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REVIEW OF PREPARATION AND PROPERTIES
OF POLYMERS FROM COPOLYMERIZATION
OF APROTIC ACRYLIC MONOMERS
WITH PROTIC ACRYLIC MONOMERS

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RESEARCH DIRECTORATE

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Configuration
Glass transition temperature,
Reactivity ratio,
Viscosity,
Copolymerization,
Polyelectrolyte. (JES) ←

PREFACE

The work described in this report was authorized under Project No. 1C162706A553I, CB Defense Data Collection and Systems Science. This work was started in June 1984 and completed in February 1988.

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REVIEW OF PREPARATION AND PROPERTIES
OF POLYMERS FROM COPOLYMERIZATION
OF APROTIC ACRYLIC MONOMERS WITH PROTIC ACRYLIC MONOMERS

1. INTRODUCTION

1.1 Polymers of Acrylic Esters.

Because of their industrial importance and theoretical interest, a considerable body of literature and patents concerned with the polymerization of acrylic esters has been developed. Most of the polymerizations of acrylic ester monomers were carried out by a free radical process, which is the predominant synthetic route for industrial polymer production. The polymerization can be performed either homogeneously (bulk or solution polymerization) or heterogeneously (emulsion or suspension polymerization).

Acrylic esters copolymerize with other vinyl monomers with relative ease. This versatility and the wide range of properties among the copolymer products led to the development of many different resins.

The reactivity ratios of acrylic esters with some other vinyl monomers are shown in Table 1. Using the reactivity ratio values r_1 and r_2 , we can predict the tendency for two monomers to copolymerize. For example, when acrylic acid (AA) is copolymerized with methyl acrylate (MA), with respective reactivity ratios of 0.95 and 1.1, little or no selectivity is expected by a polymer radical for either monomer and monomer insertion into the copolymer should be random. Thus, the resulting polymer composition is approximately equal to the composition of the monomer feed mixture. Another example of this type is the copolymerization of N,N-dimethylaminoethyl methacrylate (DMAEMA) with methacrylic acid (MAA). The idealized case of this type (both r_1 and r_2 equal to 1) is represented by line I in the Figure.

When both r_1 and r_2 are considerably less than 1, there is little tendency for either radical to react with its own monomer. As a result, an alternating copolymer can be formed. A good example of this type is the copolymerization of methyl methacrylate (MMA) with styrene. The idealized case of this type is represented by line II in the Figure.

When $r_1 \gg 1$ and $r_2 \ll 1$, a growing polymer radical for both monomers tends to react with monomer-1, thus forming a copolymer consisting mostly of monomer-1. This proceeds until the consumption of monomer-1 is almost complete. Examples of this case are the copolymerization of either t-butyl aminoethyl methacrylate (tBAEMA) or DMAEMA with vinyl chloride, where $r_1 = 49.0$ and $r_2 = 0.222$, and $r_1 = 29.7$ and $r_2 = 0.03$, respectively. Another example is the copolymerization of MMA with ethylene where $r_1 = 17$ and $r_2 = 0.2$, respectively. The idealized case of this type is shown by line III in the Figure.

