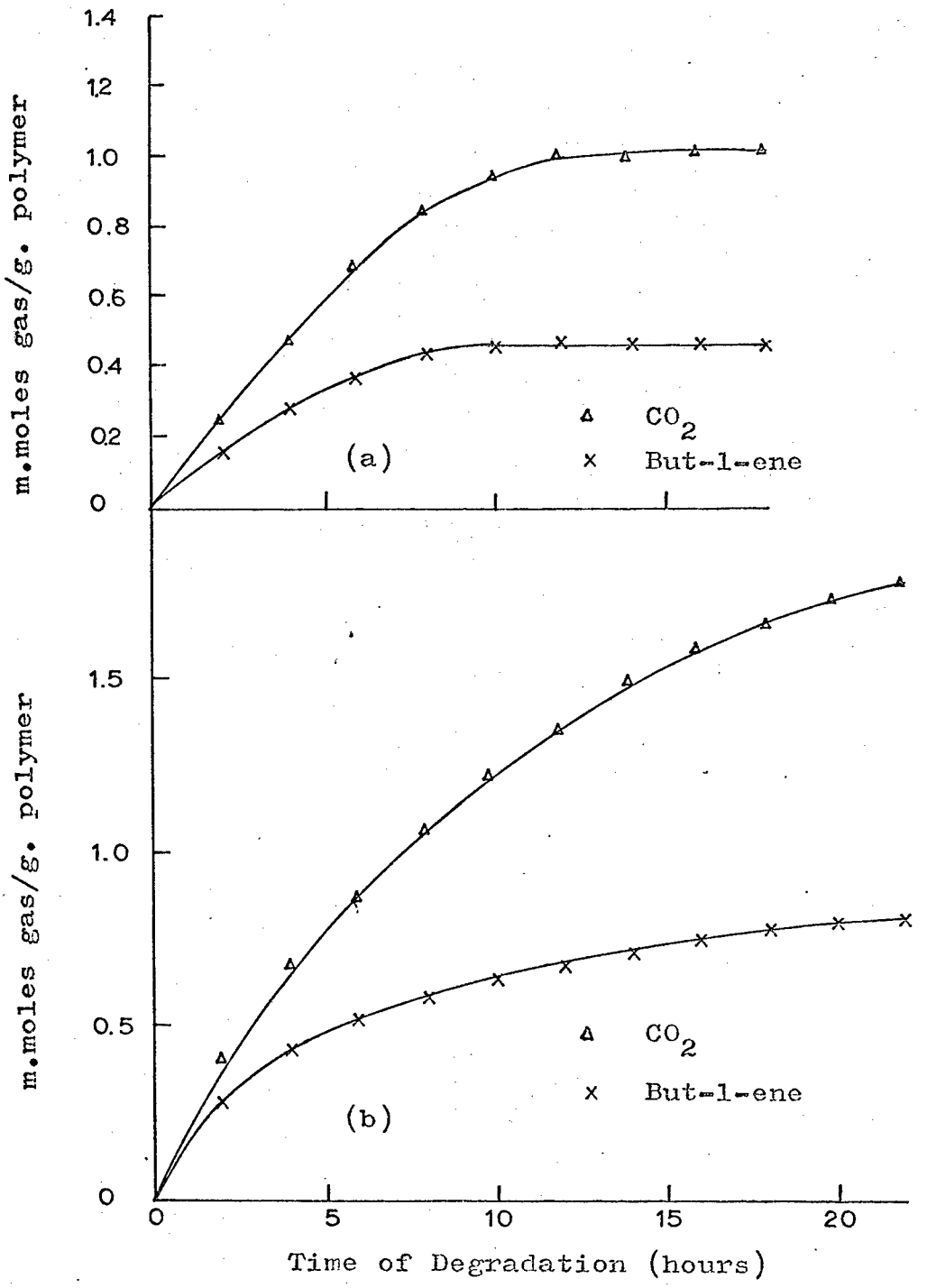
Another trend is that the molar ratio of carbon dioxide to but-1-ene at infinite degradation time, table 39, decreases both with increasing acrylate content and increasing temperature.

An interesting quantity is the amount of but-1-ene produced per gram of n-butyl acrylate in the original copolymer, for if but-1-ene production is associated with single acrylate units, then this quantity would be expected to stay constant over the copolymer composition range examined. In addition but-1-ene production would be expected to occur even when acrylate units are present as isolated entities. The fact that but-1-ene is evolved on the degradation of a 16·3 mole percent n-butyl acrylate copolymer, when more than 75% of the acrylate units present are flanked by methacrylate units, indicates that sequences of acrylate units are not required for the production of this gas. The data in table 40, however, show that the amount of but-1-ene obtained from any given n-butyl acrylate unit depends to some extent upon the acrylate content of the copolymer. This apparent anomaly might be explained by noting that a first step in the ester decomposition reaction of polyacrylates to olefin and acid is the abstraction of the tertiary hydrogen atom on the polymer chain. This initiating



(a) 3.9 mole °/o n-butyl acrylate copolymer.
(b) 16.3 mole °/o n-butyl acrylate copolymer.

Figure 58. Gas evolution plots for copolymers degraded at 313°C.



(a) 50.0 mole °/o n-butyl acrylate copolymer.

(b) 82.2 mole °/o n-butyl acrylate copolymer.

Figure 59. Gas evolution plots for copolymers degraded at 313°C.

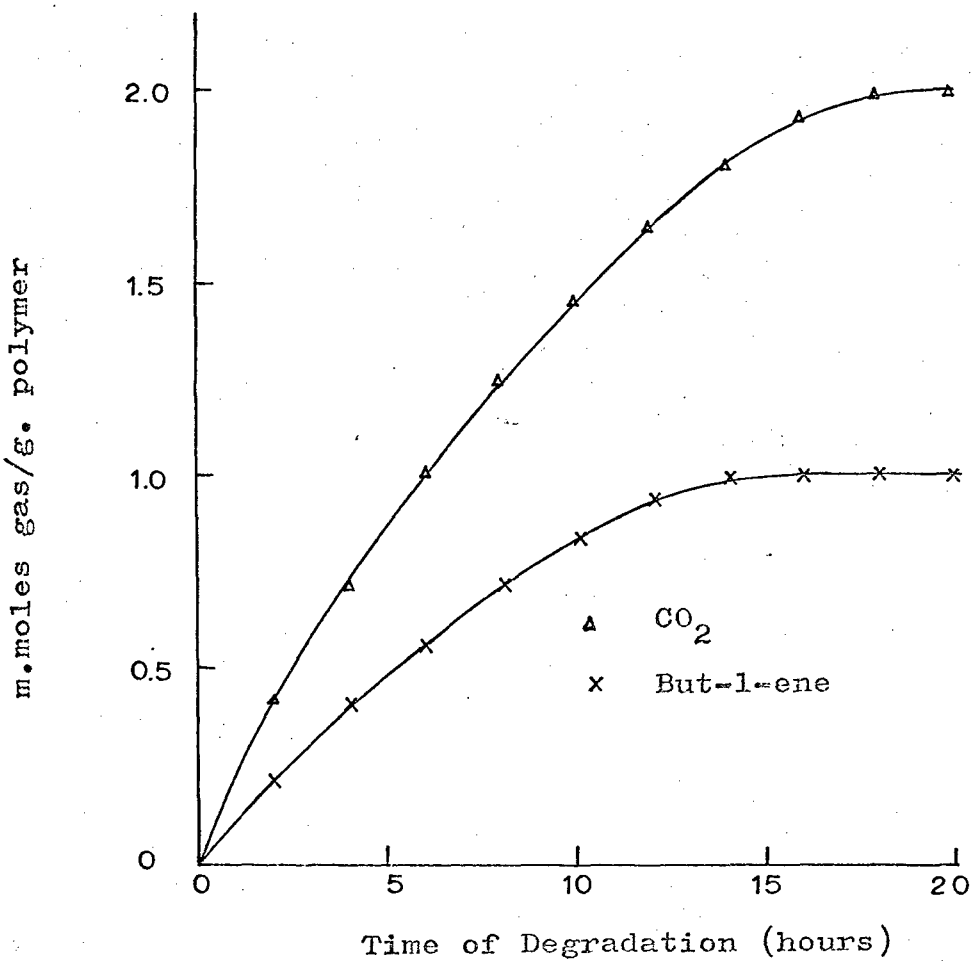


Figure 60. Gas evolution plot for a 93.4 mole °/o n-butyl acrylate copolymer degraded at 313°C.

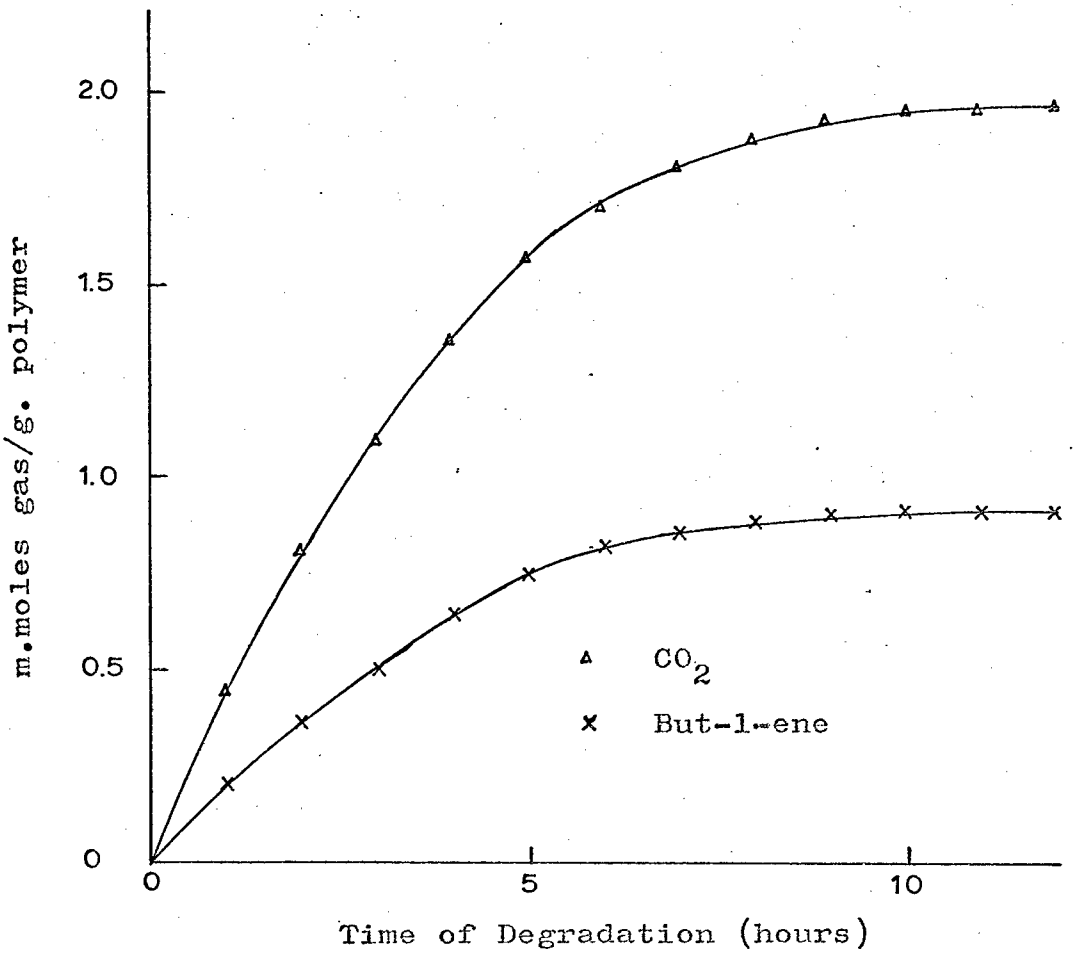


Figure 61. Gas evolution plot for a 50.0 mole °/o n-butyl acrylate copolymer degraded at 332°C.

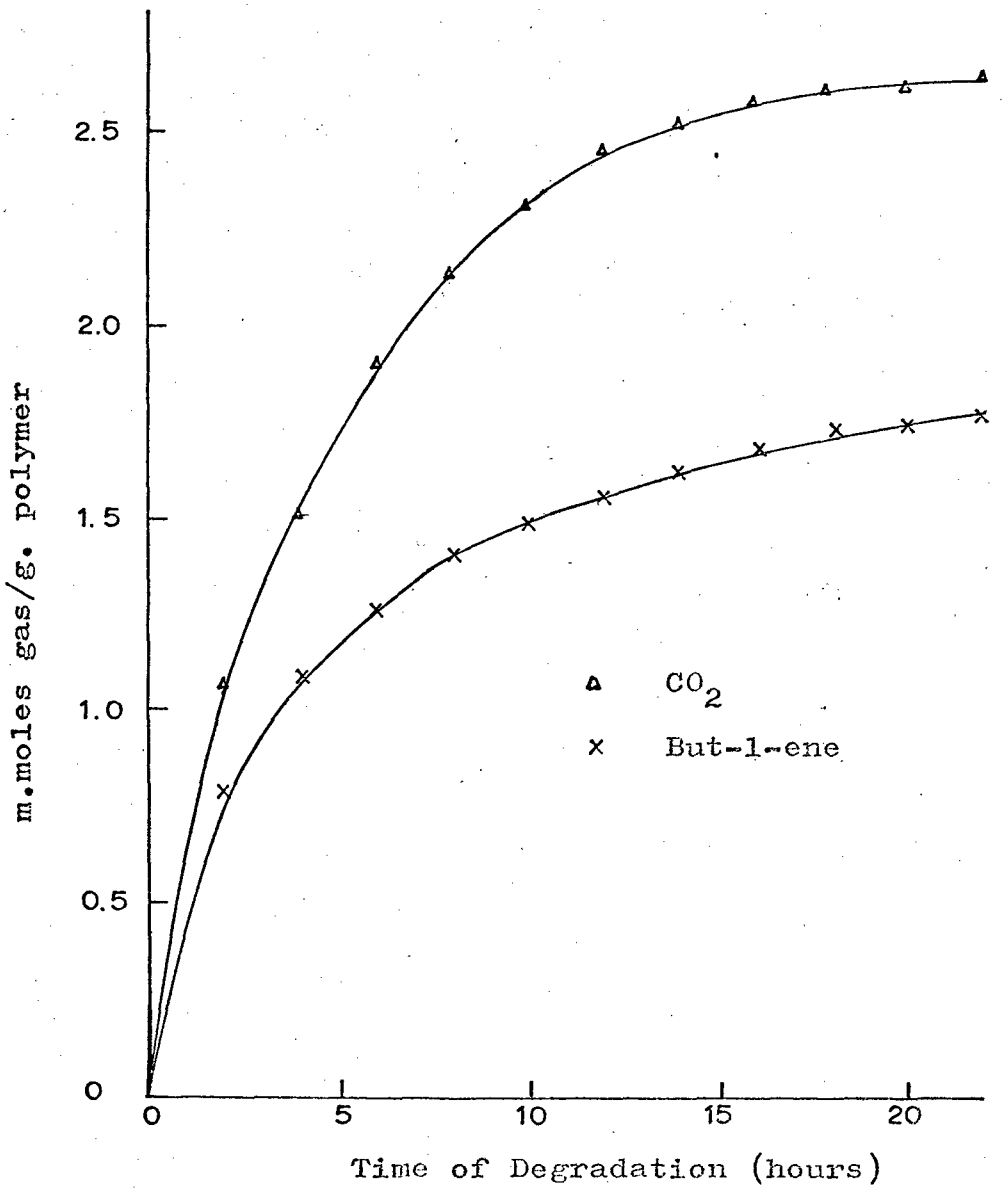


Figure 62. Gas evolution plot for a 93.4 mole °/o n-butyl acrylate copolymer degraded at 332°C.

Table 39.

Copolymer Composition (mole °/o acrylate)	Temp. of Degradation	CO_2 Pressure (mm. Hg) at t_∞	But-1-ene Pressure (mm. Hg) at t_∞	Molar Ratio(=pressure ratio) CO_2 :But-1-ene at t_∞
16.3	313	58.9	12.1	4.9
50.0	313	180.1	69.9	2.6
82.2	313	174.7	78.3	2.2
93.4	313	70.1	35.9	2.0
50.0	332	231.2	108.9	2.1
93.4	332	71.8	48.2	1.5

Table 40.

Copolymer Composition (mole °/o acrylate)	Temp. of Degradation	(g. But-1-ene/g. polymer) x 10^2	g. n-Butyl Acrylate/g. polymer	(g. But-1-ene/g. n-Butyl Acrylate) x 10^2
16.3	313	0.61	0.20	3.05
50.0	313	2.67	0.56	4.76
82.2	313	4.77	0.86	5.57
93.4	313	6.97	0.95	7.36
50.0	332	5.18	0.56	9.10
93.4	332	21.75	0.95	22.95

step is more likely to occur the higher the concentration of acrylate units since the acrylate radical is more reactive than the methacrylate radical, which prefers to depolymerize rather than to take part in hydrogen abstraction reactions such as this.

CALCULATION OF MASS BALANCE DATA

The percentage by weight of gas evolved on degradation of the copolymers has already been calculated, tables 32-38. Similar data for the liquid products, %L, and the residue, %R, are given in tables 41-47 and plotted in Figs. 63-71 as percentage of initial weight of copolymer versus time of degradation. From both the liquid product and residue curves for each polymer values of the percentage of liquids, %L', and percentage residue, %R', were read off at suitable intervals and are given in tables 41-47. In the case of copolymers of high acrylate content curves of chain fragments as a percentage of initial weight, %C, are plotted in Figs. 67, 68 and 70. The data used to construct these curves together with %C', the percentage of chain fragments with respect to initial polymer weight read off at suitable intervals from the three figures just mentioned, are given in tables 45-47. The weight of residue was determined by weighing the section of the sealed tube in which it was contained, cleaning and re-weighing, a similar procedure being adopted for measurement of chain fragments and liquid volatiles. As a check for copolymers of high methacrylate content the weight of residue was found by dissolving it in toluene, the resulting solution being made up in a standard flask and the concentration of a known volume determined. This method could not be used on all of the copolymers examined because of the insolubility of some of the residues.

ANALYSIS OF THE LIQUID DEGRADATION PRODUCTS

Analytical Techniques

The liquid products of degradation were analysed by g.l.c. (see Chapter 6). Since it was shown in the last chapter that good separation of methyl methacrylate and n-butanol was not obtained on a 1% S.E.30 column, it was decided for quantitative measurements to use a 10% dinonyl phthalate (D.N.P.) column, (table 15). A typical chromatogram is shown in Fig. 72 and table 48 gives the retention times of the peaks of interest.

Table 41

Data for the Degradation of a 3.9 Mole °/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degradation, hours.	2	4	6.5	8.5	16	18	
Weight of Liquids, g.	.144	.244	.306	.326	.349	.333	Initial Polymer Weight = 0.345g.
Weight of Residue, g.	.175	.115	.051	.035	.013	-	
°/o Liquids, °/o L.	41.7	70.7	88.7	94.5	101.2	96.5	
°/o Residue, °/o R.	50.7	33.3	14.8	10.1	3.8	-	

Time of Degradation, hours.	2	4	6	8	10	12	14	16	18
°/o L' (Fig.5.14)	43.0	67.5	84.0	94.0	98.0	99.0	99.0	99.0	99.0
°/o R' (Fig.5.14)	50.0	31.0	18.0	9.8	6.2	4.8	3.9	3.8	3.8
°/o Gas (table 5.5)	0.4	0.6	0.8	0.9	0.9	0.9	1.0	1.0	1.0
°/o Total Products	93.4	99.1	102.8	104.7	105.1	104.7	103.9	103.8	103.8

Table 42

Data for the Degradation of a 16.3 Mole °/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degradation, hours.	2	4	6	8	11	16	18	
Weight of Liquids, g.	.150	.210	.250	.290	-	.300	.300	Initial Polymer Weight = 0.331g.
Weight of Residue, g.	.232	.141	.079	.046	.033	.017	.017	
°/o Liquids, °/o L.	45.3	63.4	75.5	87.6	-	90.6	90.6	
°/o Residue, °/o R.	70.1	42.6	23.9	13.9	10.0	5.1	5.1	

Time of Degradation, hours.	2	4	6	8	10	12	14	16	18
°/o L' (Fig.5.15)	37.5	63.9	77.9	85.4	88.0	89.8	90.8	91.0	91.0
°/o R' (Fig 5.15)	69.5	43.4	24.5	14.3	10.0	7.2	5.3	5.0	5.0
°/o Gas(table 5.4)	1.0	1.6	2.0	2.3	2.5	2.6	2.8	2.9	2.9
°/o Total Products	108.0	108.9	104.4	102.0	100.5	99.6	98.9	98.9	98.9

Table 43

Data for the Degradation of a 50.0 Mole °/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degradation, hours.	2	4	6.5	8	11.5	15	16	24	
Weight of Liquids, g.	.064	.129	.148	.165	.219	-	.250	.279	Initial Polymer Weight = 0.430g.
Weight of Residue, g.	.327	-	.239	.225	.192	.178	.157	.126	
°/o Liquids, °/o L.	14.9	30.0	34.4	38.4	50.9	-	58.1	64.9	
°/o Residue, °/o R.	76.0	-	55.6	52.3	44.7	41.4	36.5	29.3	

Time of Degradation, hours.	2	4	6	8	10	12	14	16	18	20
°/o L' (Fig.5.16)	18.0	27.7	35.0	40.7	46.0	50.7	54.7	58.7	61.0	63.0
°/o R' (Fig.5.16)	76.4	65.0	57.8	52.0	48.2	44.5	41.2	38.0	35.2	32.8
°/o Gas (table 5.6)	2.0	3.7	5.1	6.2	6.8	7.2	7.6	7.9	8.1	8.1
°/o Total Products	96.4	96.4	97.9	98.9	101.0	102.4	103.5	104.6	104.3	103.9

Table 44

Data for the Degradation of an 82.2 Mole °/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degradation, hours.	2	6	10.5	13.5	15.5	24	Initial Polymer Weight = 0.270g.
Weight of Liquids, g.	.012	.079	.097	.106	.124	.149	
Weight of Residue, g.	.225	.173	.122	.125	.112	.080	
°/o Liquids, °/o L.	4.4	29.3	35.9	39.3	45.9	55.2	
°/o Residue, °/o R.	83.3	64.1	45.2	46.3	41.5	29.6	

Time of Degradation, hours.	2	4	6	8	10	12	14	16	18	20	22
°/o L' (Fig.5.17)	9.3	17.2	24.1	29.8	34.8	39.3	43.2	46.7	49.7	52.3	54.3
°/o R' (Fig.5.17)	80.0	70.5	63.0	57.4	52.0	46.8	42.5	38.5	35.3	33.0	30.9
°/o Gas (table 5.7)	3.5	5.4	6.8	8.0	9.0	9.9	10.6	11.3	11.8	12.2	12.4
°/o Total Products	92.8	93.1	93.9	95.2	95.8	96.0	96.3	96.5	96.8	97.5	97.6

Table 45

Data for the Degradation of a 93.4 Mole°/o n-Butyl Acrylate Copolymer at 313°C.