Table 1. Reactivity Ratios of Acrylic Esters with Selected Vinyl Monomers

Acrylic Ester (Monomer-1)	Vinyl Monomer (Monomer-2)	r ₁	r ₂	Literature cited
Methyl Methacrylate	Isobutyl Acrylate	1.71	0.20	1
	n-Butyl Acrylate	1.74	0.20	1
	Acrylic Acid	1.5	0.25	1
	Acrylamide	2.53	0.82	1
	Acrylonitrile	1.34	0.12	1
	1,3-Butadiene	0.25	0.75	1
	Ethylene	17	0.2	1
Methyl Acrylate	Acrylamide	0.05	1.30	1
	Acrylonitrile	0.67	1.26	1
	Acrylic Acid	0.95	1.1	1
	1,3-Butadiene	0.05	0.76	1
	Styrene	0.13	0.90	1
	Methyl Methacrylate	0.34	1.69	1
t-Butyl- aminoethyl Methacrylate	Styrene	0.83	0.47	2
	Isobutyl Methacrylate	1.38	0.72	*
	Ethyl Methacrylate	1.42	0.62	*
	Methyl methacrylate	1.38	0.69	2
	Ethyl Acrylate	3.09	0.27	2
	Butyl Acrylate	2.42	0.36	2
	2-Ethylhexyl Acrylate	2.48	0.38	2
Vinyl Chloride	49.0	0.222	2	
N,N-Diethyl- aminoethyl Methacrylate	Methacrylic Acid	2.321	0.625	3
	Isobutyl Methacrylate	2.68	0.36	*
	Ethyl Methacrylate	2.97	0.33	*
	Acrylonitrile	1.6	0.15	1
	Styrene	0.23	0.74	1
N,N-Dimethyl aminoethyl Methacrylate	Methyl Methacrylate	0.88	1.12	2
	Ethyl Acrylate	2.1	0.47	2
	Butyl Acrylate	1.61	0.61	2
	2-Ethylhexyl Acrylate	1.59	0.63	2
	Vinyl Chloride	29.7	0.03	2
	Styrene	0.37	0.53	2

*Vanderhoff, J.W., Lehigh University, Private Communication.

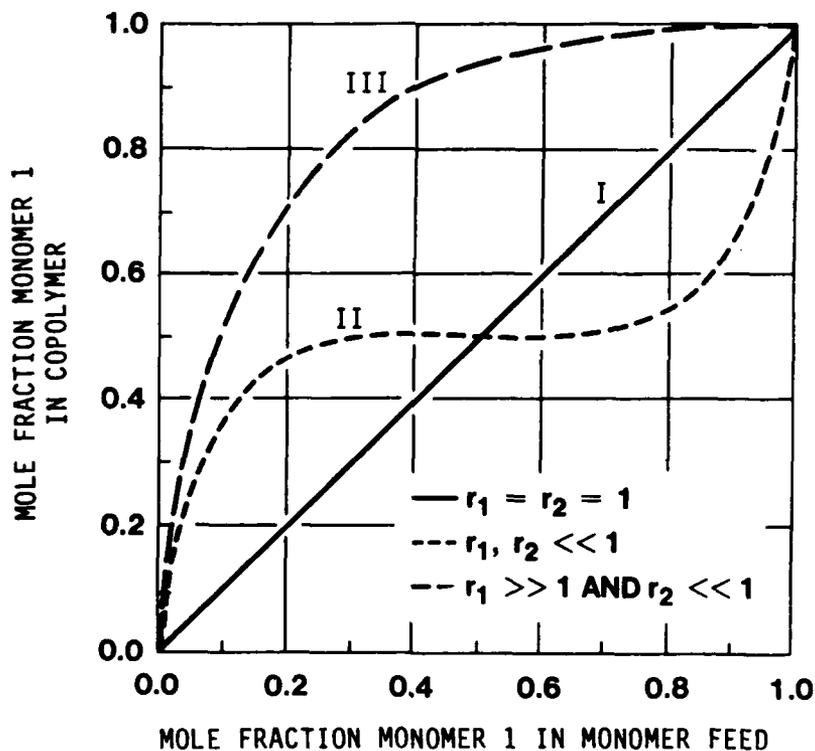


Figure. Schematic Representation of the Composition of Copolymers vs. Monomer Feed

As shown in Table 1, because of the wide differences in the reactivity ratios of many possible acrylate-containing comonomer mixtures, considerable heterogeneity in the composition of the chains and in the distribution of monomer units along the chain can be obtained.

1.2 Polymers of 1-Vinyl-2-Pyrrolidone.

Poly(1-vinyl-2-pyrrolidone), developed in Germany during World War II, has the unusual property of being soluble in both water and organic solvents. An aqueous solution of this polymer with certain added salts was used as a blood substitute. It has been used in cosmetic applications, such as hair dressing preparations and sprays. The number of investigations of its copolymerization with different types of monomers, to take advantage of its unusual properties, has increased tremendously in recent years. Selected monomer reactivity ratios of 1-vinyl-2-pyrrolidone (VP) with other vinyl monomers are shown in Table 2.