Time of Degdn.,hrs.	3	6	8	10	13.75	15.5	18	24	
Wt. of Liquids,g.	.013	.019	.022	.027	.030	.032	.039	.037	
Wt. of Residue,g.	.076	.063	-	.052	.036	.034	.044	.032	Initial Polymer Weight = 0.085g.
Wt. of Chain Fragments,g.	-	-	-	-	.002	.004	.001	.003	
°/o Liquids,°/oL.	15.3	22.4	25.9	31.8	35.3	37.6	45.9	43.5	
°/o Residue,°/oR.	89.4	74.1	-	61.2	42.4	40.0	51.8	37.6	
°/o Chain Fragments,°/oC.	-	-	-	-	2.4	4.7	1.2	3.5	

Time of Degdn.,hrs.	2	4	6	8	10	12	14	16	18	20	22	24
°/o L' (Fig.5.18)	10.8	17.7	23.8	28.1	32.4	35.5	38.3	40.5	42.6	43.9	44.7	45.5
°/o R' (Fig.5.18)	89.5	81.2	74.0	67.4	61.5	55.0	50.0	45.7	42.3	39.6	37.6	35.7
°/o C' (Fig.5.18)	0.6	1.2	1.7	1.9	2.3	2.5	2.8	3.0	3.1	3.3	3.6	3.6
°/o Gas(table 5.8)	3.2	5.7	7.8	9.6	11.2	12.7	14.0	15.1	15.8	16.5	16.9	17.2
°/o Total Products	104.1	105.8	107.3	107.0	107.4	105.7	105.1	104.3	103.8	103.3	102.8	102.0

Table 46

Data for the Degradation of a 50.0 Mole °/o n-Butyl Acrylate Copolymer at 332°C.

Time of Degdn.,hrs.	1.25	2.5	4	7	9.5	12	
Wt. of Liquids,g.	.076	.163	.197	.214	.232	.236	Initial Polymer Weight = 0.346g.
Wt. of Residue,g.	.254	.194	.126	.071	.035	.024	
Wt. of Chain Fragments,g.	-	.005	.032	.042	.028	.048	
°/o Liquids,°/oL.	22.0	47.1	56.9	61.8	67.0	68.2	
°/o Residue,°/oR.	73.4	56.1	36.4	20.5	10.1	6.9	
°/o Chain Fragments,°/oC.	-	1.4	9.2	12.1	8.1	13.9	

Time of Degdn.,hrs.	1	2	3	4	5	6	7	8	9	10	11
°/o L' (Fig.5.19)	19.2	39.1	50.3	56.9	59.8	61.9	63.4	64.4	65.4	65.9	66.3
°/o R' (Fig.5.20)	79.9	61.8	48.0	36.4	28.8	23.4	18.2	14.2	11.5	9.3	7.6
°/o C' (Fig.5.19)	2.0	3.1	5.3	6.9	8.2	9.2	9.9	10.8	11.1	11.5	11.6
°/o Gas(table 5.9)	3.2	5.6	7.7	9.6	11.2	12.1	12.8	13.3	13.7	13.8	13.8
°/o Total Products	104.3	109.6	111.3	109.8	108.0	106.6	104.3	102.7	101.7	100.5	99.3

Table 47

Data for the Degradation of a 93.4 Mole °/o n-Butyl Acrylate Copolymer at 332°C.

Time of Degdn.,hrs.	3	7	10.5	12.5	18.5	24	
Wt. of Liquids,g.	.026	.036	.036	.037	.040	.039	Initial Polymer Weight = 0.079g.
Wt. of Residue,g.	.047	.030	.028	.022	.014	.012	
Wt. of Chain Fragments,g.	.003	.007	-	.009	.009	.013	
°/o Liquids,°/oL.	32.9	45.6	45.6	46.8	50.6	49.4	
°/o Residue,°/oR.	59.5	38.0	35.4	27.8	17.7	15.2	
°/o Chain Fragments,°/oC.	3.8	8.9	-	11.4	11.4	16.5	

Time of Degdn.,hrs.	2	4	6	8	10	12	14	16	18	20	22	24
°/o L' (Fig.5.21)	27.1	35.8	41.0	44.2	46.3	47.6	48.4	48.9	49.4	49.6	49.6	49.6
°/o R' (Fig.5.22)	67.6	54.2	46.2	39.4	33.0	28.1	24.2	21.1	19.0	17.3	16.1	15.8
°/o C' (Fig.5.21)	3.2	5.3	7.2	8.8	10.0	10.9	11.8	12.4	13.1	13.5	13.8	14.1
°/o Gas(table 5.10)	9.1	12.7	15.4	17.3	18.6	19.5	20.2	20.8	21.2	21.4	21.6	21.7
°/o Total Products	107.0	108.0	109.8	109.7	107.9	106.1	104.6	103.2	102.7	101.8	101.1	101.2

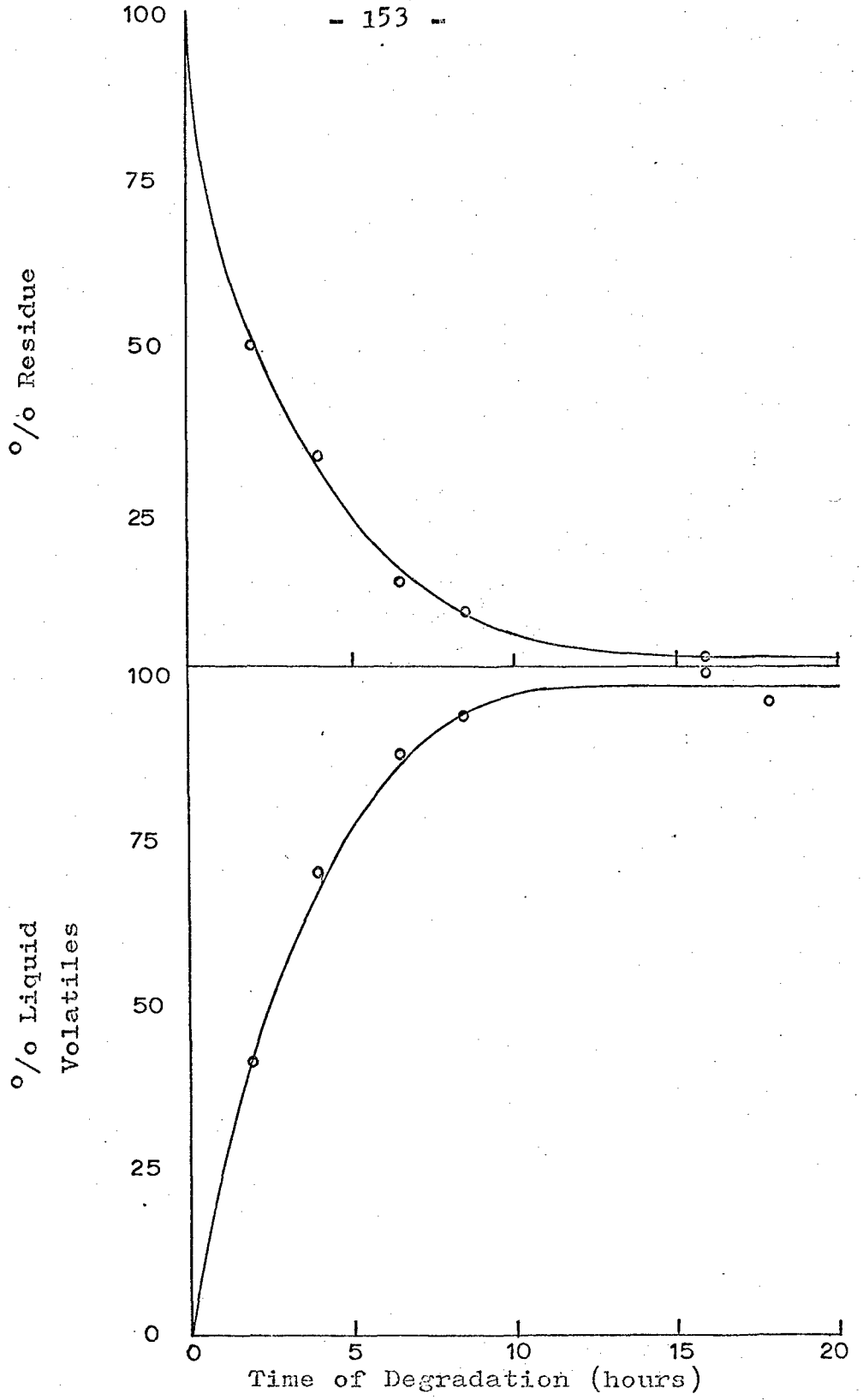


Figure 63. Residue and liquid volatile plots for a 3.9 mole percent n-butyl acrylate copolymer degraded at 313°C.

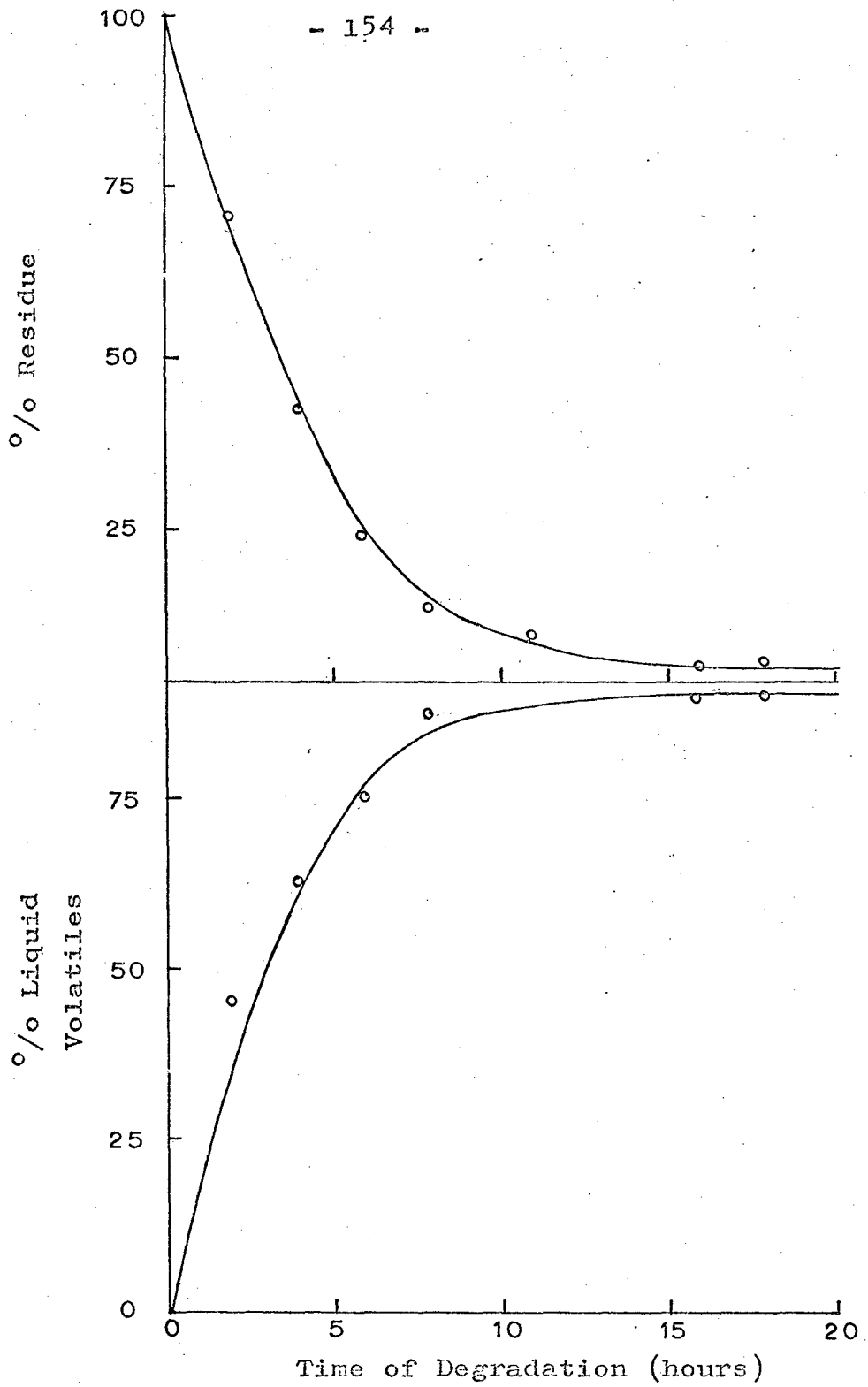


Figure 64. Residue and liquid volatile plots for a 16.3 mole percent n-butyl acrylate copolymer degraded at 313°C.

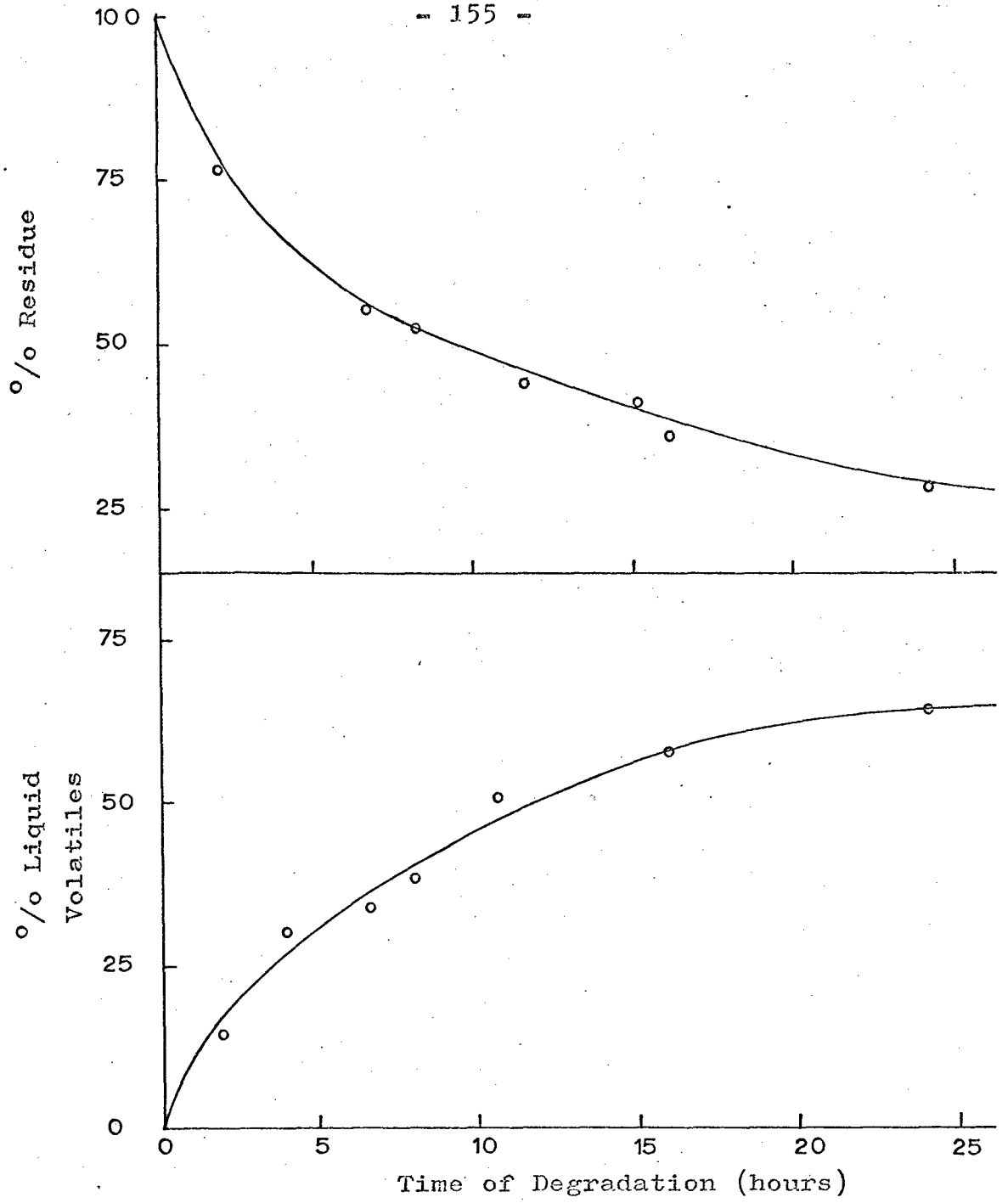


Figure 65. Residue and liquid volatile plots for a 50.0 mole percent n-butyl acrylate copolymer degraded at 313°C.

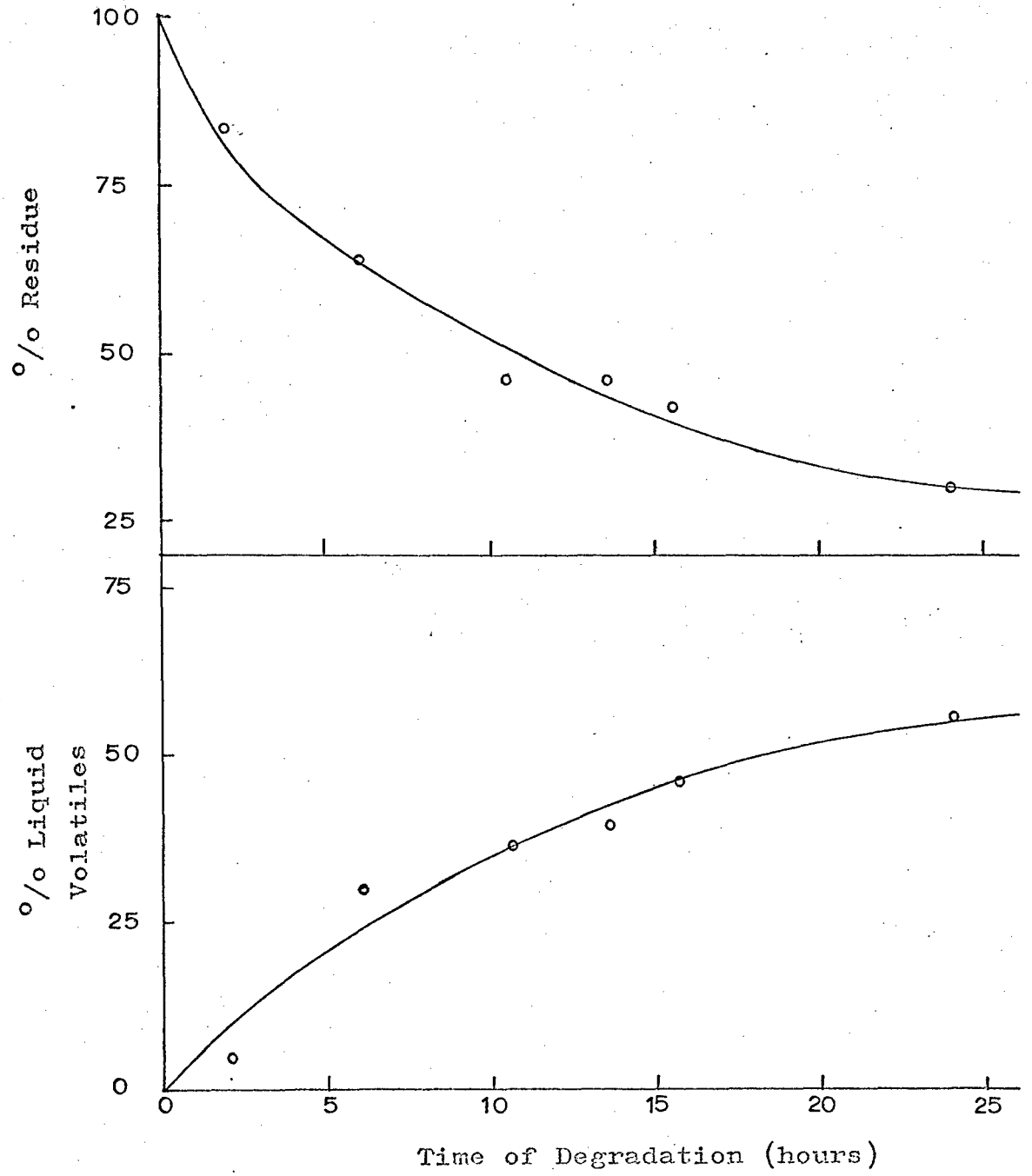


Figure 66. Residue and liquid volatile plots for an 82.2 mole percent n-butyl acrylate copolymer degraded at 313°C.

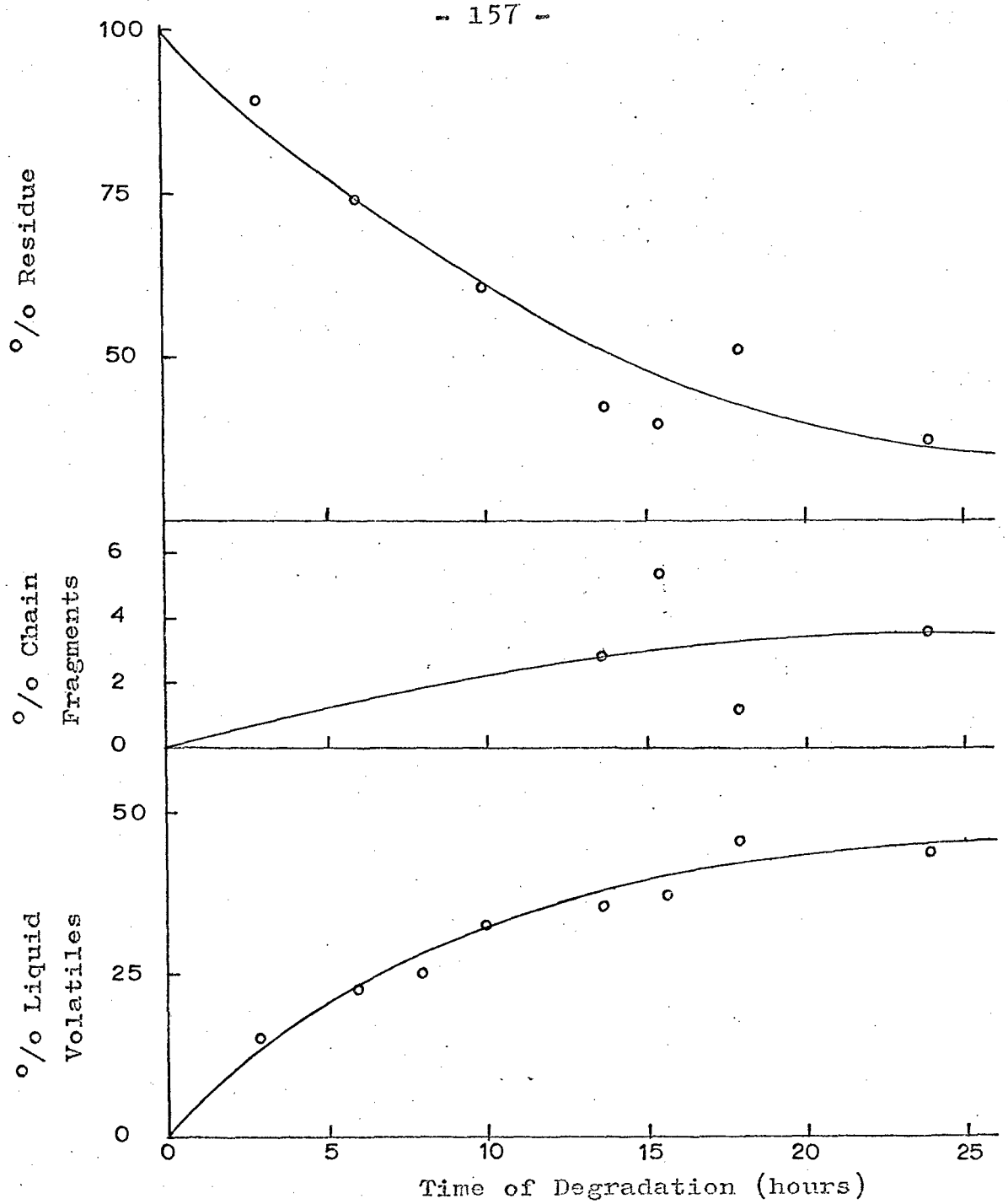


Figure 67. Residue, chain fragment, and liquid volatile plots for a 93.4 mole percent n-butyl acrylate copolymer degraded at 313°C.

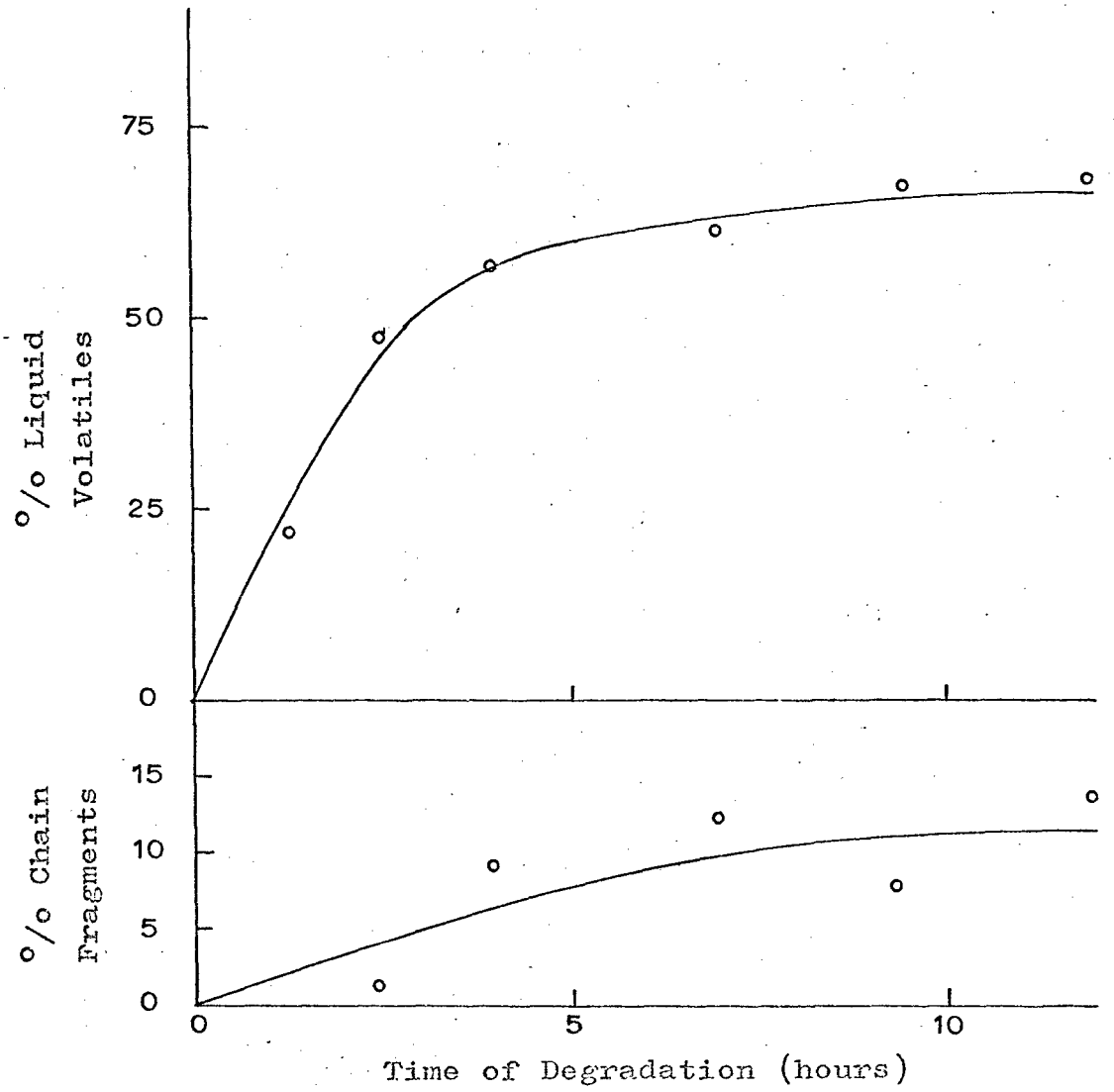


Figure 68. Liquid volatile and chain fragment plots for a 50.0 mole percent n-butyl acrylate copolymer degraded at 332°C.

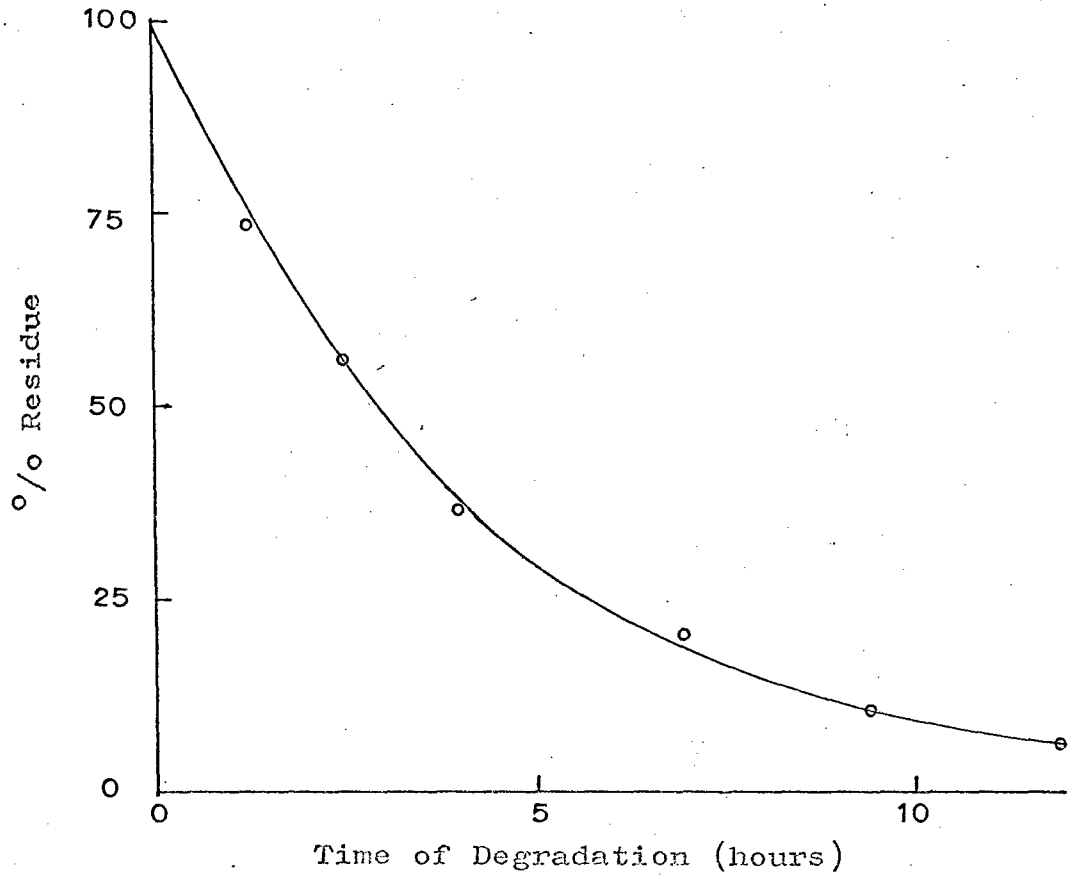


Figure 69. Residue plot for a 50.0 mole percent n-butyl acrylate copolymer degraded at 332°C.

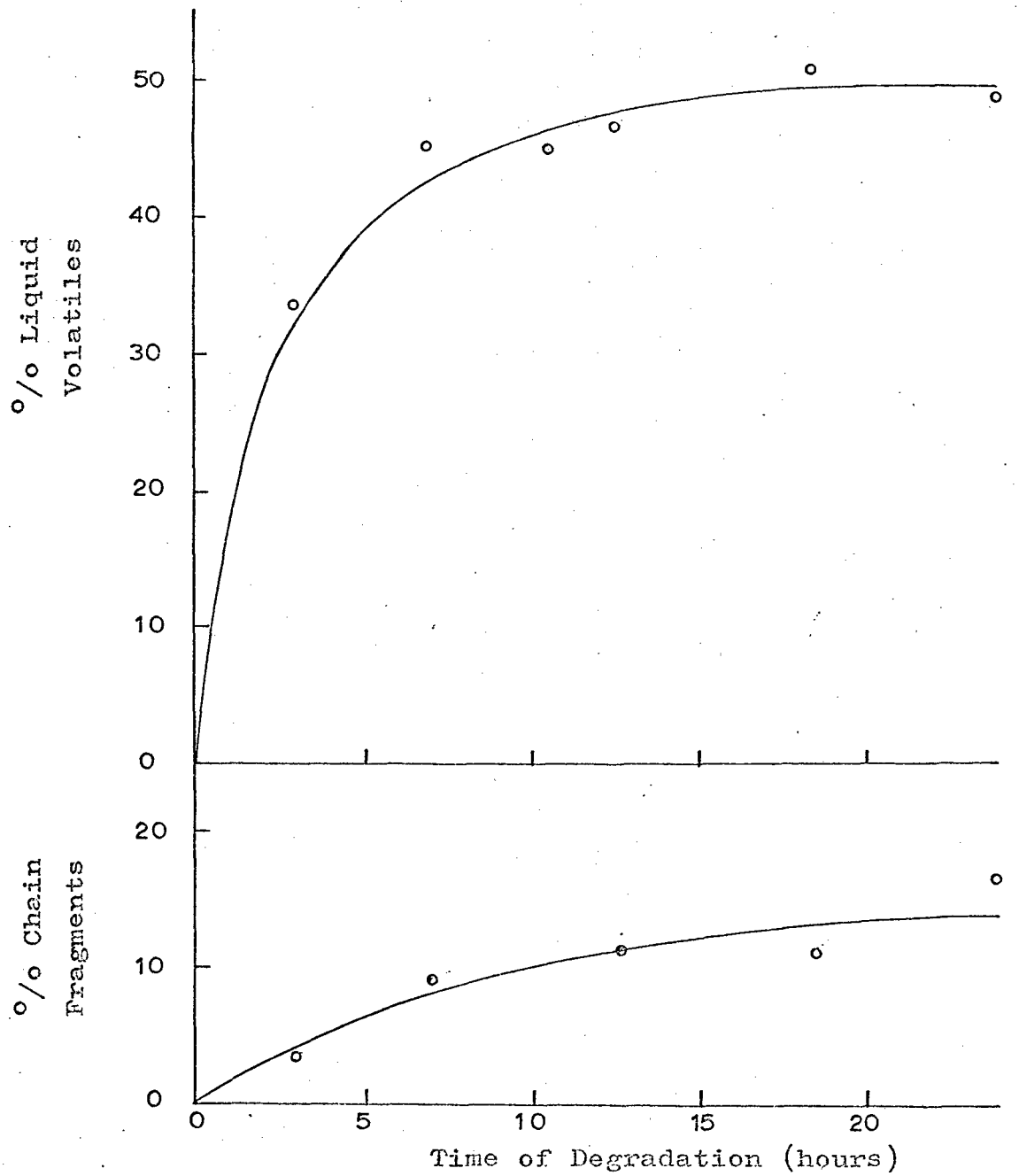


Figure 70. Liquid volatile and chain fragment plots for a 93.4 mole percent n-butyl acrylate copolymer degraded at 332°C.

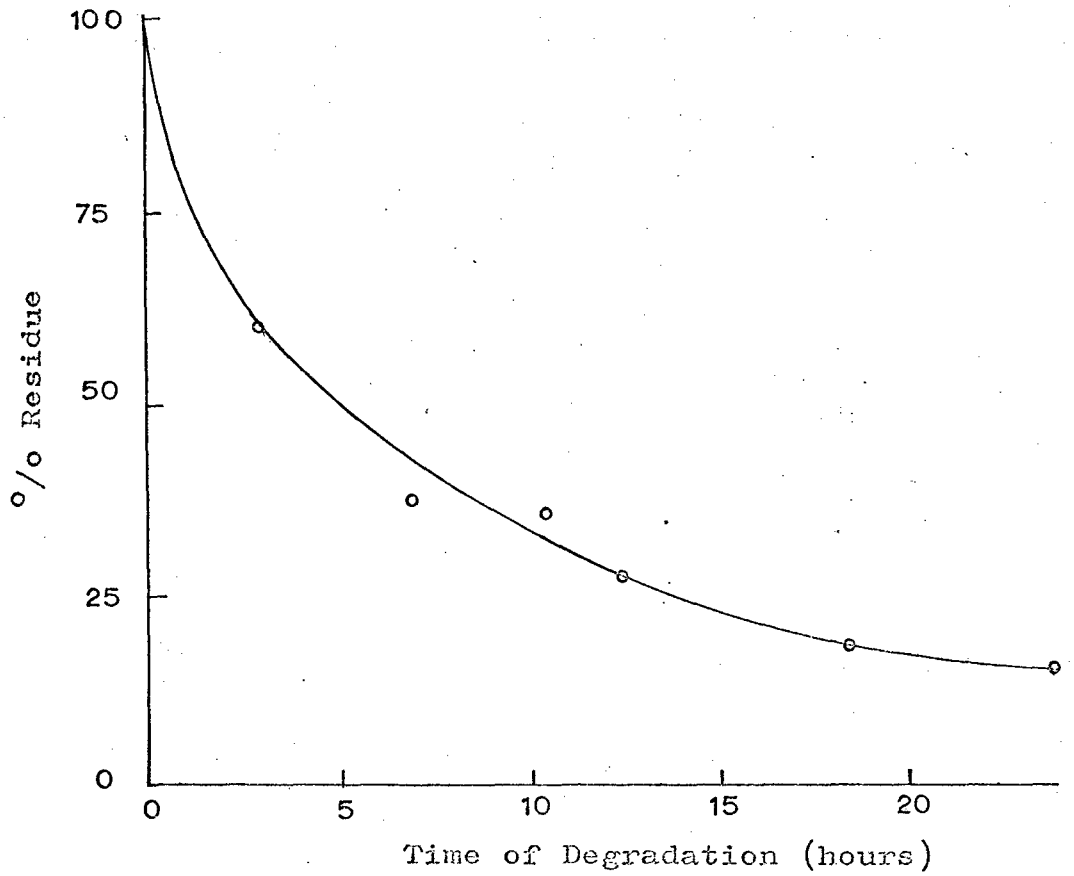


Figure 71. Residue plot for a 93.4 mole percent n-butyl acrylate copolymer degraded at 332°C.

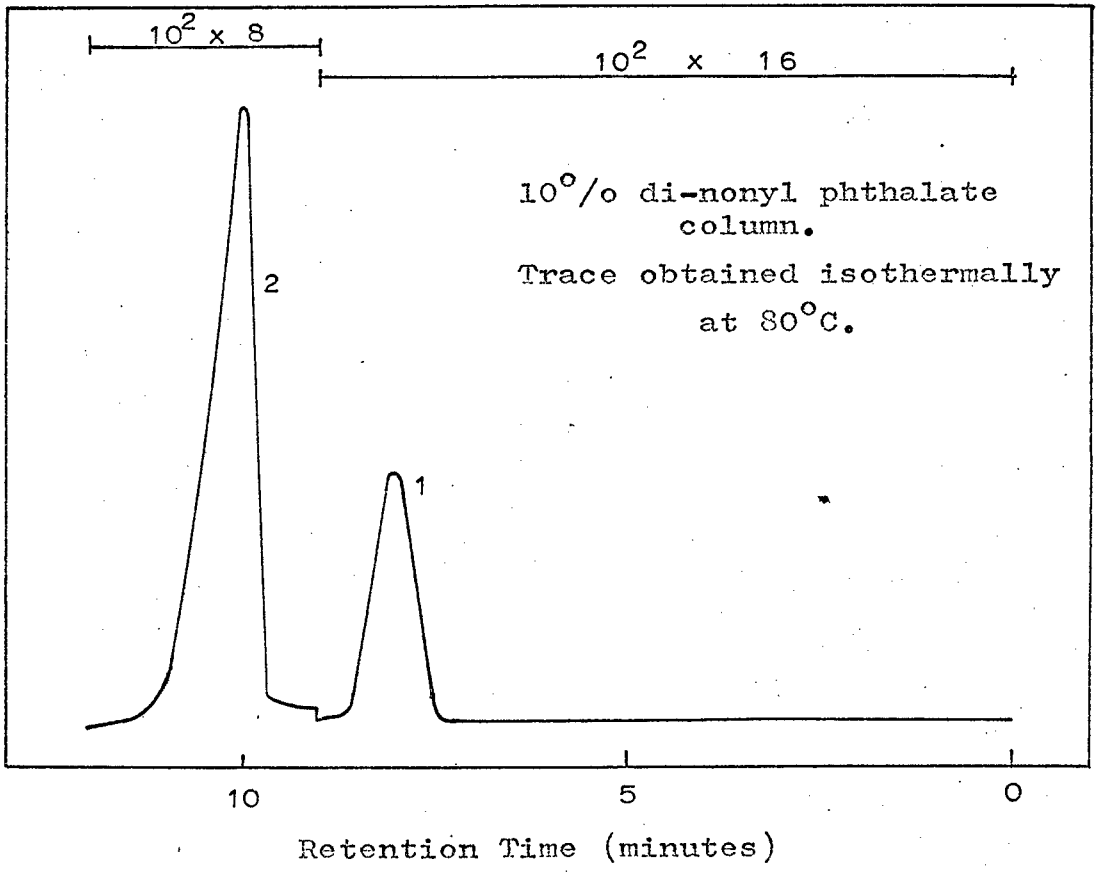


Figure 72. G.L.C. trace of the liquid degradation products from a 50.0 mole percent n-butyl acrylate copolymer pyrolyzed at 313°C for 16 hours.

TABLE 48

Peak No. in Fig. 72	Component	Retention Time (minutes)
1	Methyl Methacrylate	8
2	n-Butanol	10

For each determination a known weight of a suitable standard, cyclohexane for the D.N.P. and ethyl benzoate for the S.E.30 column, was added to a weighed amount of sample. The sensitivity of the detector to pure samples of the liquid degradation products was determined by injecting mixtures of known composition into the chromatograph, the results being quoted in table 49. Once these factors had been determined the percentage by weight of any of these components could be found as described in chapter 6. In copolymers of high methacrylate content it is very difficult to remove the last traces of toluene from the films deposited in the sealed tubes. These small amounts of solvent can be allowed for by determining the exact amounts present by quantitative g.l.c. measurements.

TABLE 49

1% S.E.30 Column

Component	Sensitivity Factor Relative to Ethyl Benzoate
n-Butyl Acrylate	0·33
n-Butyl Methacrylate	0·29

10% D.N.P. Column

Component	Sensitivity Factor Relative to Cyclohexane
Methyl Methacrylate	0·51
n-Butanol	0·40

Table 50 shows the percentages of each of the four liquid components analyzed for, with respect to the total weight of the liquid fraction. The difference between the sum of the percentages in table 50 and 100% may be accounted for in terms of short chain fragments which have distilled into the capillary portion of the sealed tube during degradation. It was not possible to put a reliable value on the small amounts of n-butyl acrylate found in the breakdown products of the 93·4 mole percent copolymer, so that the term "trace", implying less than one percent, is used in table 50. A similar situation is found with both n-butyl acrylate and n-butyl methacrylate in the degradation products of a 3·9 mole percent n-butyl acrylate copolymer.

Treatment of Results

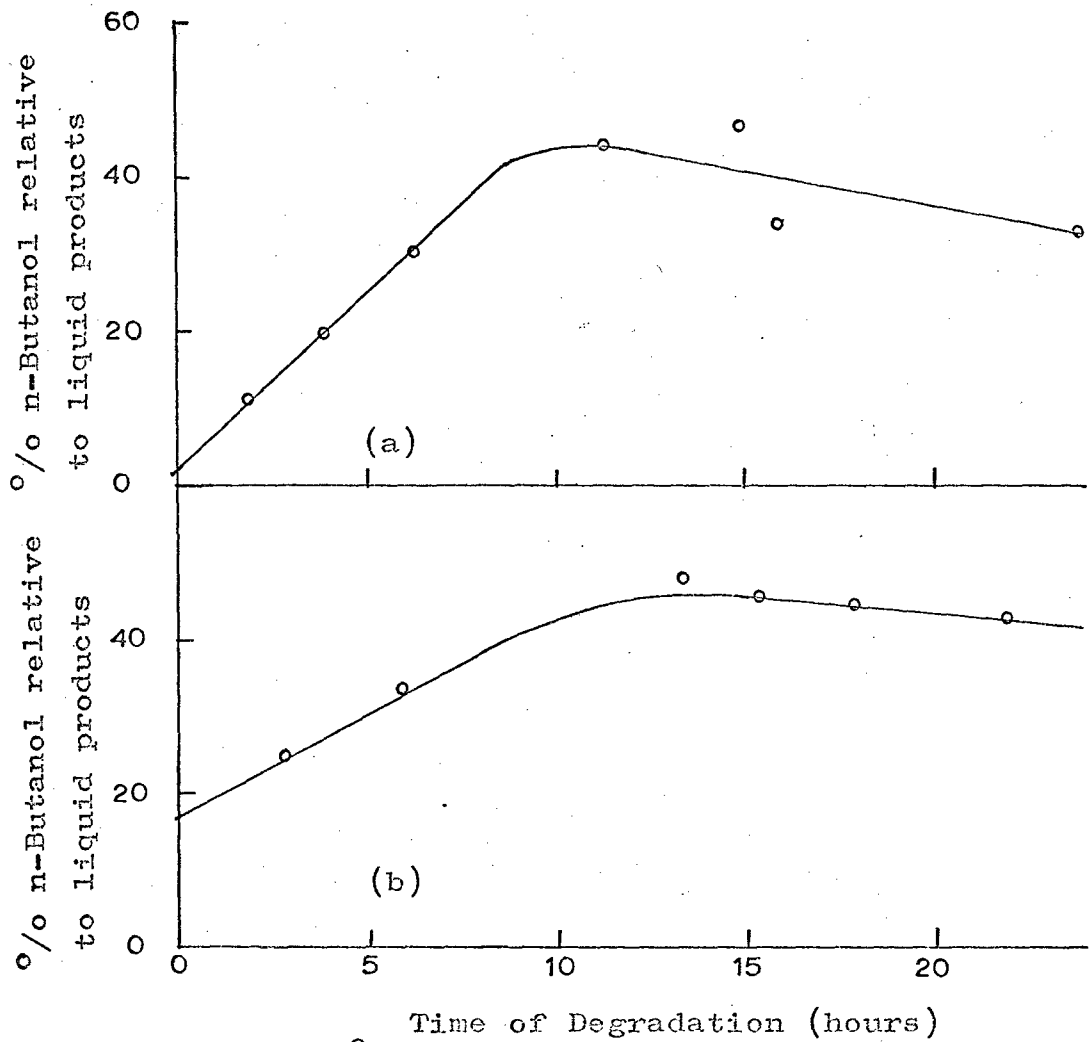
As the percentages of methyl methacrylate, n-butyl acrylate and n-butyl methacrylate noted in table 50 do not change in a systematic fashion with degradation time, an average value for these quantities, V_a, was used. V_a represents the percentage by weight of a compound with respect to the weight of the total liquid products. Since the percentage of liquid products with respect to initial polymer weight, %L', is listed in tables 41-47, the percentage of a component with respect to initial polymer weight can be calculated throughout the degradation. It is most convenient here to express the concentration of product in terms of millimoles of product per gram of initial polymer, and table 51 lists the concentrations of methyl methacrylate, n-butyl acrylate and n-butyl methacrylate in these units. For any given copolymer the percentage of n-butanol in table 50 changes in a regular fashion as the degradation proceeds, and is plotted in Figs. 73 and 74 for 50, 82·2 and 93·4 mole percent n-butyl acrylate copolymers. Values from these curves taken every two hours were used to calculate the number of millimoles of n-butanol produced per gram of initial polymer as degradation proceeds, which is listed in table 51. The production of methyl methacrylate and n-butanol is shown graphically in Figs. 75-77.