Table 2. Reactivity Ratios of Selected Vinyl Monomers

Monomer-1	Monomer-2	r1	r2	Literature cited	
1-Vinyl- 2-Pyrrolidone	Methacrylic Acid	0.98	0.68	1	
	Crotonic Acid	0.85	0.02	3	
	Crotonaldehyde	0.5	0.03	3	
	Vinylferrocene	0.4	0.66	3	
	2-Methyl-1-hexene-3,5-dione	0.02	5.38	3	
	1-Vinylimidazole	0.17	0.95	3	
	Acrylic Acid	0.15	0.13	3	
	Acrylonitrile	0.84	0.74	3	
	Methyl Methacrylate	0.005	4.7	3	
	Styrene	0.045	15.7	3	
	Vinyl Acetate	3.3	0.205	3	
	Vinyl Benzoate	2.45	0.44	3	
	Butyl Vinyl Ether	2.97	0.0	3	
	Acrylic Acid	Styrene	0.128	0.655	5
		Vinyl Acetate	9.285	0.023	5
1,1-Dichloroethylene		1.247	0.437	5	
Acrylamide		1.376	0.598	3	
N,N-Dimethyl-acrylamide		0.4	0.5	3	
Butyl Acrylate		1.15	0.78	3	
Chloroethylene		6.4	0.025	3	
1,1-Dichloroethylene		1.26	0.46	3	
1,1-Dicyanoethylene		0.26	0.29	3	
Butyl Methacrylate	0.29	3.67	3		
Methacrylic Acid	Methyl Methacrylate	1.355	0.767	5	
	Butyl Methacrylate	0.53	1.11	3	
	Styrene	0.551	0.170	5	
	2-Vinylpyridine	0.58	1.55	3	
	Butyl Acrylate	0.22	2.0	3	
	Acrylonitrile	2.5	0.093	3	
	Chlorobutadiene	0.15	2.7	3	
	Vinyl Chloride	23.8	0.034	3	

1.3 Polymers of Acrylic and Methacrylic Acids.

Acrylic acid, $\text{CH}_2=\text{CHCOOH}$, and methacrylic acid, $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOH}$, were first prepared in the late 19th century, and their polymerization was observed a few years later. Linear polymers of these acids can be prepared by general methods used with other vinyl monomers. Polymerization in aqueous solution at a monomer concentration of 25% or less is most common. Polymerization of more concentrated solutions or of undiluted monomer is not desirable because the high heat of polymerization makes polymerization difficult to control and produces an insoluble polymer. Polymerization is possible in nonaqueous media, such as benzene, which are solvents for the monomer but nonsolvents for the polymer. Acrylic and methacrylic acids are readily copolymerizable with many other monomers. Monomer reactivity ratios of acrylic and methacrylic acids with some selected vinyl monomers are also shown in Table 2. The facile polymerization of these two monomers stems from their highly reactive double bonds and from their miscibility with both oil- and water-soluble monomers.

The review of polymers prepared from acrylic esters is limited to a few articles even though there is a vast amount of literature. Primary emphasis was placed on (meth)acrylate polymers that contain amino groups. However, foreign literature on this subject was excluded because it has been adequately reviewed.⁴ Review of the literature concerning VP and (meth)acrylic acid polymers covers the time period of 1964 to 1983.

2. POLYMERS OF ACRYLIC ESTERS

2.1 Polymers of Alkyl (Meth)Acrylates.

In a 1948 article, Rehberg and Fisher⁶ documented the preparation and certain physical properties (namely, hardness and brittle point) of various alkyl (meth)acrylates. The monomers that were prepared and polymerized in the study included acrylates such as MA and ethyl acrylate (EA); methacrylates such as MMA, isobutyl methacrylate (IBMA), and 2-ethylhexyl methacrylate (EHMA); and *n*-alkyl (meth)acrylates where the *n*-alkyl group consisted of up to 14 carbon atoms.