Although the analysis of the liquid products from the degradation of a 0·4 mole percent n-butyl acrylate copolymer is given in table 50, no data appear for this copolymer in table 51 since systematic measurements of the production of volatiles were not considered to be necessary as they would add little, if anything, to the information already obtained.

TABLE 50. Analysis of the Liquid Degradation Products

Copolymer Composition (mole %BuA)	Temp. of Degdn. (°C)	Time of Degdn. (hours)	%MMA	%BuOH	%BuA	%BuMA
0·4	313	2	100	nil	nil	nil
	313	4	100	nil	nil	nil
	313	12	100	nil	nil	nil
	313	37	100	nil	nil	nil
3·9	313	2	100	nil	trace	trace
	313	4	95	nil	trace	trace
	313	6·5	99	nil	trace	trace
	313	8·5	97	nil	trace	trace
	313	16	98	nil	trace	trace
	313	18	97	nil	trace	trace
16·3	313	2	70	nil	2	4
	313	4	75	nil	3	2
	313	6	76	nil	5	4
	313	8	65	nil	3	3
	313	11	70	nil	-	-
	313	16	78	nil	-	-
	313	18	74	nil	4	3
50·0	313	2	21	11	8	6
	313	4	25	20	5	7
	313	6·5	20	31	7	5
	313	11·5	22	44	-	-
	313	15	26	47	-	-
	313	16	22	34	9	6
	313	24	22	33	9	6
82·2	313	3	1	25	1	1
	313	6	2	34	2	1
	313	13·5	1	48	-	-
	313	15·5	2	46	-	-
	313	18	2	45	2	1
	313	22	1	44	2	1
93·4	313	2	nil	22	trace	nil
	313	3	nil	28	trace	nil
	313	4	nil	32	trace	nil
	313	6	nil	53	trace	nil
	313	8	nil	77	trace	nil
	313	10	nil	71	trace	nil
	313	13·75	nil	72	trace	nil
	313	18	nil	64	trace	nil
	313	24	nil	64	trace	nil
93·4	332	3	nil	57	trace	nil
	332	7	nil	58	trace	nil
	332	10·5	nil	72	trace	nil
	332	12·5	nil	70	trace	nil
	332	18·5	nil	79	trace	nil
	332	24	nil	77	trace	nil

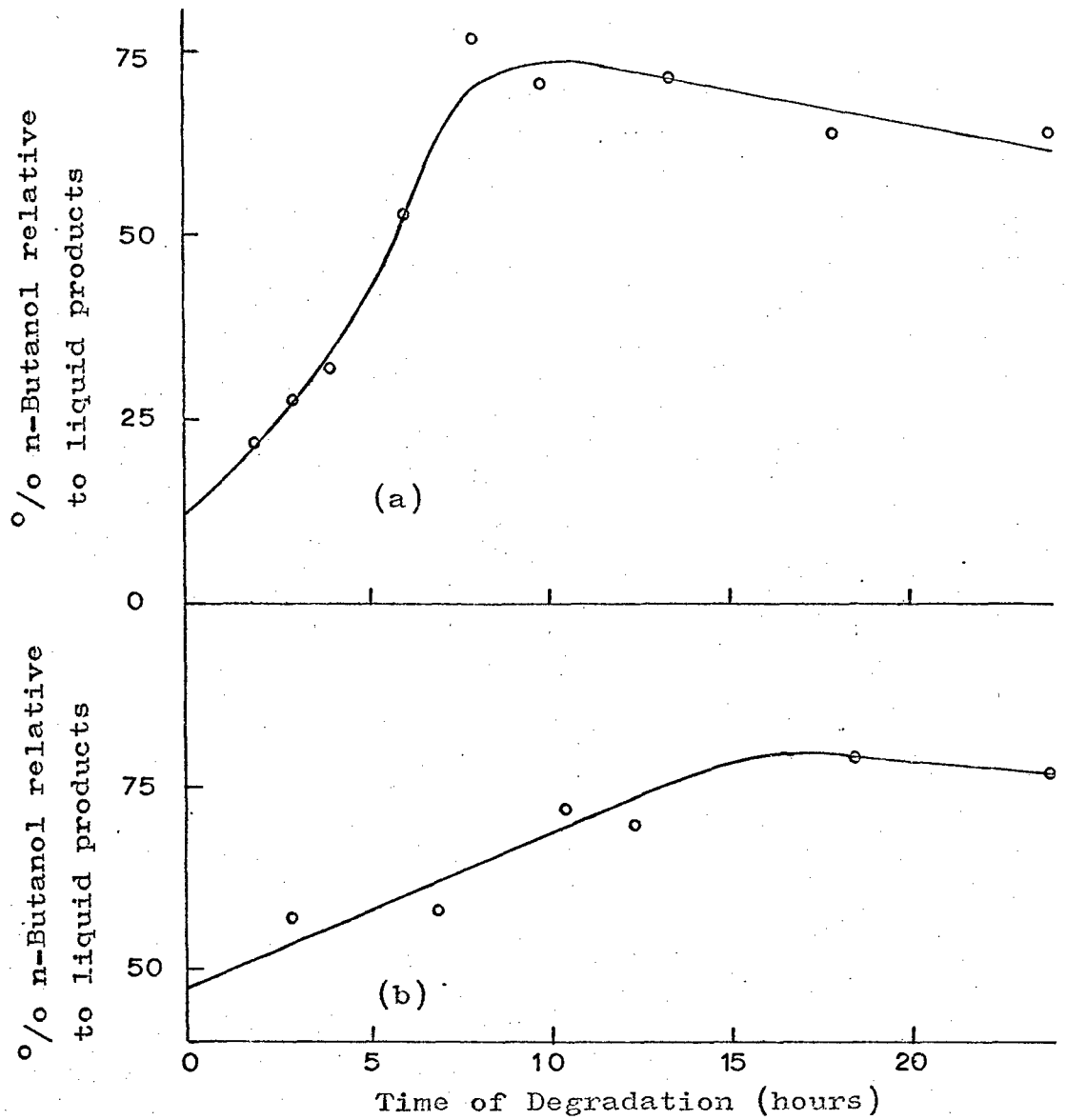
MMA = methyl methacrylate: BuOH = n-butanol: BuA = n-butyl acrylate
BuMA = n-butyl methacrylate: "trace" = less than 1%: - = value not measure



(a) 50.0 mole % n-butyl acrylate copolymer.

(b) 82.2 mole % n-butyl acrylate copolymer.

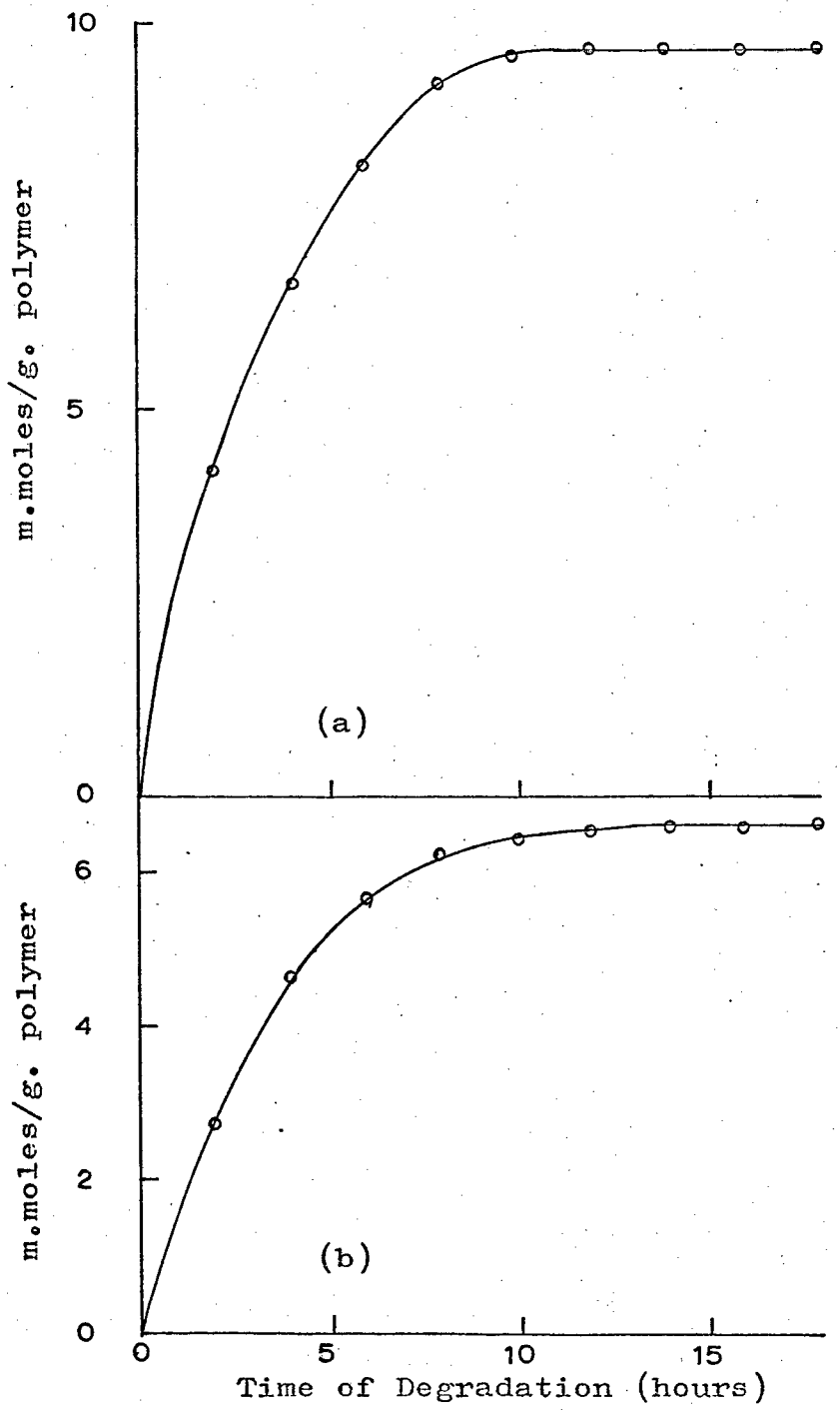
Figure 73. n-Butanol production as a percentage of the total liquid products at 313°C.



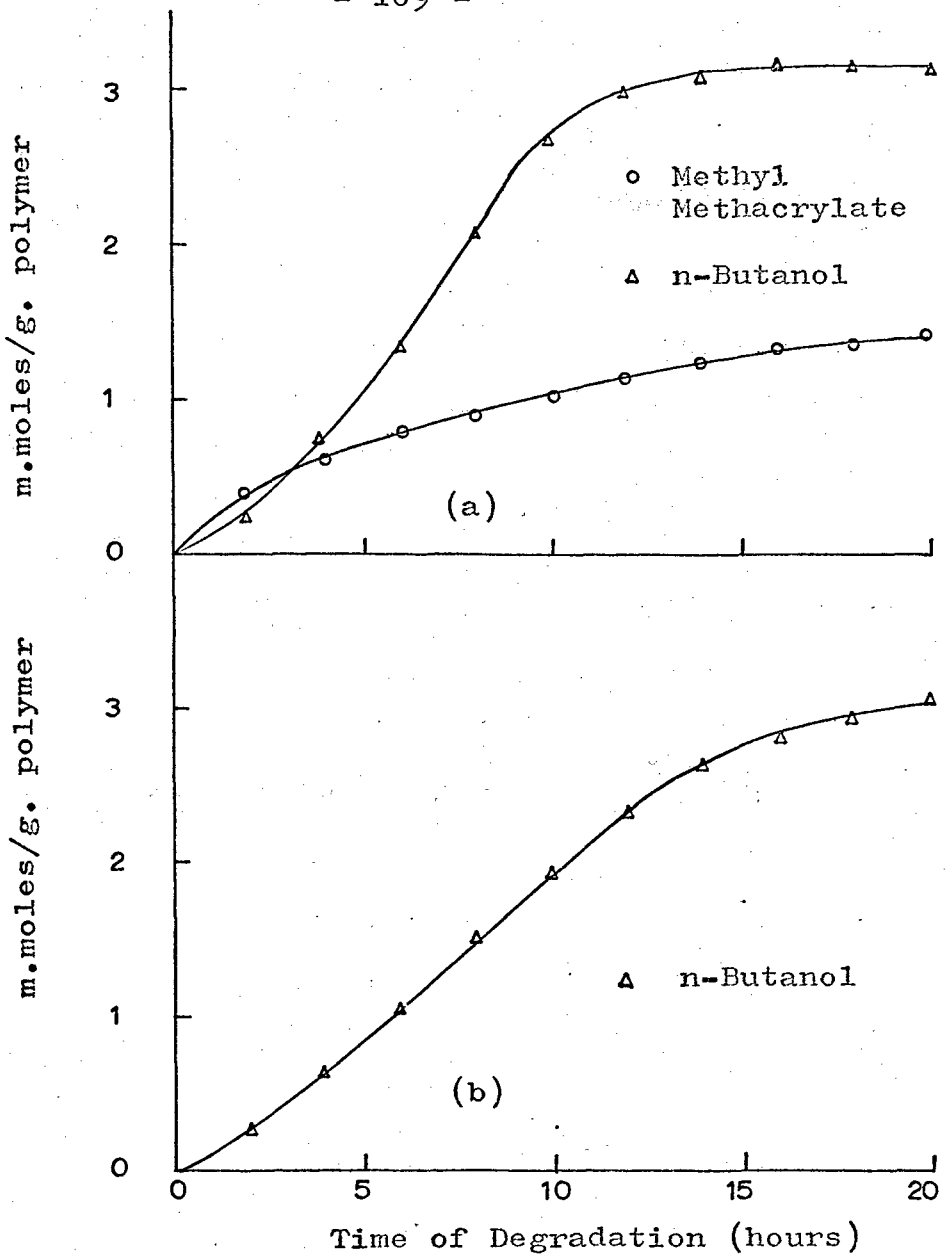
(a) Degradation temperature 313°C.

(b) Degradation temperature 332°C.

Figure 74. n-Butanol production as a percentage of the total liquid products for a 93.4 mole percent n-butyl acrylate copolymer.

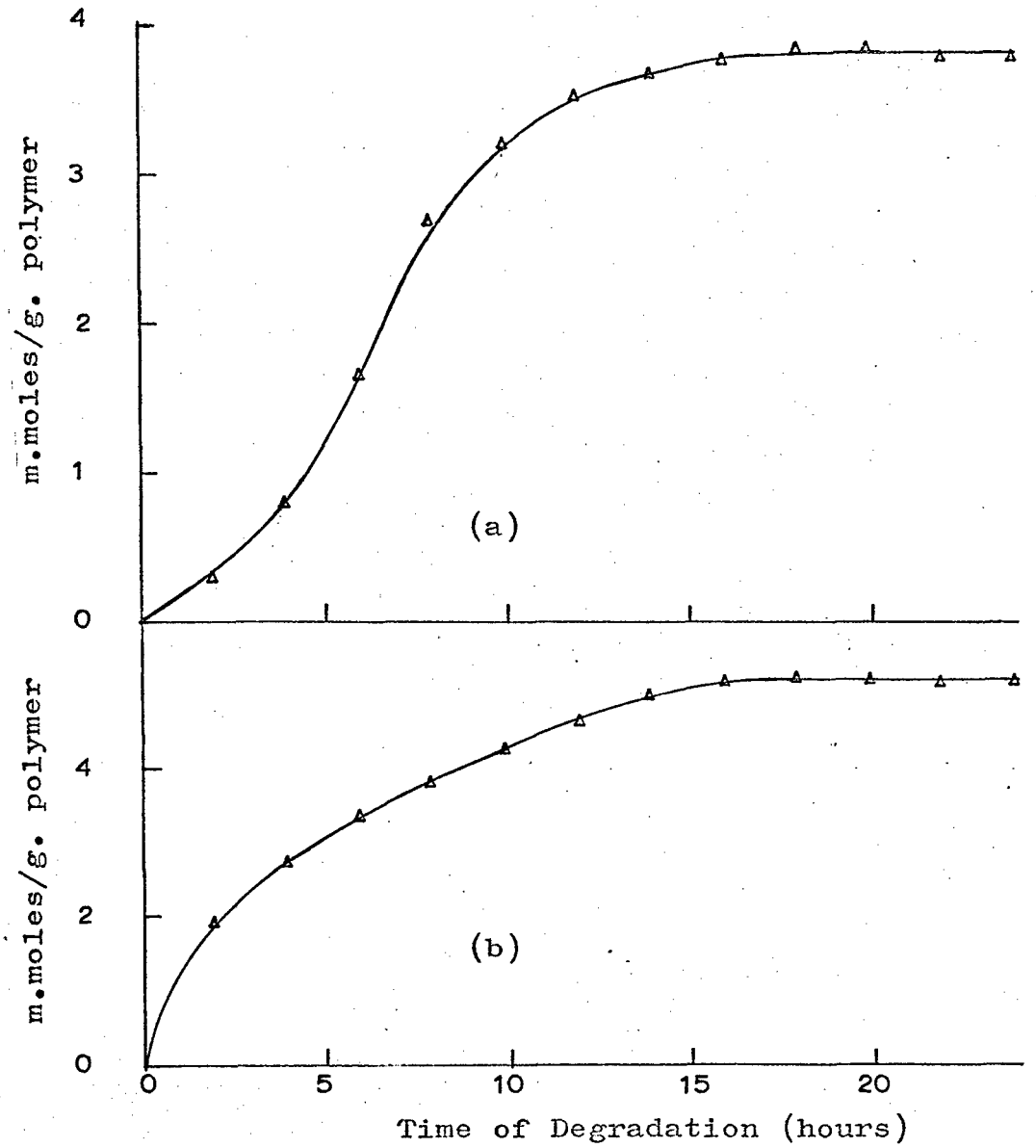


(a) 3.9 mole °/o n-butyl acrylate copolymer.
(b) 16.3 mole °/o n-butyl acrylate copolymer.
Figure 75. Plots of methyl methacrylate production at 313°C.



(a) 50.0 mole °/o n-butyl acrylate copolymer.
(b) 82.2 mole °/o n-butyl acrylate copolymer.

Figure 76. Plots of methyl methacrylate and n-butanol production at 313°C.



(a) Degradation temperature 313°C.
(b) Degradation temperature 332°C.

Figure 77. Plots of n-butanol production for a 93.4 mole °/o n-butyl acrylate copolymer.

TABLE 51. Analysis of the Liquid Degradation Products.
(Data given in terms of millimoles of product per gram initial polymer)

3·9 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time(hours)	2	4	6	8	10	12	14	16	18
Methyl Methacrylate	4·21	6·62	8·23	9·21	9·60	9·70	9·70	9·70	9·70

Traces of n-butyl acrylate and n-butyl methacrylate.

16·3 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time(hours)	2	4	6	8	10	12	14	16	18
Methyl Methacrylate	2·74	4·66	5·69	6·23	6·42	6·56	6·63	6·64	6·64
n-Butyl Acrylate	·12	·20	·24	·27	·28	·28	·28	·28	·28
n-Butyl Methacrylate	·08	·14	·17	·18	·19	·19	·19	·19	·19

50·0 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time(hours)	2	4	6	8	10	12	14	16	18	20
Methyl Methacrylate	·41	·64	·81	·94	1·06	1·17	1·26	1·35	1·40	1·45
n-Butanol	·27	·77	1·40	2·11	2·73	3·01	3·10	3·21	3·20	3·14
n-Butyl Acrylate	·11	·17	·22	·25	·29	·32	·34	·37	·38	·39
n-Butyl Methacrylate	·08	·12	·15	·17	·19	·21	·23	·25	·26	·27

82·2 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time(hours)	2	4	6	8	10	12	14	16	18	20	22
Methyl Methacrylate	·02	·03	·05	·06	·07	·08	·09	·09	·10	·10	·11
n-Butanol	·29	·65	1·07	1·53	1·98	2·35	2·64	2·85	2·97	3·10	3·08
n-Butyl Acrylate	·01	·03	·04	·05	·05	·06	·07	·07	·08	·08	·08
n-Butyl Methacrylate	·01	·01	·02	·02	·02	·03	·03	·03	·04	·04	·04

93·4 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time(hours)	2	4	6	8	10	12	14	16	18	20	22	24
n-Butanol	·32	·82	1·68	2·70	3·24	3·53	3·70	3·79	3·87	3·87	3·81	3·75

Trace of n-Butyl Acrylate.

93·4 Mole Percent n-Butyl Acrylate Copolymer at 332°C

Degradation Time(hours)	2	4	6	8	10	12	14	16	18	20	22	24
n-Butanol	1·91	2·72	3·35	3·84	4·28	4·66	5·03	5·23	5·29	5·28	5·23	5·16

Trace of n-Butyl Acrylate

A detailed mass balance for the copolymers degraded is given in table 52. The percentage by weight of total chain fragments was obtained by adding the percentage of chain fragments, if any, to the percentage of short chain fragments found in the liquid products. This latter quantity was determined, as previously mentioned, by subtracting the sum of the percentages of alcohol, n-butyl acrylate, n-butyl methacrylate and methyl methacrylate from the total percentage of liquid volatiles, and since it was determined by difference and not directly, is subject to quite large errors.

Discussion of Results

As expected the amount of methyl methacrylate found in the degradation products decreases while the amount of alcohol increases with increasing acrylate content. n-Butanol is not produced until the acrylate content reaches 50 mole percent, table 50, that is until acrylate units are present in sequences. From the curves for the production of n-butanol at 313°C, Figs. 76 and 77, it may be seen that the rate of alcohol evolution reaches a maximum after about seven hours degradation, which could imply that the formation of alcohol is autocatalytic in nature. Although Cameron and Kane (56) made no mention of a similar effect for methanol evolution in the degradation of poly(methyl acrylate), this kind of behaviour has been noted in other investigations of alcohol production from polyacrylates (2). It has been suggested that this effect is a result of the increasing rigidity of the polymer molecule as degradation proceeds (2). If this is correct, then as the temperature of degradation is raised, it would be reasonable to suppose that the occurrence of such a rate maximum would be less pronounced. At 332°C, Fig. 77 shows that, for the degradation of a 93·4 mole percent n-butyl acrylate copolymer, no rate maximum is evident. This will be discussed more fully in a later chapter.

In table 53 the concentrations of n-butyl acrylate and n-butyl methacrylate at infinite degradation times are listed, the data applying to a pyrolysis temperature of 313°C.

At first sight it appears anomalous that while a 60·0 mole percent n-butyl acrylate copolymer produces on degradation 0·39 m.moles/g. polymer of n-butyl acrylate monomer, a copolymer containing 93·4 mole percent acrylate only evolves trace amounts of this compound. This kind of effect, however, has also been reported by McCormick (57) who found that the amount of ethyl acrylate evolved from a 25 mole percent ethyl acrylate-methyl methacrylate copolymer was more than twice that evolved by the acrylate homopolymer, although the copolymer contained only one quarter the amount of acrylate. One explanation is that

TABLE 52. Mass Balance Data
(Data given in terms of percentage of the initial polymer weight).

3·9 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time (hours)	2	4	6	8	10	12	14	16	18
Carbon Dioxide	·4	·6	·8	·9	·9	·9	1·0	1·0	1·0
Methyl Methacrylate	42·1	66·2	82·3	92·1	96·0	97·0	97·0	97·0	97·0
Total Chain Fragments	·9	1·3	1·7	1·9	2·0	2·0	2·0	2·0	2·0
Residue	50·0	31·0	18·0	9·8	6·2	4·8	3·9	3·8	3·8
Total Products	93·4	99·1	102·8	104·7	105·1	104·7	103·9	103·8	103·8

16·3 Mole Percent n-Butyl Acrylate Copolymer at 313°C

Degradation Time (hours)	2	4	6	8	10	12	16	18	20
Carbon Dioxide	·8	1·2	1·5	1·7	1·9	2·0	2·2	2·3	2·3
But-1-ene	·2	·4	·5	·6	·6	·6	·6	·6	·6
Methyl Methacrylate	27·4	46·6	56·9	62·3	64·2	65·6	66·3	66·4	66·4
n-Butyl Acrylate	1·5	2·5	3·1	3·4	3·5	3·6	3·6	3·6	3·6
n-Butyl Methacrylate	1·1	2·0	2·3	2·6	2·6	2·7	2·7	2·7	2·7
Total Chain Fragments	7·5	12·8	15·6	17·1	17·7	17·9	18·2	18·3	18·3
Residue	69·5	43·4	24·5	14·3	10·0	7·2	5·3	5·0	5·0
Total Products	108·0	108·9	104·4	102·0	100·5	99·6	98·9	98·9	98·9

Table 52 (cont'd.)

50·0 Mole Percent n-Butyl Acrylate Copolymer at 313°C.

Degradation Time(hours)	2	4	6	8	10	12	14	16	18	20
Carbon Dioxide	1·1	2·1	3·0	3·7	4·2	4·6	5·0	5·3	5·5	5·5
But-1-ene	·9	1·6	2·1	2·5	2·6	2·6	2·6	2·6	2·6	2·6
Methyl Methacrylate	4·1	6·4	8·1	9·4	10·6	11·7	12·6	13·5	14·0	14·5
n-Butyl Acrylate	1·4	2·2	2·8	3·3	3·7	4·1	4·4	4·7	4·9	5·0
n-Butyl Methacrylate	1·1	1·7	2·1	2·4	2·8	3·0	3·3	3·5	3·7	3·8
n-Butanol	2·0	5·7	10·3	15·6	20·2	22·3	23·0	23·8	23·7	23·3
Total Chain Fragments	9·4	11·7	11·7	10·0	8·7	9·6	11·4	13·2	14·7	16·4
Residue	76·4	65·0	57·8	52·0	48·2	44·5	41·2	38·0	35·2	32·8
Total Products	96·4	96·4	97·9	98·9	101·0	102·4	103·5	104·6	104·3	103·9

82·2 Mole Percent n-Butyl Acrylate Copolymer at 313°C.

Degradation Time(hours)	2	4	6	8	10	12	14	16	18	20	22
Carbon Dioxide	1·9	3·0	3·9	4·7	5·4	6·1	6·6	7·2	7·4	7·8	7·9
But-1-ene	1·6	2·4	2·9	3·3	3·6	3·3	4·0	4·1	4·4	4·4	4·5
Methyl Methacrylate	·2	·3	·5	·6	·7	·8	·9	·9	1·0	1·0	1·1
n-Butyl Acrylate	·2	·3	·5	·6	·7	·8	·9	·9	1·0	1·0	1·1
n-Butyl Methacrylate	·1	·2	·2	·3	·3	·4	·4	·5	·5	·5	·5
n-Butanol	2·1	4·8	8·0	11·3	14·6	17·4	19·6	21·1	22·0	22·6	22·8
Total Chain Fragments	6·7	11·6	14·9	17·0	18·5	19·9	21·4	23·3	25·2	27·2	28·8
Residue	80·0	70·5	63·0	57·4	52·0	46·8	42·5	38·5	35·3	33·0	30·9
Total Products	92·8	93·1	93·9	95·2	95·8	96·0	96·3	96·5	96·8	97·5	97·6

TABLE 52 (cont'd.)

93·4 Mole Percent n-Butyl Acrylate Copolymer at 313°C.

Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20	22	24
Carbon Dioxide	1·9	3·3	4·6	5·6	6·5	7·4	8·1	8·7	9·2	9·6	9·9	10·2
But-1-ene	1·3	2·4	3·2	4·0	4·7	5·3	5·9	6·4	6·6	6·9	7·0	7·0
n-Butanol	2·4	6·1	12·4	20·0	24·0	26·1	27·4	28·1	28·6	28·6	28·2	27·8
Total Chain Fragments	9·0	12·8	13·1	10·0	10·7	11·9	13·7	15·4	17·1	18·6	20·1	21·3
Residue	89·5	81·2	74·0	67·4	61·5	55·0	50·0	45·7	42·3	39·6	37·6	35·7
Total Products	104·1	105·8	107·3	107·0	107·4	105·7	105·1	104·3	103·8	103·3	102·8	102·0

93·4 Mole Percent n-Butyl Acrylate Copolymer at 332°C.

Degradation Time (hours)	2	4	6	8	10	12	14	16	18	20	22	24
Carbon Dioxide	4·7	6·6	8·4	9·4	10·2	10·8	11·1	11·4	11·5	11·6	11·7	11·7
But-1-ene	4·4	6·1	7·0	7·9	8·4	8·7	9·1	9·4	9·7	9·8	9·9	10·0
n-Butanol	14·2	20·0	24·8	28·4	31·7	34·5	37·2	38·7	39·1	39·1	38·7	38·2
Total Chain Fragments	16·1	20·9	23·4	24·6	24·6	24·0	23·0	22·6	23·4	24·0	24·7	25·5
Residue	67·6	54·2	46·2	39·4	33·0	28·1	24·2	21·1	19·0	17·3	16·1	15·8
Total Products	107·0	108·0	109·8	109·7	107·9	106·1	104·6	103·2	102·7	101·8	101·1	101·2

TABLE 53

Copolymer Composition (mole % n-butyl acrylate)	n-Butyl Acrylate (m.moles per g. polymer)	n-Butyl Methacrylate (m.moles per g. polymer)
3·9	trace	trace
16·3	0·28	0·19
50·0	0·39	0·27
82·2	0·08	0·04
93·4	trace	nil

the acrylate monomer is produced in a depolymerization reaction initiated at methacrylate chain units, capable of unzipping through some of the acrylate units, before termination occurs. In the acrylate homopolymer no methacrylate units are available to initiate such depolymerizations, and since acrylate radicals prefer to take part in transfer reactions rather than to depolymerize, very little monomer is produced.

n-Butyl methacrylate is obtained in highest yield from the 50·0 mole percent n-butyl acrylate copolymer, which is consistent with the idea that its production depends upon the number of acrylate-methacrylate linkages in the chain.

With increasing acrylate content the percentage of chain fragments increases reflecting the increasing number of transfer reactions taking place during breakdown. The stability of the copolymers is shown by the greater percentage of residue found for any given time of degradation the greater the percentage of n-butyl acrylate in the original copolymer.

Use of a higher degradation temperature favours the production of gases, liquids and chain fragments at the expense of the residue.

CHAPTER 10

THERMAL DEGRADATION OF COPOLYMERS OF METHYL METHACRYLATE AND n-BUTYL ACRYLATE. E. THE RESIDUE AND CHAIN FRAGMENTS.

INTRODUCTION

In the last chapter a thorough examination of the gaseous and liquid degradation products was made. It is also appropriate to investigate the other products of decomposition, namely the residue and chain fragments.

INVESTIGATION OF THE RESIDUE

Spectroscopic Techniques

Infra-red

For copolymers of high methacrylate content the entire residue was found to be soluble in carbon tetrachloride, so that spectra of both the degraded and undegraded material could be run in solution. As the acrylate content of the copolymer is increased, the residue becomes increasingly insoluble in organic solvents so that some other technique must be used to obtain spectra. Grinding the residue with potassium bromide and pressing the mixture to form discs was not very successful because of the difficulties of grinding a rubbery material. The best method found for such copolymers consisted of applying a solution of the undegraded polymer in toluene to two salt plates and removing the solvent in a vacuum oven at 80°C. The plates were then placed together, the polymer film being sandwiched between them, and the whole assembly degraded in a sealed tube. Fig. 78 shows a typical spectrum of an undegraded copolymer together with a spectrum of the same material after degradation between salt plates at 313°C. These differ in that the spectrum of the pyrolyzed copolymer has a shoulder at 1760 cm^{-1} on the carbonyl peak, and a new peak at 1560 cm^{-1}, while the other absorptions have broadened. Only degradations carried out on salt plates

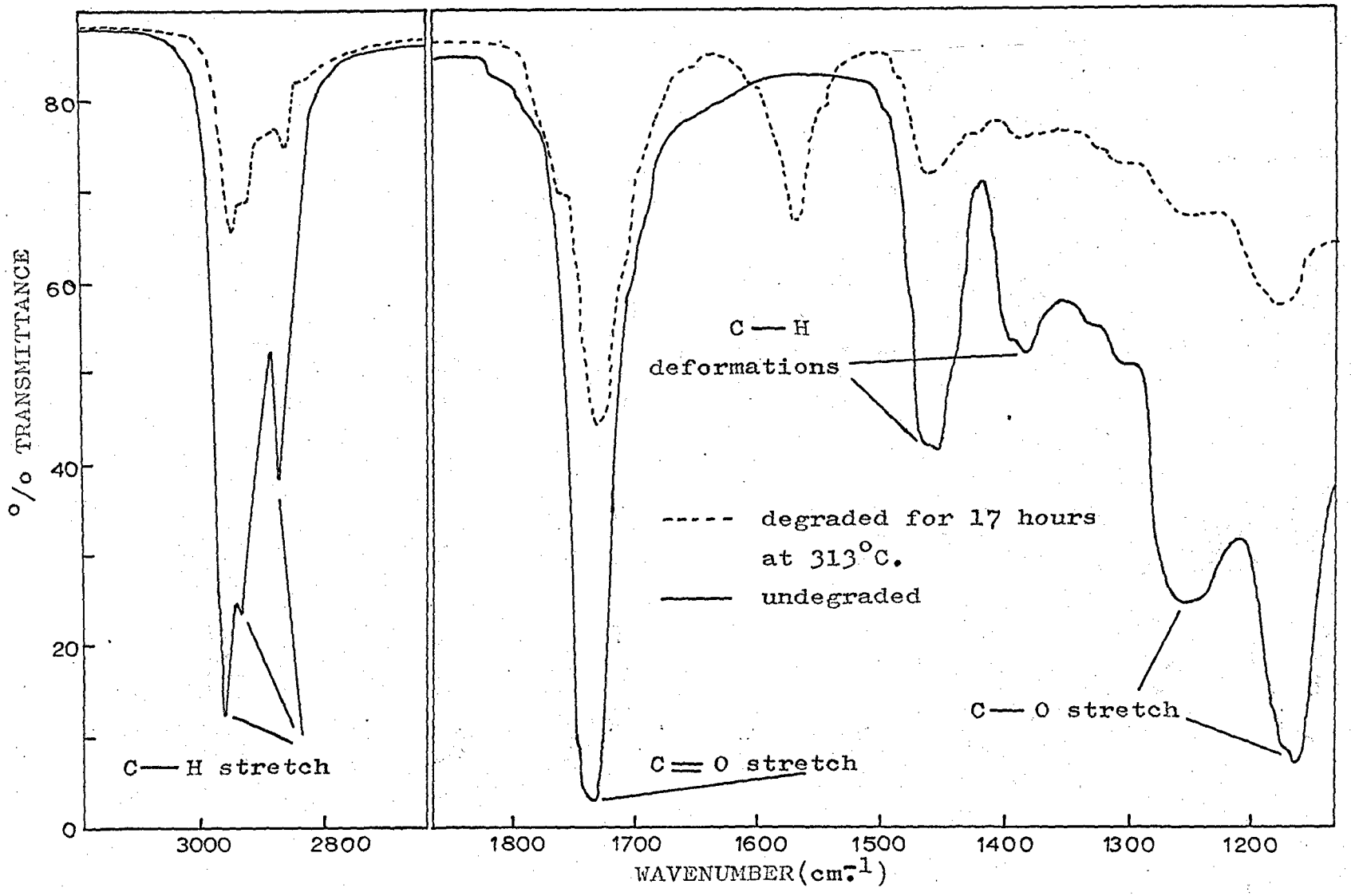


Figure 78. Infra-red spectra of an 82.2 mole °/o n-butyl acrylate copolymer.

showed the new absorption. The shoulder at 1760 cm^{-1} becomes better defined when both the acrylate content of the starting material and the time of degradation are increased. In addition to these absorptions, the 93·4 mole percent n-butyl acrylate copolymer exhibits a small peak at 1605 cm^{-1}, which has also been reported for the degradation of pure poly(n-butyl acrylate) (2).

Dealing first with the absorption at 1560 cm^{-1}, the possibilities are strictly limited, the only likely assignment being that of a carboxylate ion $\left(\begin{array}{c}C{=}O\\ |\\ O(-)\end{array}\right)$ The most reasonable explanation is that ester decomposition reactions leave carboxylic acid residues pendant to the main chain. Under the experimental conditions these may react with the salt plates to form the appropriate sodium salt. If this explanation is correct, a polymer such as poly(methacrylic acid) should, under similar conditions of degradation, show a similar absorption at 1560 cm^{-1}. Because of the insolubility of this polymer in solvents suitable for coating on salt plates it was ground up with sodium chloride and degraded in a sealed tube at 313°C for seven hours. A sample of pure poly(methacrylic acid) was similarly degraded under identical conditions as a control. The sample heated with sodium chloride had an absorption at 1560 cm^{-1}, while the control sample had not. Neither does undegraded poly(methacrylic acid) absorb in this region. To check that copolymers of high acrylate content showed this absorption when degraded as a mixture with sodium chloride, a sample of the 82·2 mole percent n-butyl acrylate copolymer was degraded in this way, the new absorption appearing as expected. These experiments confirm the general nature of this absorption.

The shoulder on the carbonyl peak at 1760 cm^{-1} may be ascribed to a γ lactone, an $\alpha\beta$ unsaturated γ lactone, or a $\beta\gamma$ unsaturated δ lactone. It has been postulated that anhydride groups have a doublet absorption at about 1800 cm^{-1} and 1760 cm^{-1}. No peak at 1800 cm^{-1} was observed in the decomposition of the copolymers, but it should be pointed out that the reaction of the acid residue with the salt plates may take place in preference to anhydride formation so that production of anhydride units cannot definitely be ruled out by this result. Recently, however, an RM-100 Rotomill (Research and Industrial Instr. Co.) has become available, and can be used to prepare acceptable potassium bromide discs from the residue resulting from

decomposition of copolymers of high acrylate content. An examination of the 82·2 mole percent n-butyl acrylate copolymer by this technique showed no absorption at 1800 $cm.^{-1}$ so that production of anhydride in the residue can be dismissed.

The absorption at 1605 $cm.^{-1}$ can be attributed to conjugated carbon-carbon double bonds.

U.V.-Visible

As degradation proceeds the colour of the residual polymer goes through yellow to brown and for similar extents of decomposition the copolymers of greater acrylate content exhibit more pronounced coloration. U.V.-Visible spectra were run of polymeric films deposited on the base of a silica flange, a procedure which was found to be necessary since suitable solvents for the copolymers did not have sufficient transmittance in the U.V. The copolymers examined were the 3·9 mole percent and 82·2 mole percent n-butyl acrylate copolymers. 2 ml. of a 50 mg./ml. solution of the sample in toluene was pipetted on to the flat base of a silica flange and the solvent removed in a vacuum oven at 80°C. The samples were degraded at 313°C using the glass still (see Chapter 6), spectra being run by placing the whole flange in the beam of the spectrometer. Scans were run from 880 mμ to 200 mμ, the undegraded copolymers showing an absorption maximum at about 227 mμ corresponding to absorption by the ester group. As the 82·2 mole percent copolymer was degraded there was a general increase in absorption in the region from 420 mμ down to 227 mμ, while in the case of the 3·9 mole percent copolymer, increasing absorption in this region did not become important till long degradation times, and was still much less than that exhibited by the material richer in acrylate. This new absorption, Fig. 79, has no characteristic maximum, and may be attributed to the presence of varying lengths of ethylenic unsaturation, the maximum length of such conjugation being about eight double bonds which corresponds to a μ_{max} of 415 mμ.

N.M.R.

The soluble residue from breakdown of the 50·0 mole percent n-butyl acrylate copolymer at 313°C was examined by N.M.R. A spectrum of degraded material is shown in Fig. 80, run in carbon tetrachloride with tetramethyl silane as standard. No new absorptions appeared on decomposition, and the ratio of the two kinds of ester group present as given by the ratio of $-OCH_2-$ to $-OCH_3$ protons also remained constant.

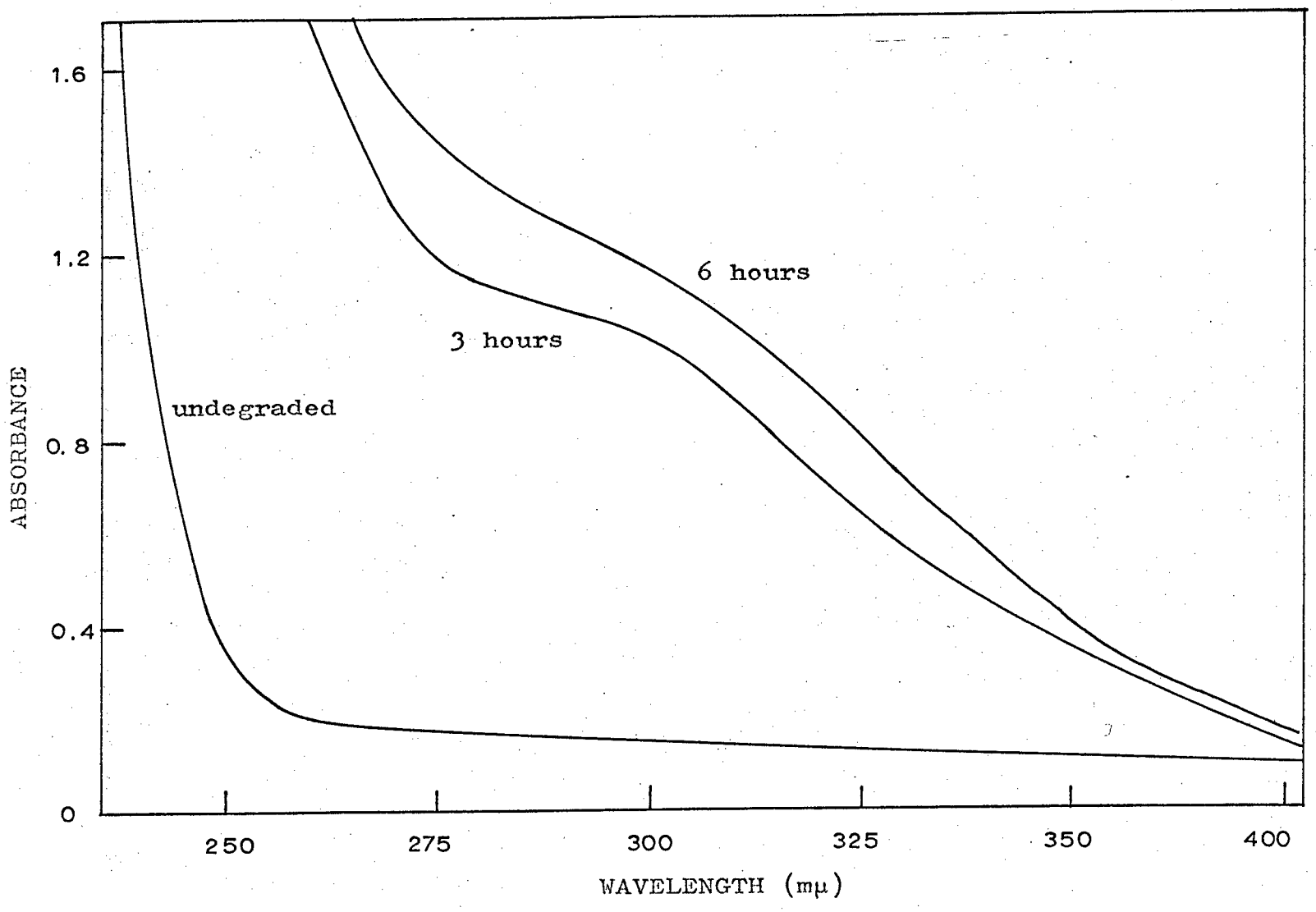


Figure 79. U.V. spectra of an 82.2 mole °/o n-butyl acrylate copolymer degraded for the times shown.

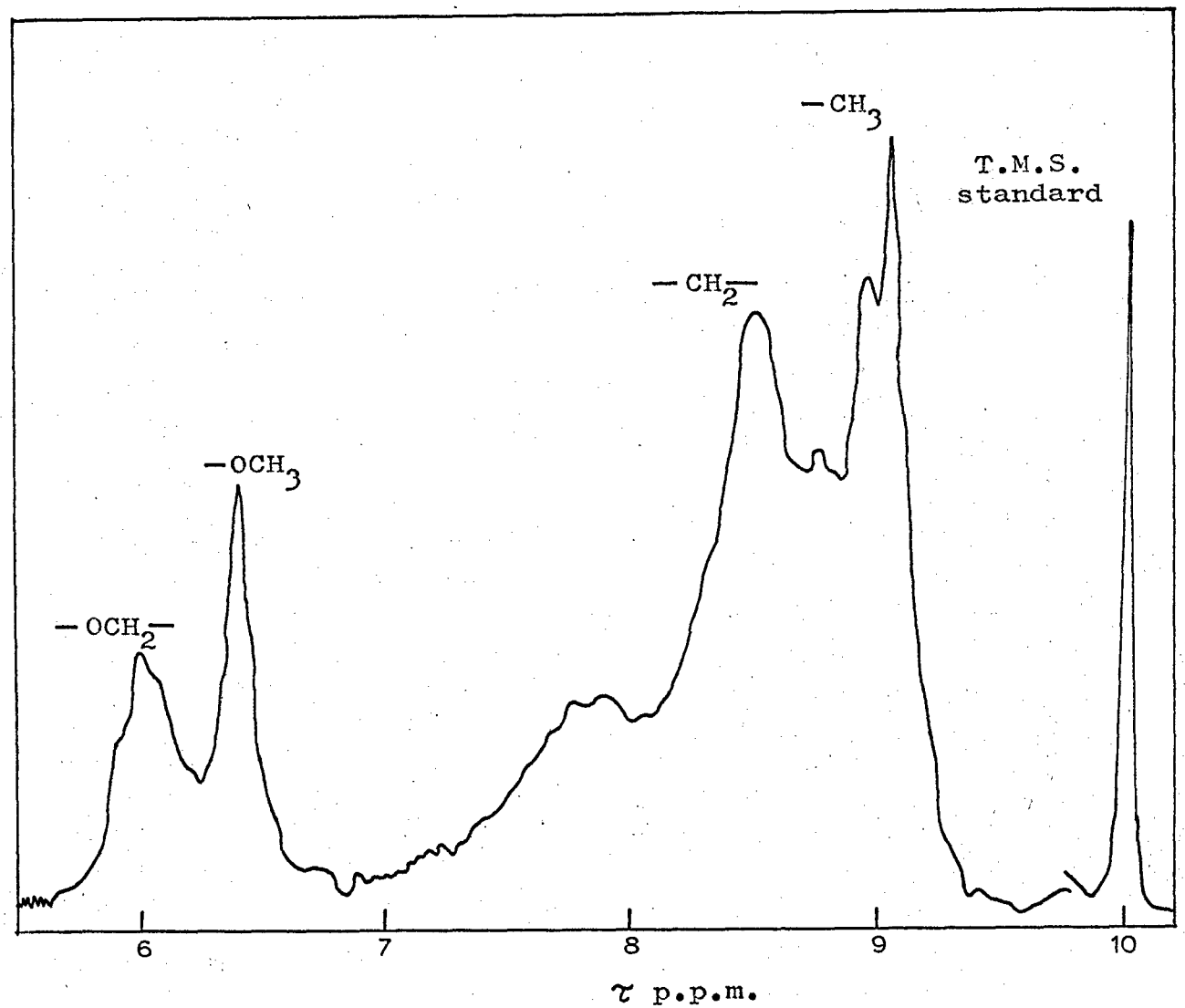


Figure 80. N.M.R. of a 50.0 mole °/o n-butyl acrylate copolymer degraded at 313°C for 16 hours. (Run in carbon tetrachloride solution.)