Cooper⁷ studied the alkaline hydrolysis of polyacrylates; that is, poly(EA) and a 70:30 copolymer of butadiene and EA. The author found that the rate constant for the hydrolysis of poly(EA) was concentration dependent and, unlike the copolymer, was dependent on the degree of hydrolysis.

The hydrolysis of poly(MMA) was reported by Glavis of Rohm and Haas Company in 1959.⁸ Glavis found that the rate of hydrolysis was affected significantly by the tacticity of the polymer. Atactic or syndiotactic polymers hydrolyzed relatively slowly, whereas isotactic polymers hydrolyzed rather rapidly and to a higher final conversion than either of the other two types. However, the molecular weight (MW) of the polymers, especially in the isotactic structure, affected the rate of hydrolysis only slightly.

The effect of stereoregularity on the glass transition temperatures (T_g) of various acrylate and methacrylate polymers was reported by Shetter in 1963.⁹ Isotactic methacrylate polymers, prepared by anionic polymerization in nonpolar solvents, showed much lower T_g 's than corresponding polymers having a random configuration. For example, T_g 's of isotactic poly(MMA) and isotactic poly(IBMA) were determined to be 43 to 50 and 8 °C, respectively, whereas the same polymers with a random structure showed T_g 's of 104 and 53 °C, respectively. Contrary to this result, however, the T_g 's of the acrylate polymers were not affected by the tacticity of the polymer chain. For example, the T_g of isotactic poly(MA) was 10 °C, whereas the T_g of random poly(MA) was 8 °C. Also, the effect of the size of the alkyl groups on T_g 's was quite significant in methacrylate polymers, but it was insignificant in the case of acrylate polymers.

A study of the protective effect of some organophosphorous compounds on the degradation of poly(MMA) was reported by Kondrat'yeva and co-workers in 1967.¹⁰ Poly(MMA) was prepared by radiation polymerization (gamma-irradiation using a cobalt-60 source) at 60 °C. The resulting polymer was soluble in acetone, insoluble in methanol, and had a MW of around 1 megadalton. The organophosphorous compounds used in this study were triphenyl phosphate, triphenyl phosphite, and triphenyl phosphine. All three showed a protective effect with regard to the degradation of poly(MMA). Triphenyl phosphite had the best antiradiation property. The degree and probable mechanism of the protection were determined by analysis of the structure of the organophosphorous additives.

A U.S. patent concerning polymeric additives in oil compositions was granted to Mottus in 1967.¹¹ A typical polymer of this invention was an interpolymer of tetrahydrofurfuryl methacrylate, an alkyl methacrylate such as MMA, ethyl methacrylate (EMA), n-propyl methacrylate (nPMA), isopropyl methacrylate (IPMA), n-butyl methacrylate (nBMA), IBMA, and many other vinyl monomers. The vinyl monomers used also included olefins such as ethylene or propylene, ethers containing ethylenic group, and esters containing ethylenic group. The polymers were prepared by solution polymerization in benzene with benzoyl peroxide as the initiator. Base oil was added to the polymerization mixture at the end of the polymerization period, and the viscosity of this mixture was determined. Other monomers used in this invention were VP, vinylpyridine, vinyl acetate (VA), methacrylamide (MAM), alkylaminoalkyl (meth)acrylates such as tBAEMA, and hydroxy- and aminoalkyl derivatives of fumaric and maleic acids.

A series of alkyl methacrylate polymers was studied by linear expansion and torsion-pendulum measurements in the temperature range from -180 °C to just above their T_g 's.¹² As a result, linear expansion coefficients below the T_g increased as a result of lengthening the n-alkyl side chain. This is probably due to the retention of some excess free volume below the T_g for larger side chains. Also, in the butyl isomer series, the linear expansion coefficient decreased from n-butyl to sec-butyl/isobutyl to t-butyl, probably due to the packing of the side chains. Torsion-pendulum measurements of mechanical damping versus temperature showed poly(MMA) had two distinct maxima, the lower peak being broader and the higher peak being at the glass transition. Similar results were obtained for poly(EMA) and poly(nPMA), with the two maxima moving closer together. In poly(nBMA), the lower peak appeared as a shoulder on the glass transition maximum.