Elemental Analysis

Micro analysis was carried out on the residue obtained by the degradation of a 50·0 mole percent n-butyl acrylate copolymer at 332°C. Because of the tendency of the residue to adhere to the walls of the glass pyrolysis tube, it was quite difficult to obtain a sample for combustion. Table 54 lists the relative weights of carbon, hydrogen and oxygen in the sample, the oxygen figure being found by difference.

TABLE 54

Time of Degradation (hours)	%C	%H	%O
0 (calculated data)	63·13	8·83	28·04
14·5	78·98	6·73	14·29
24·0	77·80	6·53	15·63

These results show that on degradation the carbon content rises while the hydrogen and oxygen content falls. A similar result has been reported for decomposition of the homopolymer, poly(n-butyl acrylate) (2). The complexity of the degradation of the copolymers as reflected by the variety of products obtained makes interpretation of data such as this extremely difficult, so that extensive examination of copolymer residues by this technique was not undertaken.

Molecular Weight Measurements

The molecular weight changes which occur on degradation at 313°C of the 0·4 mole percent and 50·0 mole percent n-butyl acrylate copolymers are plotted in Fig. 81. On this type of plot polymers breaking down by depolymerization processes give curves lying above the diagonal AC while those degrading by random scission lie along ABC (34). The behaviour of the 0·4 mole percent copolymer is much nearer to that displayed by pure poly(methyl methacrylate) than is the behaviour of the 50·0 mole percent copolymer. This is to be expected, but it is interesting to note the disproportionate effect of a small amount of acrylate. A similar type of result has been found for other copolymer systems. In Chapter 7 copolymers with acrylate contents of up to 50·0 mole percent were treated from a thermogravimetric point of view as degrading by a first order type of process whereas Fig. 81 would seem to indicate that even with as little as 0·4 mole percent n-butyl acrylate, the copolymers should be treated as randomly degrading entities.

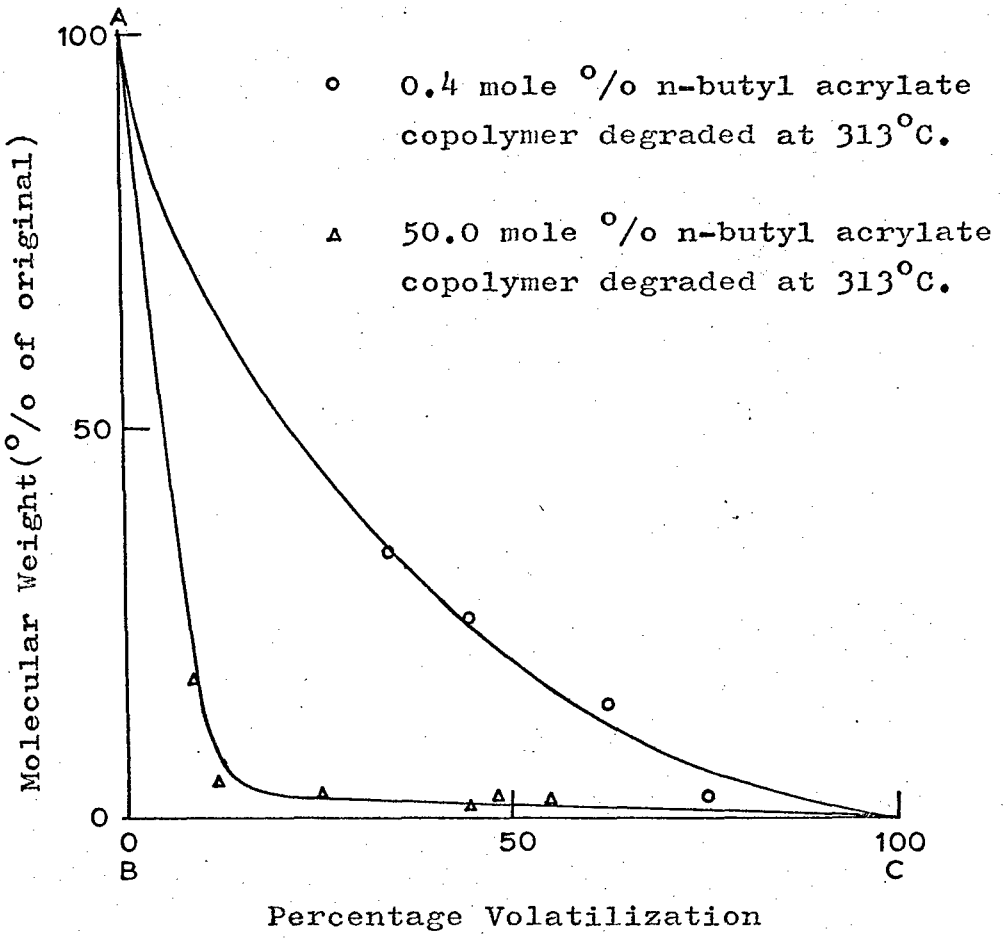


Figure 81. Molecular weight versus percentage volatilization plots.

The reason for this apparent contradiction is that a few scissions occurring at random in a polymer molecule will make a great difference to the molecular weight of the sample, but will not lead to any weight loss, unless some scissions occur close together. If a copolymer can degrade both by random scission and by depropagation simultaneously, it is clear that molecular weight measurements will be more sensitive to the random reaction, while weight loss methods will tend to follow the depropagation reaction. It is therefore the relative sensitivity of these two differing methods of following thermal breakdown which leads to an apparently anomalous situation.

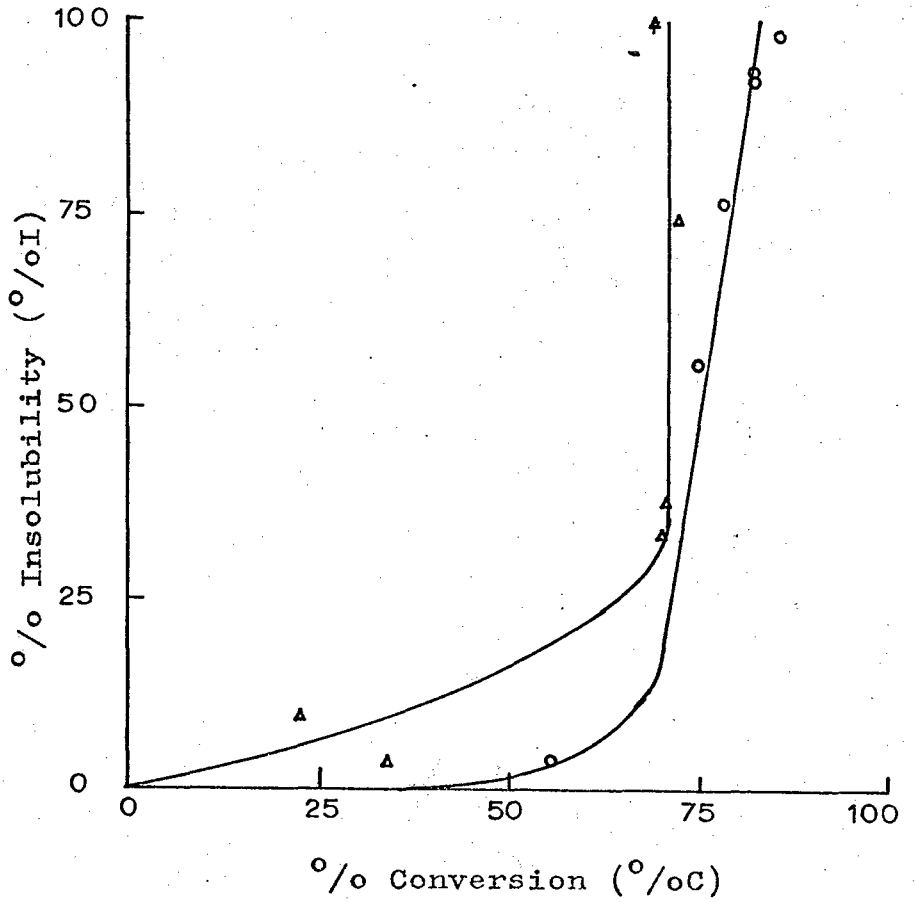
Sol-Gel Analysis

The Soxhlet extraction technique described in chapter 6 was used to investigate the relative amounts of soluble and insoluble material in the polymeric residues. This method ensures a constant supply of fresh solvent with which to perform efficient extraction. Benzene was used since it is desirable to use a fairly low boiling solvent in order to prevent further decomposition of the polymer during extraction. This investigation was extended to include measurements on homopolymers of n-butyl acrylate. The polymers examined and the degradation conditions employed are listed in table 55.

TABLE 55

Polymer Composition (mole % n-butyl acrylate)	Molecular Weight, $\overline{M}_n$	Temperature of Degradation, °C
100	870,000	313 and 329
93·4	76,500	329
93·4	3,160,000	329
52·4	1,330,000	313

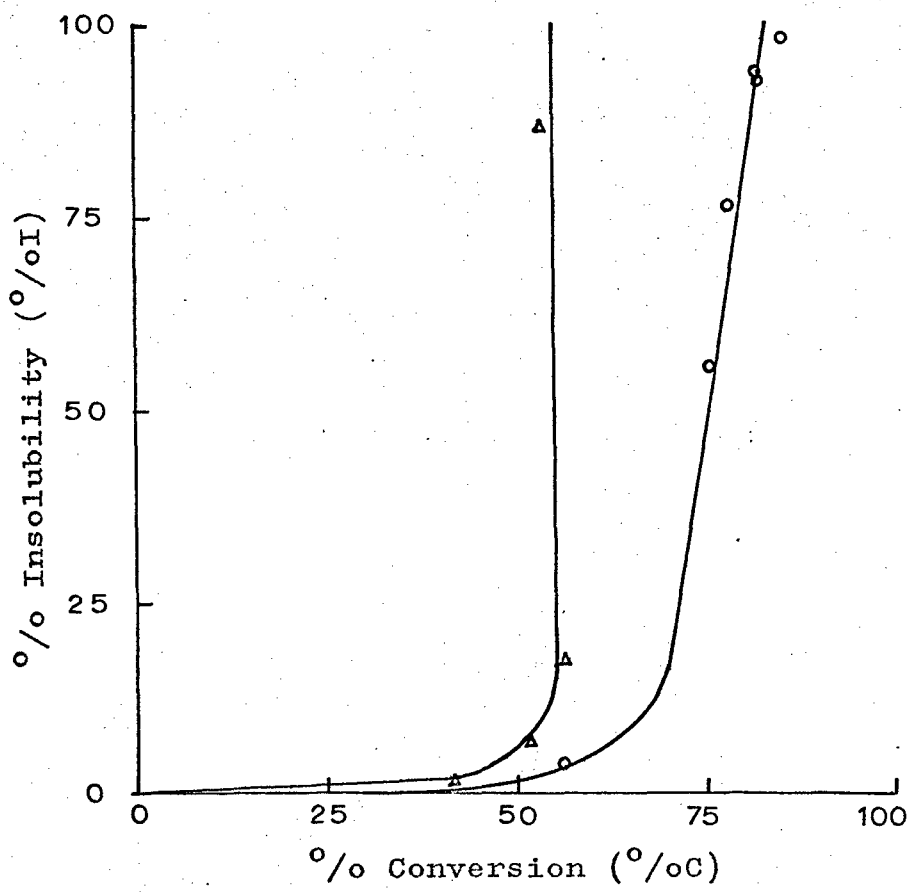
As detailed in chapter 6, for each run the weight of gel, $(\Delta Q+\Delta S)$, weight of sol, $(\Delta P-\Delta S)$, and total weight of residue, $(\Delta P+\Delta Q)$, were determined. Knowing in addition the initial weight of polymer degraded, W, the percentage insolubility, $\% I = [(\Delta Q+\Delta S)/(\Delta P+\Delta Q)] \times 100$, and percentage conversion, $\%C = [1 - (\Delta P+\Delta Q)/W] \times 100$, were found. The effect of composition, Fig. 82, molecular weight, Fig. 83, and temperature



▲ n-butyl acrylate homopolymer, $\overline{M}_n$ 870,000.

o 93.4 mole °/o n-butyl acrylate copolymer, $\overline{M}_n$ 76,500.

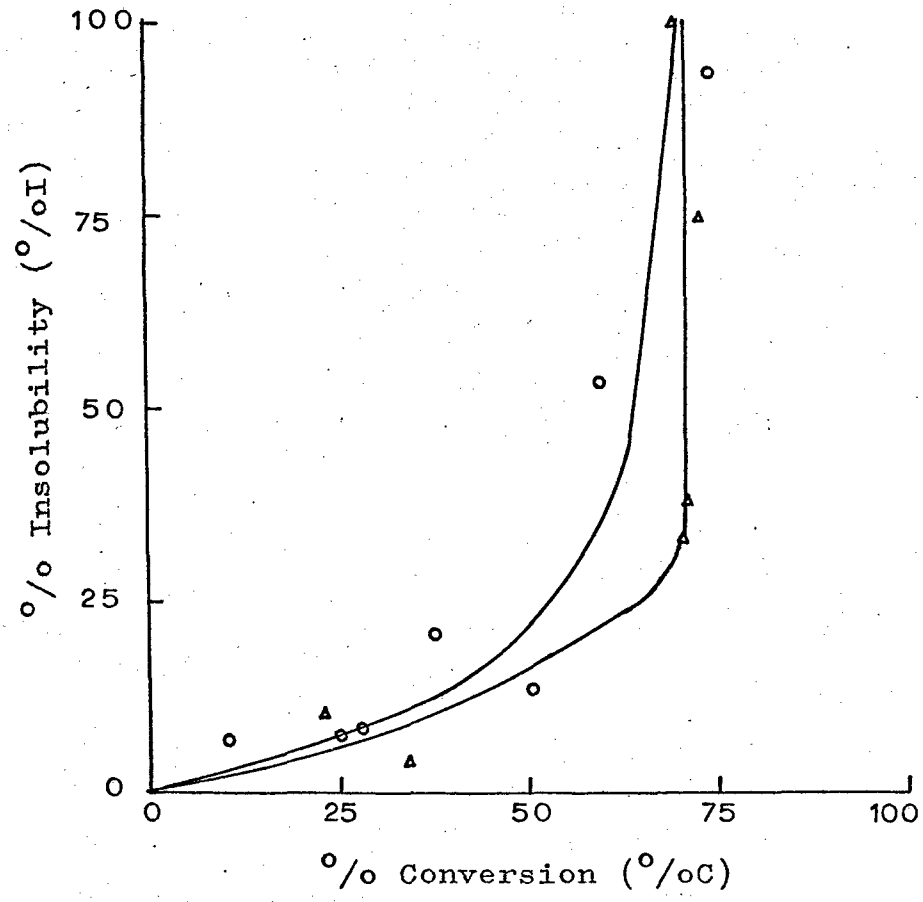
Figure 82. Effect of composition on gel formation at 329°C.



▲ 93.4 mole % n-butyl acrylate copolymer $\bar{M}_n$ 3,160,000.

o 93.4 mole % n-butyl acrylate copolymer $\bar{M}_n$ 76,500.

Figure 83. Effect of molecular weight on gel formation at 329°C.



△ Degradation temperature 329°C.

○ Degradation temperature 313°C.

Figure 84. Effect of temperature of degradation on gel formation in poly(n-butyl acrylate) $\overline{M}_n$ 870,000.

of degradation, Fig. 84, are shown by appropriate plots of %I versus %C in the figures mentioned, using the values listed in tables 56-59.

Solubility depends upon the flexibility of the polymer chain and on its ability to adopt any orientation with respect to solvent molecules. Factors which tend to reduce the possibility of attaining such orientations will therefore tend to reduce solubility. The development of insolubility in a polymer as degradation proceeds can be associated with cross linking reactions or the formation of rigid structures by intramolecular processes. The occurrence in the n-butyl acrylate - methyl methacrylate copolymer system of such cross links or rigid structures due to inter- and intramolecular anhydride formation respectively may be discounted as there is no evidence for the existence of such functional groups in the residue, so that it seems likely that insolubility is caused by cross linking of n-butyl acrylate units through their tertiary carbon atoms, a contribution also being made by the formation of ring systems which increase the rigidity of the polymer chain.

Effect of Copolymer Composition on Gel Formation

Fig. 82 shows that for a fixed degree of conversion the amount of gel formation in the acrylate homopolymer is always greater than that in the copolymer containing 93·5 mole percent acrylate, when both are degraded at 329°C. Comparison of the data given in tables 56 and 60 for degradations carried out at 313°C confirm the observation that increasing the acrylate content of the system increases gelation at any given conversion. These results reflect the different modes of breakdown of acrylates and methacrylates.

Effect of Molecular Weight on Gel Formation

From the introductory discussion it would appear that gel formation should be a function of both cross link density and the length of the chains being cross linked. Fig. 83 shows the effect of molecular weight on the formation of gel for 93·4 mole percent n-butyl acrylate copolymers. As predicted, for a given degree of conversion the higher molecular weight material contains a greater proportion of insoluble residue than does the lower molecular weight sample.

Effect of Degradation Temperature on Gel Formation

In the case of poly(n-butyl acrylate) degraded at 313°C and at 329°C, Fig. 84 shows that there is greater insolubility

Table 56

Sol-gel Analysis Data for Poly(n-butyl acrylate)

$\overline{M}_n$ 870,000 Degraded at 313°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
1	10	7
2	25	8
4	28	8
10	38	20
16	51	14
20	60	53
24	75	94

Table 57

Sol-gel Analysis Data for Poly(n-butyl acrylate)

$\overline{M}_n$ 870,000 Degraded at 329°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
2	23	11
5	34	4
10	71	38
19	72	75
24	69	100

Table 58

Sol-gel Analysis Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer, $\overline{M}_n$ 76,500, Degraded at 329°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
4	56	4
10	76	56
21	82	94
24	86	98

Table 59

Sol-gel Analysis Data for a 93.4 Mole °/o n-Butyl Acrylate Copolymer, $\overline{M}_n$ 3,160,000, Degraded at 329°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
1	43	2
8	52	7
12	57	18
24	55	87

Table 60

Sol-gel Analysis Data for a 52.4 Mole °/o n-Butyl Acrylate Copolymer, $\overline{M}_n$ 1,330,000, Degraded at 313°C.

Time of Degradation (hours)	°/oConversion (°/oC)	°/oInsolubility (°/oI)
4	34	.4
6	38	.3
17	27	.6

at the lower temperature of decomposition than at the higher when the same degree of conversion is considered. This result reflects the effect of temperature on the competing processes of depolymerization, random scission, and cross linking.

Degradation at a Lower Temperature

An investigation of the relationship between chain scission and carbon dioxide production in the methyl acrylate - methyl methacrylate copolymer system established that there is a one to one correspondence between these processes (18,33). It was thus considered to be of interest to investigate what relationship, if any, these reactions bear to one another in the n-butyl acrylate - methyl methacrylate system. In order to study this aspect of the degradation reaction, a lower pyrolysis temperature was chosen than those previously used so that this relationship might be investigated unaccompanied by large scale volatilization reactions.

Carbon Dioxide Production and Chain Scission

The number of chain scissions, N, which have occurred per molecule of copolymer is given by,

$$N = (M_o / M_t - 1)$$

in which M_o and M_t are the initial molecular weight and the molecular weight after degradation for time t respectively. This equation only applies strictly if there is neither cross linking nor loss of polymer molecules from the system. Consequently degradation conditions were chosen such that a large fall in molecular weight could be observed without accompanying detectable weight loss.

All degradations were carried out in the glass still at 237°C. The sample size used was approximately 130 mg., the polymer being degraded as a film cast on the base of a flange from toluene solution. Measurements of the pressure of carbon dioxide evolved were made using a McLeod gauge, and the number of moles of gas produced calculated. After degradation the residue was dissolved in toluene, its molecular weight measured, and the number of chain scissions per molecule of original polymer, N, calculated. Knowing the exact weight of sample used and the molecular weight of the undegraded copolymer, the number of moles of carbon dioxide evolved per mole of initial sample may be found.

The results of these measurements are given in table 61. The plot of carbon dioxide evolved per molecule versus the number of chain scissions per molecule is given, for a 52·4 mole percent n-butyl acrylate copolymer, in Fig. 85, which shows that the amount of this gas produced per chain scission is not constant as degradation proceeds, but increases with time of pyrolysis. This straightforward interpretation of Fig. 85 applies providing that it is assumed that no cross linking occurs. If cross linking does take place to a small extent, however, and this would not seem to be unlikely, then the molecular weight measured after degradation for time t, M_t, would be greater than that found if no cross linking had occurred, so that the value of N calculated would be smaller, and the calculated amount of carbon dioxide per chain scission greater, than the correct value. Thus the data in table 61 and Fig. 85 can also be interpreted in terms of a fixed relationship between chain scission and carbon dioxide production as degradation proceeds, in conjunction with a cross linking reaction. Whichever interpretation is correct, it is clear that simple measurement of carbon dioxide production cannot be used, as it was in the methyl acrylate-methyl methacrylate copolymer system, to determine the extent of chain scission.

Mass Spectrometry

The mass spectrum of the volatile materials evolved from a 52·4 mole percent n-butyl acrylate copolymer heated at 237°C for seven hours is shown in Fig. 86. This spectrum may be interpreted largely in terms of that expected from a mixture of methyl methacrylate and but-1-ene. The small peaks at mass 31 and at mass 44 may be attributed to n-butanol and carbon dioxide respectively. Although these peaks are much smaller than those ascribed to methyl methacrylate and but-1-ene, without calibration of the mass spectrometer no conclusions can be drawn as to their relative importance.

INVESTIGATION OF CHAIN FRAGMENTS

No detailed investigation of the chain fragments was undertaken. As in the case of the residue, the colour of these fragments becomes deeper with increasing acrylate content ranging from yellow to brown. Infra-red spectra of this fraction were run as liquid films between salt plates and were essentially similar to that of the residue shown in Fig. 78. A typical g.l.c. trace of the short chain fragments which distilled into the capillary section of the sealed tube during degradation is shown in Fig.87. A 1% S.E.30 column was used in this work, the retention times for some n-alkanes being shown for comparison.

Table 61.

Data for the Degradation of a 52.4 Mole Percent n-Butyl Acrylate Copolymer at 237°C.

Time of Degradation (hours)	Molecular Weight, M_t	No. of Chain Scissions, N, per Molecule of Polymer	Moles CO_2 per Mole Polymer	Molecules of CO_2 per Chain Scission
0	1,330,000	0	0	0
1	342,000	2.89	1.74	0.60
2	236,000	4.64	3.66	0.79
3	186,000	6.15	4.23	0.69
4	170,000	6.83	6.28	0.92
6	145,000	8.17	8.76	1.07
7	127,000	9.47	10.62	1.12

Sample size 0.133g.

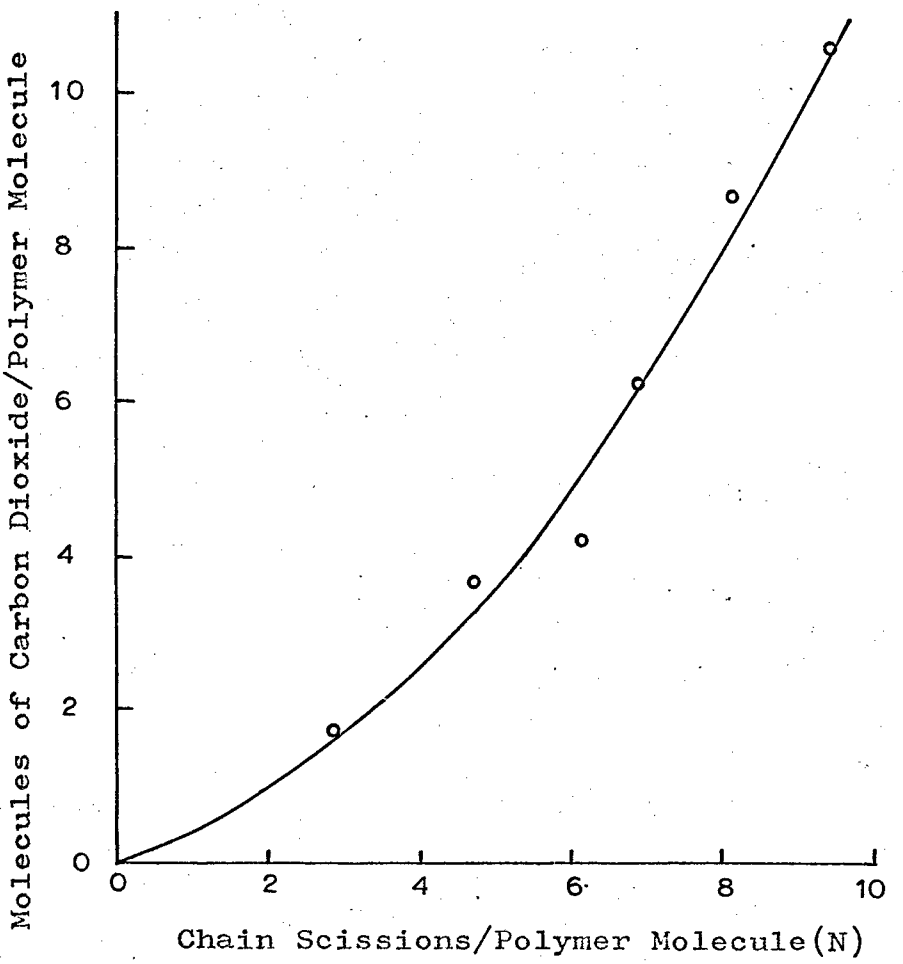


Figure 85. Carbon dioxide evolution versus chain scission plot for a 52.4 mole °/o n-butyl acrylate copolymer degraded at 237°C.

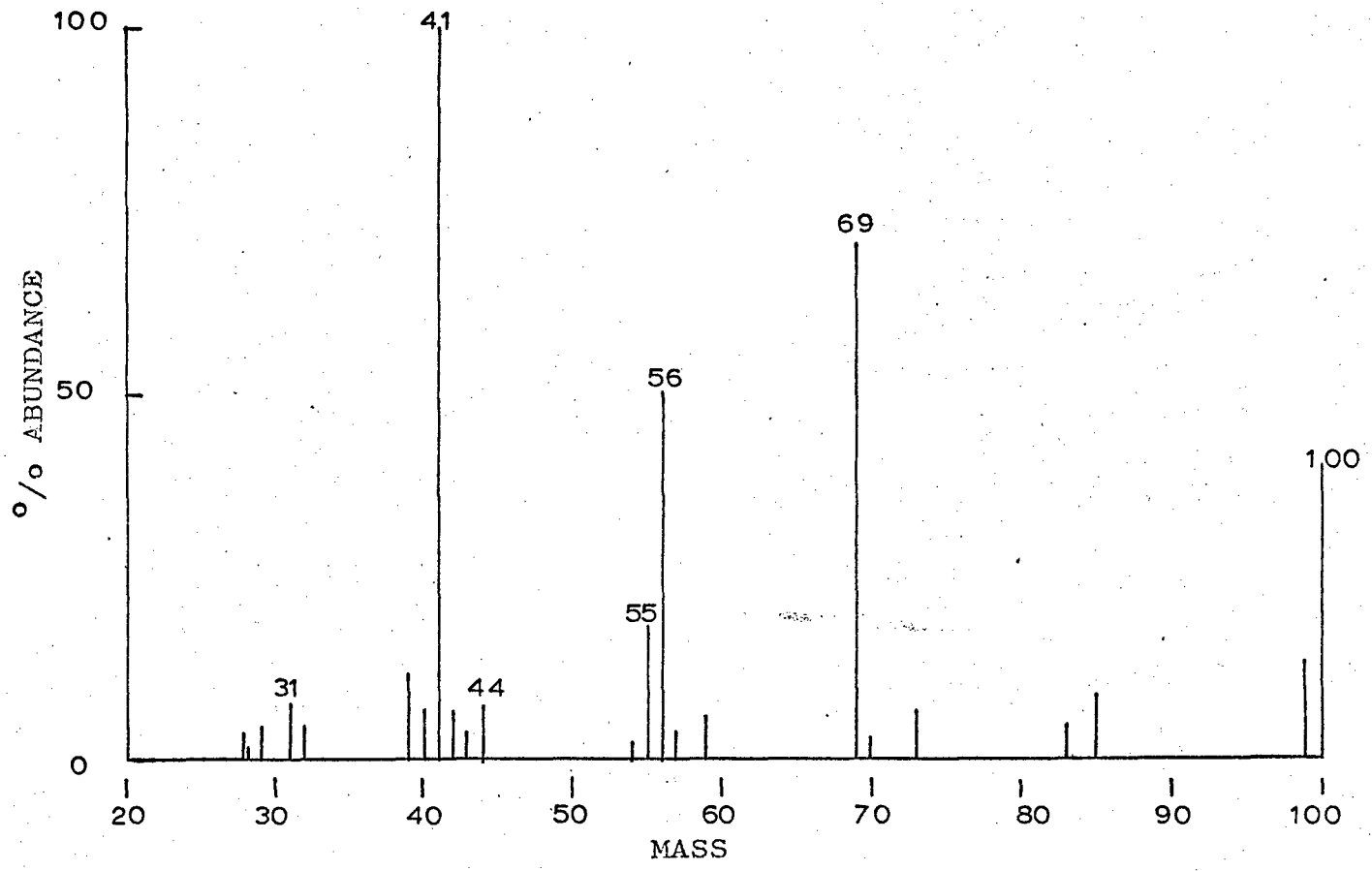


Figure 86. Mass spectrum (20ev) of products from the degradation of a 52.4 mole percent n-butyl acrylate copolymer for seven hours at 237°C.

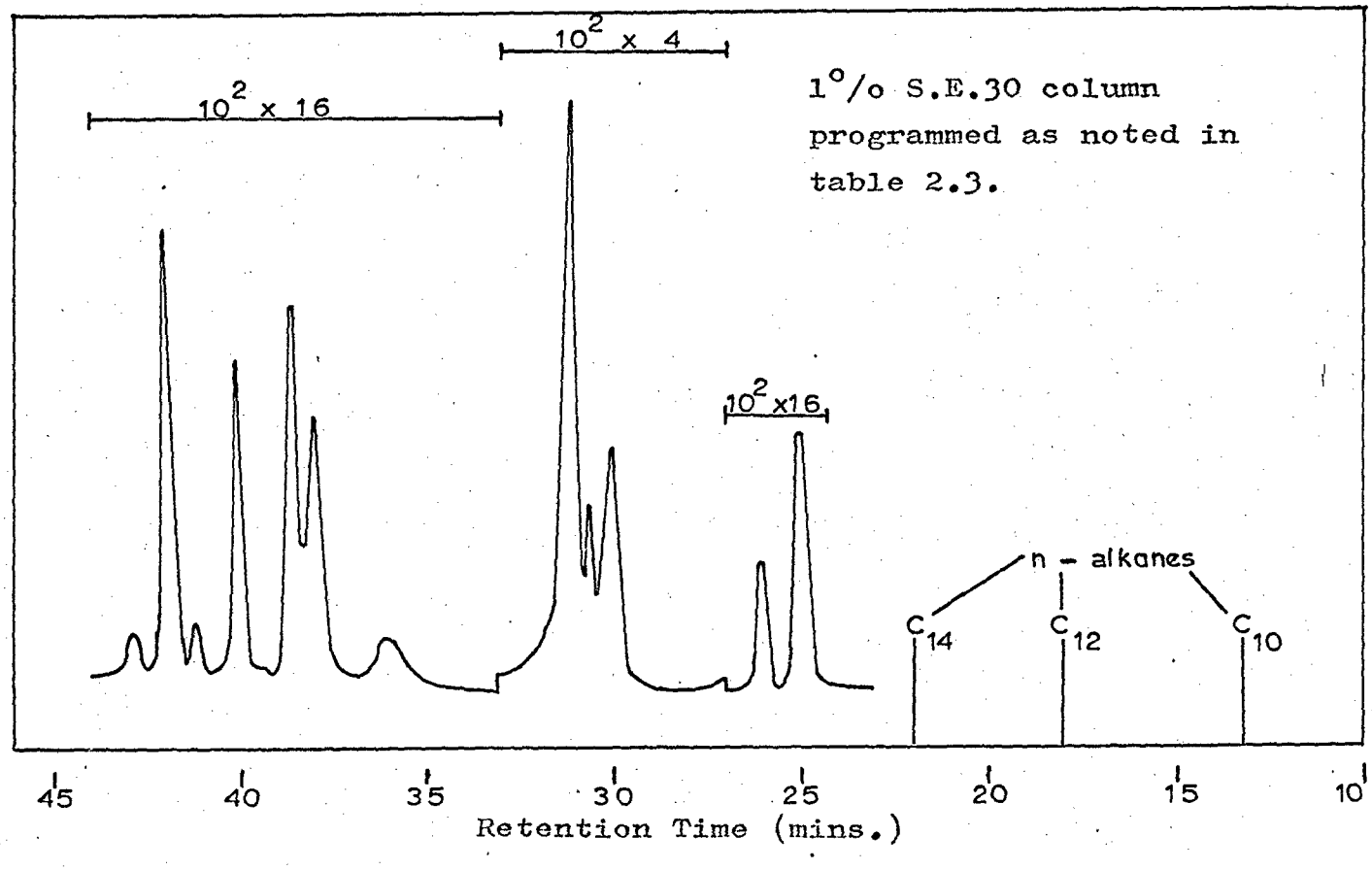


Figure 87. G.L.C. trace of short chain fragments from the degradation of a 50.0 mole percent n-butyl acrylate copolymer at 313°C for 11.5 hours.

CHAPTER 11

SURVEY OF RESULTS AND GENERAL DISCUSSION

INTRODUCTION

As a preliminary to studies of the thermal degradation of copolymers of methyl methacrylate with methyl and butyl acrylates it was necessary to estimate the reactivity ratios for these two systems. Values had not previously been reported, probably because the closely similar chemical structures of the two comonomers made analysis extremely difficult. N.M.R. spectroscopy was used to analyse the copolymers since it can distinguish quantitatively between protons in different environments in the two monomer units. The values of reactivity ratios obtained in this way are in good agreement with values published, for the methyl methacrylate/methyl acrylate system, since this work was started. This method has been extended to a wider series of methacrylate/acrylate copolymers with excellent results. N.M.R. spectroscopy clearly offers a general method of analysis of copolymers whose constituent monomers are similar, provided they have protons in different environments.

METHYL METHACRYLATE/METHYL ACRYLATE COPOLYMERS

The methyl methacrylate/methyl acrylate copolymer system was found to degrade in approximately the same fashion thermally and photochemically. It is therefore convenient to discuss the two reactions together. Copolymer degradation may be treated most conveniently from the point of view of the effect of a second monomer on the degradation of a homopolymer. Thus in the case of poly(methyl methacrylate) the incorporation of only 1% methyl acrylate has a profound effect on the thermal and photochemical degradation. The methyl acrylate units block the normal depolymerization from unsaturated chain ends. After all these unsaturated chain ends have reacted, depropagation only occurs from points of random chain scission and of course is blocked by the methyl acrylate units in the chain. Thus the methyl methacrylate/methyl acrylate copolymers are very much more stable thermally than poly(methyl methacrylate)

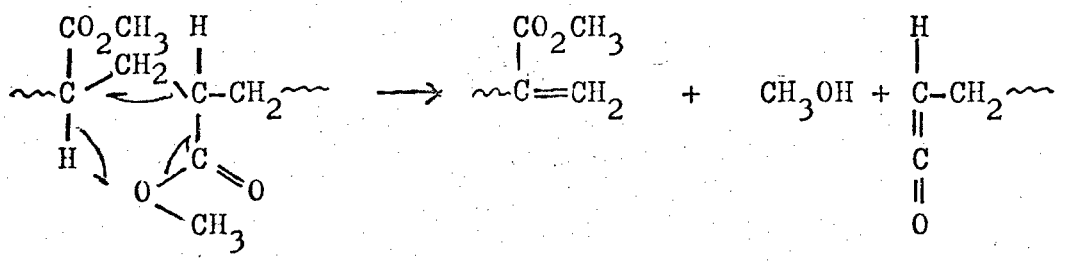
as shown by the temperature at which reaction occurs at a conveniently measurable rate (260°C for copolymers compared to 220°C for poly(methyl methacrylate)). In the photochemical degradation much less volatilization occurs in the copolymers than in poly(methyl methacrylate) at similar temperatures. This again indicates stabilisation by the comonomer methyl acrylate. In both the thermal and photochemical reactions, as expected, stability increases with increasing methyl acrylate content.

Sequence distribution studies show that in the copolymer molecules the large majority of methyl acrylate units are separated from each other by blocks of methyl methacrylate. There are, however, small amounts of pairs of adjacent methyl acrylate units. The experimental zip lengths from points of chain scission, for the thermal degradation of copolymers of low methyl acrylate content, show that the depropagation reaction is effectively blocked by isolated methyl acrylate units. In copolymers of higher methyl acrylate content the zip length indicates that the reaction can pass through single methyl acrylate units, but very much less readily through adjacent pairs of methyl acrylate units. This blocking reaction at methyl acrylate pairs can be explained in terms of intermolecular transfer reactions occurring at the unstable methyl acrylate radicals to form stable saturated chain ends. Some depropagation through the methyl acrylate pairs does occur during the thermal degradation and this could be explained by intramolecular transfer to form a chain fragment larger than monomer and a methyl methacrylate radical, which can readily depropagate. In photochemical degradation the zip lengths are much longer than in the thermal reaction showing that depropagation can occur more readily through methyl acrylate pairs. In this case the copolymer samples are very viscous and it is possible that this favours the intramolecular rather than intermolecular transfer reaction.

Much more work is necessary on this aspect of the degradation since it is not clear why the blocking efficiency should alter with increasing methyl acrylate content of the copolymers. This explanation of longer zip lengths in the photochemical degradation is only tentative and this needs further investigation. A study of copolymers with higher methyl acrylate content and also copolymers of methyl methacrylate with other monomers capable of transfer and thus having blocking ability, should produce interesting results.

The degradation behaviour of poly(methyl acrylate) is also affected by the addition of a comonomer. Thus the production of methanol, which forms approximately 15% of the

volatile products of thermal degradation of poly(methyl acrylate), is suppressed in the copolymers. This surprising result can be related to the isolation of the methyl acrylate units in the methyl methacrylate chain. It appears that it is necessary to have a block of methyl acrylate units before methanol is liberated. It may be tentatively suggested that a mechanism of the type shown is involved, which depends upon the existence of adjacent methyl acrylate units.



This mechanism could be thoroughly investigated by degrading copolymers with the methyl acrylate labelled in the $-O-CH_3$ position with C^{14} thus allowing any methanol produced to be estimated with a high degree of accuracy. By covering a range of copolymer compositions, it should be possible to determine very exactly the conditions required for methanol production.

This work illustrates one of the advantages of copolymer degradation studies. Thus in the thermal degradation of poly(methyl acrylate) the various reactions occurring are superimposed and it is difficult to determine the individual degradation mechanisms. In copolymers the methyl acrylate units are "diluted" by isolation in the methyl methacrylate chain, thus removing some of the masking reactions which occur in the homopolymer. This allows the mechanism of methanol production to be investigated in detail.

Apart from methanol, the volatile products of the thermal and photochemical degradations are as expected by comparison with the products of degradation of the homopolymers. It is obvious, however, that greater amounts of methyl acrylate monomer are liberated when the methyl acrylate units are isolated in a methyl methacrylate chain.

The chain scission reaction which occurs during the thermal degradation of the copolymers also illustrates a variation from the expected behaviour. The polymer chains do not break directly at methyl acrylate units as might be expected. A complicated reaction mechanism is operative which, from a

study of the kinetics of chain scission, proceeds by means of a radical chain reaction. The initiation step of this chain reaction is the formation of radicals at methyl acrylate units in the chain, hydrogen being liberated. The propagating radical, however, can attack any main chain methylene group to liberate eventually, as the result of a five-membered ring mechanism, one molecule of carbon dioxide for every chain scission. This type of chain scission might possibly occur in poly(methyl acrylate), accounting for the observed carbon dioxide formation, although no data is yet available, due to the masking cross linking reaction. However, it is probable that the mechanism only applies to the copolymer system and occurs because the separation of the methyl acrylate units allows the propagation step of the chain reaction to proceed. This point is worthy of further study and could lead to an understanding of the chain scission mechanism in poly(methyl acrylate).

The chain reaction mechanism is particularly open to criticism in the assumption that hydrogen is produced in the initiation step. Although the experimental results indicate that this is true, unsaturation is observed in the copolymers and hydrogen can obviously be liberated in reactions leading to unsaturation and cross linking. Further study of the initial stages of degradation of copolymers containing methyl acrylate with the tertiary hydrogen atom replaced by deuterium could clear up this point. This system would serve a double purpose since at higher extents of degradation methanol production could be investigated.

The molecular weight changes on photodegradation show that the chains do not break initially at methyl acrylate units, therefore it is probable that a radical chain scission mechanism is operative as for thermal degradation. Carbon dioxide production does not appear to bear a simple 1/1 relationship with chain scission, however, so it is possible that the chain scission mechanism is slightly different. However, it is difficult to obtain kinetic data to confirm the mechanism in this case due to the viscous nature of the sample. This aspect of the work requires further investigation.

The copolymers show an apparent induction effect when photodegraded in the form of powder. However, when the sample is degraded in the form of a film this effect disappears. It is not possible to explain this interesting result on the limited experimental evidence available; however, it is probably due in some way to the nature of the powdered form of the

polymer below its melting point and not to the fundamental nature of the chain scission reaction. This result illustrates the difficulty of interpreting polymer degradation behaviour where the physical form of the sample can affect the degradation characteristics as discussed in chapter 6. Before any further detailed study of the photodegradation of this copolymer system is undertaken, therefore, it is obviously important to investigate fully the effect of the physical form of the sample on its degradation behaviour.

METHYL METHACRYLATE/BUTYL ACRYLATE COPOLYMERS

Copolymerization of two monomers can lead to a variety of copolymers differing in composition and arrangement of monomer units. The two kinds of monomer unit may be randomly distributed, may tend to alternate, or may tend to group themselves in blocks of like units. For the investigation of the degradation of copolymers a knowledge of sequence distribution as well as composition is necessary. Methods of calculating sequence distribution have been devised by Harwood (58,59) using the concept of run numbers. The run number, R, of a copolymer is defined as the average number of uninterrupted monomer sequences which occur in a copolymer chain per hundred monomer units, and may be calculated for the n-butyl acrylate - methyl methacrylate system from a knowledge of the monomer reactivity ratios and the molar percentages of acrylate and methacrylate in the polymerization mixture. Denoting acrylate units by A and methacrylate units by M it is possible, having found R, to calculate the percentage of A-A, M-M and A-M linkages in the copolymers. Looking at longer sequences, the percentage of A in the centre of the three possible triads, AAA, MAM and MAA, which is equivalent to AAM, may be found. It is also of interest to look at the number average length of acrylate sequences, and this quantity $\overline{A}_n$ is listed with other sequence distribution data in table 62. The percentage of acrylate in the middle of AAA triads, relative to all possible triads in the copolymer including those centred on methacrylate units, is also a useful quantity and is given in table 62 as the relative total percentage acrylate in AAA triads, A_{tp}.

Production of Alcohol

The importance of n-butanol among the products of degradation of the copolymers increases as the proportion of acrylate in the initial polymer rises. It is interesting to note that the

Table 62

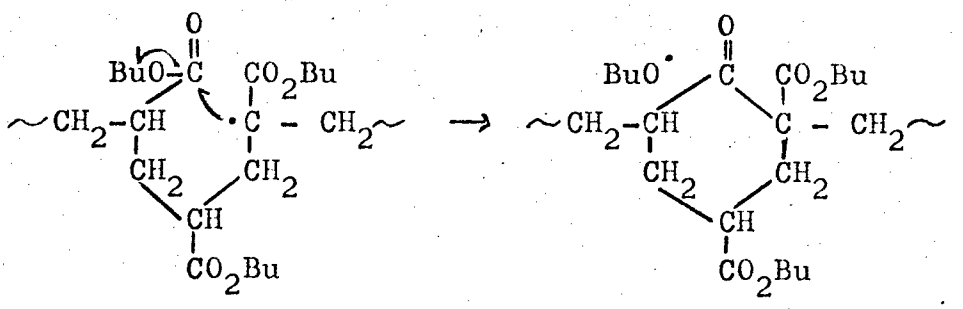
Sequence Distribution Data for Copolymers of n-Butyl Acrylate and Methyl Methacrylate.