The effect of stereoregularity on the low temperature polymer relaxation process was investigated using isotactic and syndiotactic poly(IBMA)'s by Japanese researchers at Hiroshima University.¹³ Isotactic poly(IBMA) was prepared by solution polymerization in toluene at -70 °C with lithium aluminum hydride as the initiator. Syndiotactic poly(IBMA) was obtained by solution polymerization in tetrahydrofuran (THF) at -70 °C using the same initiator. The resulting isotactic poly(IBMA) showed 90% isotacticity with a Tg of 7 °C, whereas syndiotactic poly(IBMA) showed 80% syndiotacticity with a Tg of 53 °C.

The effect of a filler on the relaxation behavior of filled poly(MMA) was investigated by Russian researchers Surovtsev, Vovkotrub, and Solomko.¹⁴ The fillers, with properly directed modification of particle surfaces, led to structural changes in the polymer. As a result, the relaxation time of the system broadened; and, consequently, the composition showed different characteristics.

Potolovskiy and co-workers reported the determination of MWs of MMA polymers in lubricating oils by various methods.¹⁵ Each sample of poly(MMA) was obtained by dissolving it in benzene with subsequent precipitation from dehydrated ethanol. The MWs of the polymer samples were obtained by treatment of the viscosity data using the Staudinger equation as well as the Mark-Houwink equation. For comparison, the absolute MWs of the same polymers were determined by ebullioscopy. When the numerical values of the polymer MWs were compared to each other, the divergence between the values was regular. However, the viscometric method was simpler because it required neither a thorough purification nor much measuring time.

Kuramshin and co-workers investigated the polymerization of MMA using a system of 4-phenyl-1,3-dioxane hydroperoxide (PDHP) and cobalt(II) chloride dicyclohexylsulfoxide as the initiator.¹⁶ The researchers showed that cyclic acetal hydroxides could initiate free radical polymerization. Also, the kinetics of polymerization were studied dilatometrically using a 5 mL mercury dilatometer. As a result, PDHP without the cobalt salt effectively initiated polymerization only at a temperature higher than 70 °C. Introduction of the catalyst, a cobalt(II) salt, significantly increased the rate of the process and helped to initiate the polymerization at a lower temperature.

Microsuspension polymerization of MMA and styrene, based on the use of a surface-active initiator, was investigated by Semchikov, Slavitskaya, and Myakova.¹⁷ The group of initiators studied included benzoyl peroxide (BP), azobisisobutyronitrile (AIBN), dicyclohexylperoxydicarbonate, and lauryl peroxide (LP). The only effective initiator/stabilizer was LP. In the presence of a surface active initiator, the kinetics of microsuspension polymerization of MMA had very distinct characteristics. At the same concentration of LP, the initial rate of polymerization of MMA was several times higher and the MW of the polymer formed was an order of magnitude higher than the corresponding parameters of block polymerization. Investigators observed that during the polymerization of styrene, there was a small difference in polymerization rate but a large difference in MW.

Kozlov¹⁸ reported the results of a study on the copolymerization of MMA with styrene in the presence of ammonium salts containing an unsaturated radical. The polymerization of MMA and copolymerization of MMA with styrene were conducted at 60 and 70 °C, respectively, with AIBN as the initiator. The allylic radical containing quaternary ammonium salt was used as an antistatic agent. The presence of the antistatic agent appeared to lower the rate of polymerization although the difference was not significantly large. Kinetic studies also indicated that an increased amount of MMA accelerated the rate of the copolymerization.

Polymers discussed above are summarized in Table 3.