Copolymer Composition (mole °/o n-butyl acrylate)	Diads			°/o Acrylate in centre of triads			Number av. run length $\bar{A}_n$	Relative total °/o acrylate in AAA triads, A_{tp}
	°/o A-A linkages	°/o M-M linkages	°/o A-M linkages	MAA AAM	MAM	AAA		
93.4	87.1	0.3	12.6	12.6	0.5	86.9	14.9	81.3
82.2	66.7	2.4	30.9	30.5	3.5	66.0	5.3	54.2
50.0	22.5	22.5	55.0	49.5	30.3	20.2	1.8	10.1
16.3	2.0	69.4	28.6	21.3	77.2	1.5	1.1	0.2
3.9	0.1	92.4	7.5	7.0	92.9	0.1	1.0	0
0.4	0	99.3	0.7	0	100.0	0	0.7	0

50·0 mole percent n-butyl acrylate copolymer is the material of lowest acrylate content which is found to produce alcohol on pyrolysis. It is clear then from table 62 that n-butanol is only evolved when non-isolated acrylate units occur, but it is not certain from this data whether the sequence length required is three or only two acrylate units, since the threshold of alcohol formation at the 50·0 mole percent copolymer corresponds to a marked increase in both the number of A-A linkages, from 2·0 to 22·5, and in the relative total percentage acrylate in AAA triads, A_{tp}, from 0·2 to 10·1.

In view of the dependence of alcohol formation on the presence of sequences of acrylate units it would be interesting to test the hypothesis in chapter 4 that a similar situation occurs in the methyl acrylate - methyl methacrylate copolymer system. No methanol at all is produced from copolymers containing up to 33·3 mole percent acrylate, but this was the highest acrylate content copolymer examined. It was concluded that this value of 33·3 mole percent methyl acrylate is near the threshold for methanol production. Consequently a methyl methacrylate - methyl acrylate copolymer containing 66·7 mole percent acrylate was synthesised and purified by dissolving in acetone and precipitating from water, care being taken to use no methanol in the purification process, so that if this alcohol were detected on degradation there could be no ambiguity as to its source. On degradation at 313°C this copolymer gave liquid products which contained 11% by weight of methanol. The relevant sequence distribution data are given in table 63.

In addition to the mechanism for the production of alcohol from acrylates shown below (I) Cameron and Kane (56) have proposed an alternative route (II) which again takes into account the need for sequences of acrylate units.

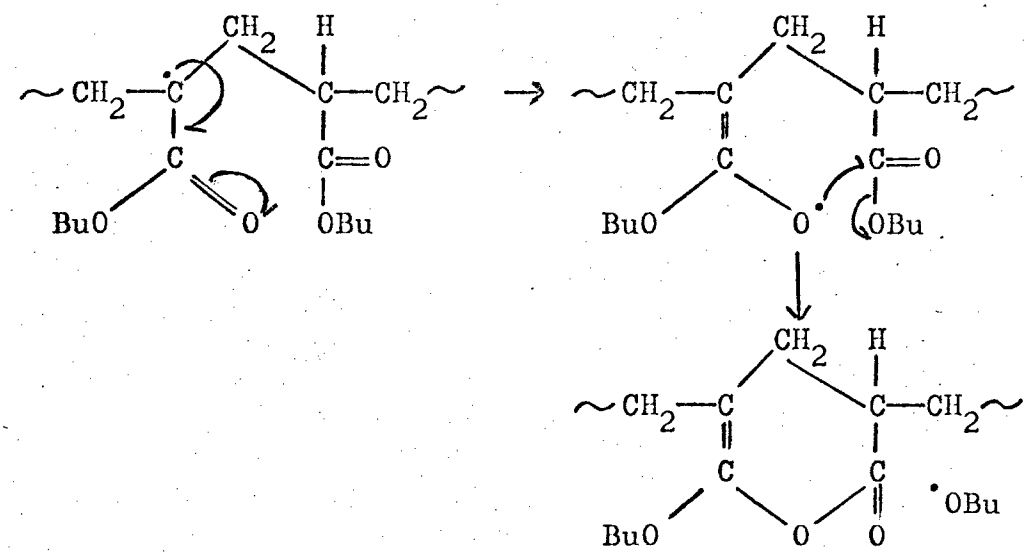


I (B)

Table 63

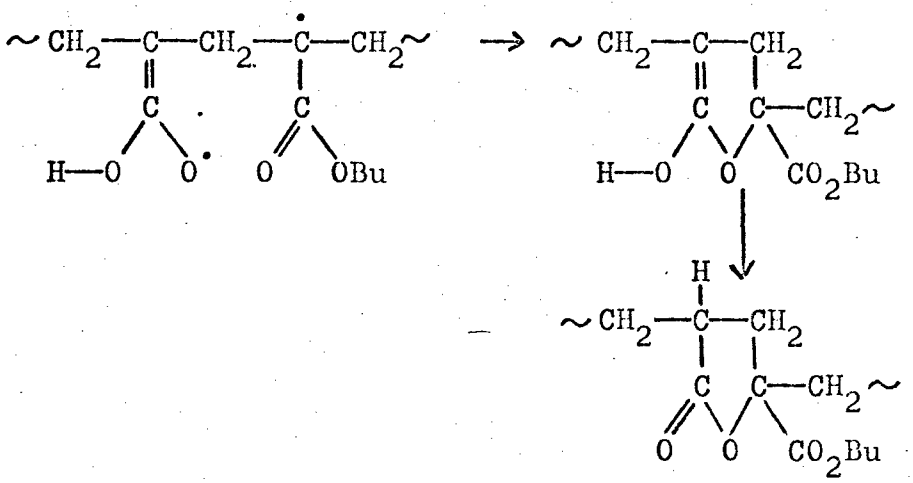
Sequence Distribution Data for Copolymers of Methyl Acrylate and Methyl Methacrylate.

Copolymer Composition (mole °/o methyl acrylate)	Methanol Occurrence	Diads °/o A-A linkages	°/o Acrylate in centre of triads			Number av. run length, $\bar{A}_n$	Relative total °/o acrylate in AAA triads, A_{tp}
			MAA AAM	MAM	AAA		
33.3	No	8.9	39.2	53.6	7.2	1.4	2.4
66.7	Yes	42.3	46.4	13.4	40.2	2.7	26.8



II (C)

Route I leads to the formation of structure (B), a β keto ester. Since this particular β keto ester cannot exist in the enol form it will exhibit the characteristic absorptions due to the ketone (1700-1720 cm^{-1}) and ester carbonyl group (1735-1750 cm^{-1}) separately. Any new absorptions in these regions could well be masked by the strong carbonyl absorption due to ester groups already present. The second mechanism (II) results in formation of a γδ unsaturated δ lactone (C) which would absorb at around 1764 cm^{-1}, and would thus account for the shoulder noted at 1760 cm^{-1}. Although this shoulder increases in importance with both time of degradation and the acrylate content of the initial polymer, it could well be unconnected with butanol formation. Route III indicates a route by which such an absorption could be accounted for, involving a radical coupling reaction between two adjacent acrylate groups, one of which has undergone ester decomposition as in V.

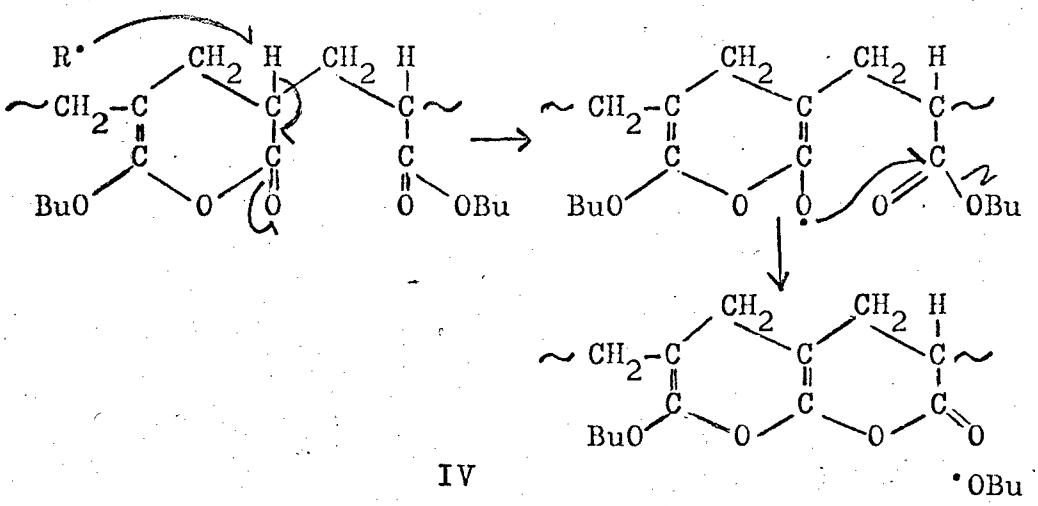


III (D)

(D) is a δ lactone absorbing in the region (1760-1780 cm^{-1}). U.V. spectra showing as they do no characteristic absorptions, do not make any real contribution to deciding the route by which alcohol is formed.

Both of the mechanisms shown in I and II involve attack on an ester group by an acrylate radical. In homopolymers of acrylates there is only one kind of ester group which can be attacked, but when copolymers of acrylates and methacrylates are considered two types of ester are present. If both the methyl and butyl ester groups in the n-butyl acrylate - methyl methacrylate copolymers studied were attacked by an acrylate radical then both methanol and butanol should be evolved. This means that any route proposed for alcohol production must be able to explain the non-appearance of methanol in the degradation products. Molecular models for the structure (B) of reaction I suggest that in triads such as AMA, AAM and AMM sterically unfavourable 1-3 diaxial interactions involving the α methyl substituent of methacrylate units and the butyl ester of the attacking n-butyl acrylate group occur. Such interactions could explain the absence of methanol among the degradation products. Similar considerations for the lactone (C) of reaction II tend to suggest that both A-A and A-M sequences could react by this route, implying that some methanol at least would be produced.

The mechanisms I and II suggest that only one acrylate unit in 2 or 3 respectively can degrade to n-butanol. For the pyrolysis of a 93·4 mole percent n-butyl acrylate copolymer in which it is supposed that acrylate units break down to n-butanol exclusively by the routes shown in reactions I and II the concentration of butanol expected would be 3·5 and 2·5 millimoles per gram initial polymer. The value actually found for degradation at 313°C for an infinite time is 3·8 (table 51). Similar results have been obtained for other acrylate polymers (2). In order to attempt to reconcile the requirement of sequences of acrylate with these results, the mechanism in IV is tentatively suggested, and is an extension of the route of reaction II



IV

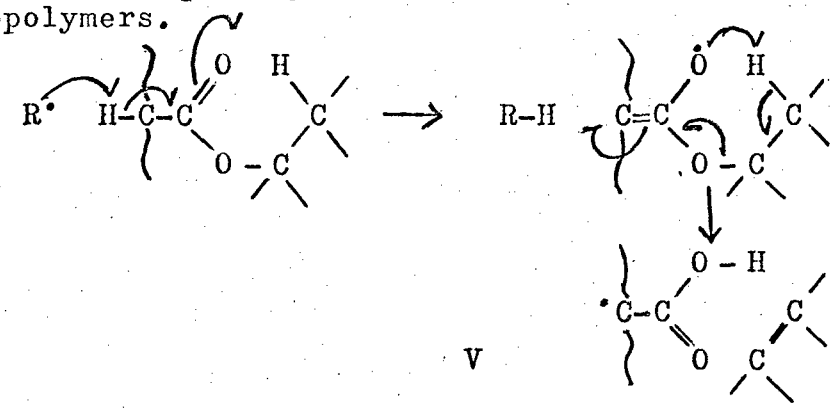
Repetition of this scheme would carry the alcohol elimination reaction on along the polymer chain. Such a reaction could be stopped by the first methacrylate unit encountered after one molecule of methanol has been formed, because there is no suitable tertiary hydrogen to continue this process. Since each sequence of acrylate units produces at most one methanol molecule it is possible that such a low concentration of this alcohol could escape detection in copolymers rich in acrylate. It is difficult to see, however, why methanol should not be produced in significant amounts from copolymers such as the 50·0 mole percent n-butyl acrylate copolymer which contains 55% of A-M bonds. Again, if the scheme shown in IV is an important process a strong band in the infra-red at 1580-1600 cm^{-1} should be present, but was not found.

The autocatalytic nature of alcohol production at 313°C, Figs. 76 and 77, has been explained in terms of changes in the physical nature of the polymer molecule brought about by this reaction (2). All the mechanisms so far advocated involve the formation of cyclic structures which decrease flexibility of the polymer chain thus increasing the possibility of reactions considered in this section, at the expense of intermolecular processes such as cross linking.

None of the proposed mechanisms can satisfactorily account for all of the experimental data. Other schemes have been suggested such as an intermolecular version of the route shown in Reaction I, but this explains neither the requirement of sequences of acrylate units for alcohol elimination nor the absence of methanol. Thus the picture presented for this reaction is not very satisfactory and further study of this aspect of acrylate-methacrylate degradation is required.

Production of But-1-ene

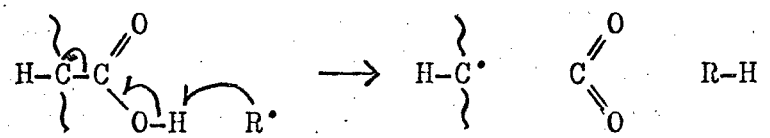
The fact that but-1-ene is evolved on the degradation of a 16·3 mole percent n-butyl acrylate copolymer when only 2% A-A linkages are present and the number average run length is 1·1 (table 62), indicates that in contrast to alcohol production elimination of this gas does not depend upon acrylate sequences. This view is supported by the data given in chapter 9. Thus the mechanism proposed below (V) appears to account adequately for the elimination of but-1-ene from the copolymers.



V

Production of Carbon Dioxide

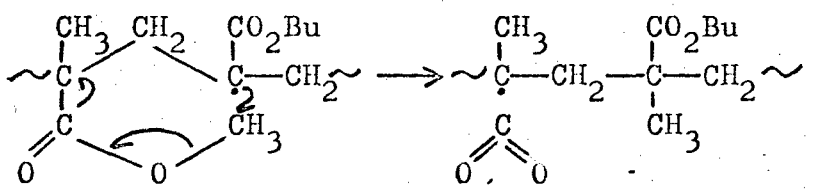
Carbon dioxide may be produced by decarboxylation of acid groups pendant to the main polymer chain after ester decomposition has occurred, VI. Such a mechanism would mean that the highest possible value for the molar ratio of carbon dioxide to but-1-ene would be unity.



VI

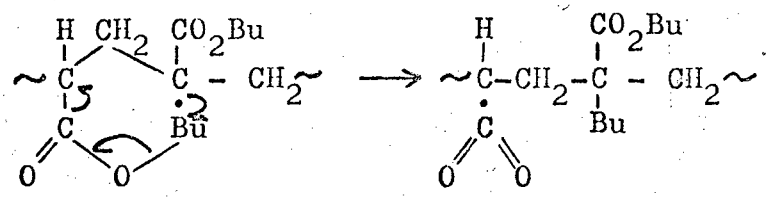
Experimentally (chapter 9) it was found that the above ratio for degradations carried out at 313°C ranges from 4·9 for the 16·3 mole percent n-butyl acrylate copolymer to 2·0 for the 93·4 mole percent copolymer. These results must mean that route VI is not the only one operating.

The reaction scheme VII has also been suggested.



(G)

VIIa



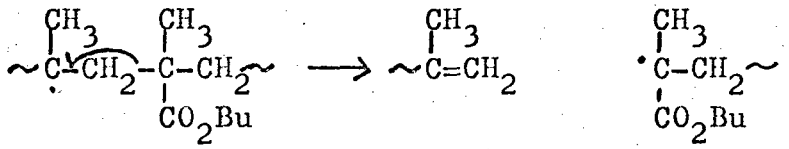
VIIb (H)

This elimination reaction can occur between an acrylate and a methacrylate unit, VIIa, or between two acrylate units, VIIb. If the scheme shown in VIIb is followed it requires the shift of the rather bulky n-butyl group. However, this type of reaction scheme has been proposed for the degradation of poly(benzyl acrylate (60) in which the shift of the large benzyl group is involved. The routes shown in VIIa and b allow elimination of carbon dioxide without simultaneous production of but-1-ene and do not require that a sequence of two acrylate units is present, it being sufficient for one acrylate unit to be present which can attack a neighbouring methacrylate unit. These points are important since the evolution of carbon dioxide is found to take place when the acrylate content is only 3·9 mole percent, there being only 0·1 percent A-A links in the polymer, and no but-1-ene is evolved.

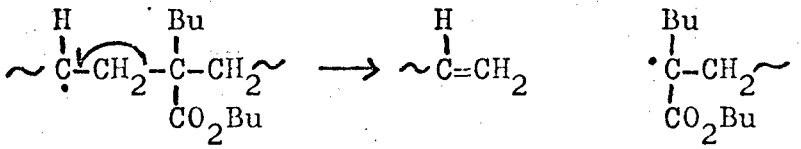
The relationship between evolution of carbon dioxide and chain scission was reported in chapter 10. These results show that at 237°C there is no definite connection between these two processes.

Production of n-Butyl Methacrylate

The reaction shown in VIIa results in the formation of the chain radical (G) which can then break down as shown in VIIIa.



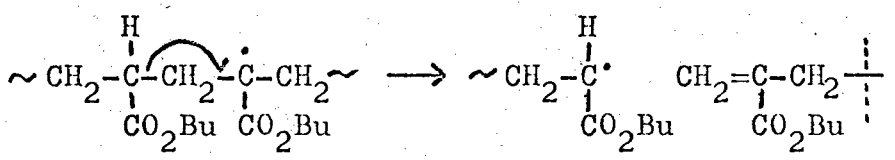
(G) VIIIa unzips to produce n-butyl methacrylate



(H) VIIIb should unzip to produce α n-butyl n-butyl acrylate

If, however, a similar reaction between two acrylate units takes place the radical which results, (H), VIIIb, could, on unzipping, produce a molecule of n-butyl acrylate substituted at the α position by an n-butyl group. None of this compound was available so that its retention time on the g.l.c. columns used is not known, but it is feasible that such a compound would appear on the g.l.c. trace among the short chain fragments.

n-Butyl methacrylate can also be formed in a reaction of the type shown in IX



n-butyl methacrylate produced by scission of the bond indicated

IX

This mechanism would lead, for degradation of acrylate homopolymers in general, to the evolution of the corresponding monomeric acrylate substituted in the α position by a methyl group. These compounds have been reported for all of the primary acrylates so far studied (2).

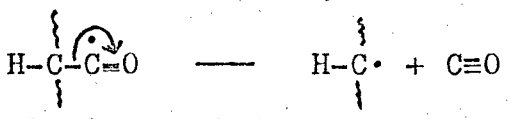
Production of n-Butyl Acrylate

The amount of this product evolved on degradation of the copolymers initially increases with acrylate content as expected but then falls off again (chapter 9), This was explained in terms of acrylate units being evolved in depolymerizations initiated at methacrylate linkages, so that increasing the acrylate content decreases the possibility of such depolymerizations since homopolymers of acrylates take part in transfer reactions rather than unzipping.

Other Products

The production of chain fragments is obviously the result of intramolecular transfer.

Both carbon monoxide and hydrogen are evolved in small amounts on copolymer breakdown. The formation of hydrogen has already been discussed and carbon monoxide may be formed by the breakdown of carbonyl radicals.



Methane evolution probably corresponds mechanistically to hydrogen elimination, involving the α methyl group of methyl methacrylate units. It could also be formed from the methyl ester group of methyl methacrylate or by breakdown of the n-butyl group in the ester part of the n-butyl acrylate molecule.

The other minor products may be considered as deriving from the breakdown of the n-butyl side chain of the acrylate units.

Methyl methacrylate formation can be adequately accounted for in terms of unzipping of methacrylate units along the polymer backbone.

SUMMARY

The initiation step in the degradation of the copolymer system studied can be described in terms of random chain scission, as confirmed by molecular weight measurements to produce terminal chain radicals. The increasing difficulty of breaking the linkages in the series methacrylate-methacrylate, acrylate-methacrylate and acrylate-acrylate is reflected by the greater stability of acrylate rich copolymers. If any of the terminal chain radicals involve a methyl methacrylate unit, depolymerization will take place until the unzipping process is blocked by the first n-butyl acrylate unit encountered. Thus two n-butyl acrylate terminated chain radicals have been produced, with or without monomeric methyl methacrylate, depending upon the site of the initial break. These terminal radicals can then depropagate to produce n-butyl acrylate monomer or take part in transfer reactions involving hydrogen abstraction to produce a chain radical. This chain radical may then undergo scission to produce chain fragments or react according to any of the schemes discussed in this chapter resulting in formation of the appropriate product. As the acrylate content of the copolymer increases, transfer reactions producing chain fragments and reactions depending upon sequences of acrylate units, such as alcohol evolution, become important. Termination may take place by mutual destruction of pairs of radicals in processes such as cross linking. During the course of the reaction coloration develops in the residue and in the chain fragments, the colour going through yellow to brown with both increasing time of degradation and rising acrylate content. This has been associated with the formation of conjugated carbon-carbon double bonds along the polymer backbone.

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ABSTRACT

This report is principally concerned with the thermal degradation of two copolymer systems, namely methyl methacrylate/methyl acrylate and methyl methacrylate/butyl acrylate. The photo-degradation of the methyl methacrylate/methyl acrylate system was also studied insofar as it is relevant to the thermal reaction. In view of the similarity of the monomers, reliable values of reactivity ratios were not available. An accurate method, making use of nuclear magnetic resonance spectroscopy, was devised and applied to these and other acrylate/methacrylate systems.

For both systems a series of copolymers covering the whole composition range was synthesised. Degradations were carried out under vacuum either in a dynamic molecular still or using a new technique developed in these laboratories. Thermal methods of analysis, such as thermogravimetric analysis (TGA) and thermal volatilisation analysis (TVA), showed that the copolymers became more stable to thermal breakdown as the acrylate content was increased. These techniques allowed a suitable temperature range to be chosen in which to study the reactions isothermally. The gaseous degradation products, liquid products, chain fragments and residue were each examined separately, using, among other techniques, infra-red spectroscopy, gas-liquid chromatography, mass spectrometry and

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13. ABSTRACT (Cont'd.)

combined gas chromatography - mass spectrometry. The complex nature of the pyrolysis of these copolymer systems is reflected by the variety of products obtained.

The main gaseous products were found to be carbon dioxide and smaller amounts of hydrogen from the methyl acrylate copolymer and carbon dioxide and but-1-ene from the butyl acrylate copolymer. The most important liquid products are methyl methacrylate from both systems and n-butanol from the butyl acrylate copolymers with high butyl acrylate contents. Quantitative measurements enabled the build-up of these products to be followed as degradation proceeds, and mass balance tables were drawn up for each copolymer studied. The large chain fragments were only briefly examined. Molecular weight measurements on the residue indicated that breakdown by random scission processes becomes more important relative to breakdown by depolymerization processes as the acrylate content is increased. Degradation schemes and mechanisms are postulated to account for the formation of all of the important products, although no really satisfactory route for alcohol evolution has been found.

14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
Thermal Degradation						
Copolymers						
Methyl Methacrylate						
Methyl Acrylate						
Butyl Acrylate						
Photo Degradation						
Copolymer Reactivity Ratios						
Nuclear Magnetic Resonance Spectroscopy						
TGA						
TVA						
Products of degradation of polymers						
Infra-red spectroscopy						
Gas-liquid chromatography						
Mass spectrometry						
Pyrolysis of polymers						
Mechanism of Degradation						