2.2 Polymers of Alkylaminoalkyl (Meth)Acrylates with Alkyl (Meth)Acrylates.

Gruntfest and Fordyce of the Rohm and Haas Company were granted a U.S. patent concerning polymerization of aminoalkyl esters of acrylic and methacrylic acids and the subsequent quaternization of the resulting linear polymers.¹⁹ These polymeric esters were homopolymers or copolymers containing at least 10 mole % and up to 50 mole % of aminoalkyl esters such as DMAEMA. The MWs of these polymers were at least 0.1 megadalton and in most cases were up to several megadaltons. The comonomers used by the authors were vinyl group containing compounds including VA, AA, MAA, acrylonitrile (AN), methacrylonitrile (MAN), acrylamide (AM), MAM, styrene, ethylene, isobutylene, and acrylic and methacrylic esters such as MA, MMA, t-butyl methacrylate (tBMA), and n-octyl methacrylate.

In 1960, Maeder of Switzerland was granted a U.S. patent concerning stable emulsions of water-dispersible polymerization products.²⁰ These products were obtained from the polymerization of the quaternary ammonium salt of aminoalkyl (meth)acrylate with other polymerizable vinyl monomers such as styrene, AN, or alkyl acrylate. Examples of the aminoalkyl (meth)acrylates used are N,N-diethylaminoethyl acrylate (DEAEA) and N,N-diethylaminoethyl methacrylate (DEAEMA). Also claimed in this investigation was the invention of a water-dispersible polymerization product made from the copolymerization of N,N-diethylaminoethyl fumarate with styrene and n-butyl acrylate. An emulsion polymerization technique was employed in the presence of the free radical initiator, potassium persulfate.

Tobolsky and Shen reported the results of their study on the effect of hydrogen-bonding (H-bonding) on the viscoelastic properties of amorphous polymer networks.²¹ Various methacrylate homopolymers and copolymers including poly(DEAEMA), poly(tBAEMA), and poly(DEAEMA-co-tBAEMA) were investigated. Some of these polymers were H-bonded, and some were not. However, all were completely amorphous under the conditions employed. The polymers were obtained by photopolymerization. As a result, it was concluded that the H-bonded polymers showed generally higher values of Tg's and rubbery moduli than the polymers that did not hydrogen bond.

Table 3. Summary of the Polymerization and Properties of Alkyl(Meth)Acrylates, [Alkyl(M)A], Polymers

Acrylate Monomer	Comonomer(s)	Polymerization Method	Physical Properties		Literature cited
			Solvent	Other	
AlkylMA: MA, MMA, EA, IBMA, EHMA, etc.	---	---	---	hardness, brittle- point	6
EA	---	---	---	hydrolysis	7
EA	butadiene	---	---	rate	
MMA	---	---	---	hydrolysis (tacticity)	8
acrylates and methacrylates	---	---	---	Tg	9
MMA	---	---	---	degradation	10
AlkylMA: MMA, EMA nPMA, IPMA, THFFMA,* etc.	vinyl monomers, ethylene, propylene (VP, VA, MAM, tBAEMA, etc.)	solution (free radical)	---	viscosity	11
AlkylMA: MMA, EMA nPMA, nBMA	---	---	---	linear expansion (torsion pendulum)	12
IBMA	---	solution (anionic)	---	stereo- regularity, Tg	13
MMA	---	---	---	relaxation behavior	14
MMA	---	---	benzene	viscosity (ebullioscopy)	15
MMA	---	free radical	---	dilatometry	16
MMA	styrene	micro- suspension (free radical)	---	---	17
MMA	---	---	---	kinetics of	18
MMA	styrene	---	---	polymerization	

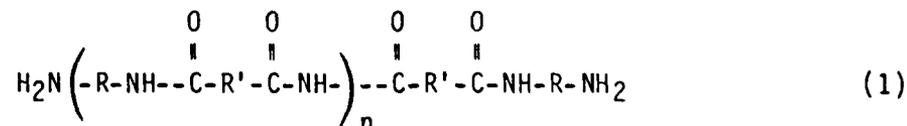
*tetrahydrofurfuryl methacrylate

The Tg's and thermal expansion coefficients of different polymers, most of them acrylates, were reported by Krause and co-workers of the Rohm and Haas Company.²² The polymers reported included: acrylates such as isopropyl acrylate (IPA), benzyl acrylate (BzA), and m-(N,N-dimethylamino) phenyl acrylate; and methacrylates such as IPMA, IBMA, tBAEMA, and DMAEMA. The monomers were synthesized at Rohm and Haas Company and were subsequently polymerized by free radical initiation with the exception of a few that were polymerized thermally. Polymerizations were carried out by solution, bulk, or emulsion polymerization techniques depending on which was more appropriate for the monomer of interest. For example, poly(tBAEMA) was prepared by bulk polymerization at 60 °C, and poly(DMAEMA) was prepared by bulk polymerization at -20 °C or solution polymerization in benzene at 44.1 °C. The Tg of poly(tBAEMA) was reported to be 33 °C, and the Tg's for poly(DMAEMA) were 19 and 17 °C for bulk polymerized and solution polymerized samples, respectively.

Harrison, in 1967, documented the process of the preparation of ammonium salts containing a methacrylic group by reacting aminoalkyl methacrylate with hexafluoroarsenic or hexafluorophosphoric acids.²³ The resulting salts were useful as parasiticides for the control of a number of mites, insects, and other organisms.

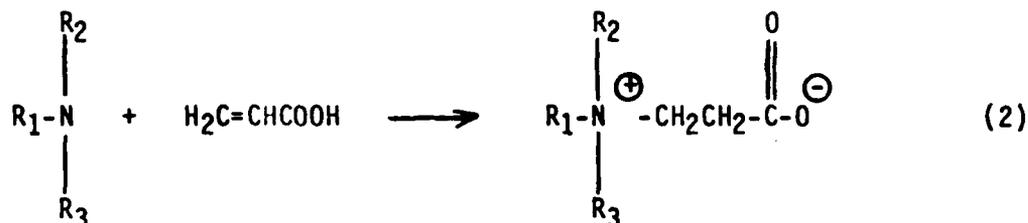
Jamrog and Podlewski were able to prepare linear copolymers of tBAEMA (0.1 to 5 wt %) with vinyl monomers such as AA, MAA, alkyl acrylates (MA, EA, n-butyl acrylate, cyclohexyl acrylate, BzA, n-hexyl acrylate, or 2-ethylhexyl acrylate), alkyl methacrylates (MMA, EMA, IPMA, tBMA, cyclohexyl methacrylate, benzyl methacrylate, n-hexyl methacrylate, EHMA, lauryl methacrylate, or stearyl methacrylate), styrene, and vinyl toluene.²⁴ These polymers were produced by solution polymerization in the presence of free radical initiators such as AIBN or BP. Examples of the solvents that were used for the polymerization included toluene, xylene, butyl acetate, acetone, methyl ethyl ketone (MEK), isopropanol, ethylene glycol monoethyl ether acetate, and butylene glycol monoethyl ether acetate. The resulting polymers were soluble in conventional organic solvents such as acetone, toluene, xylene, ethylene glycol monoethyl ether acetate, and other aliphatic and aromatic hydrocarbons, esters, ethers, ketones, and alcohols.

In a 1973 U.S. patent, Cremeans and co-workers reported the invention of a surface coating (paint) that reacts with vapor-phase iodine or methyl iodide.²⁵ The invention describes a safety system for preventing the escape of radioactive iodine with a paint containing a cross-linked poly(amino acrylate) or a cross-linked combination of poly(amino acrylate) and an amine-terminated polyamide. The poly(amino acrylate) used was poly(tBAEMA) or a copolymer of tBAEMA with DMAEMA. The amine-terminated polyamide can be characterized by the following structure:



where R and R' are aliphatic groups, and n is an integer.

A U.S. patent about a method to produce organic compounds containing betaines was granted to Shachat, Haggard, and Lewis.²⁶ A betaine is formed by a tertiary amine reacting with AA according to the following equation:



where R_1 , R_2 , and R_3 are alkyl groups. The tertiary amines used by the authors included dialkylaminoalkyl (meth)acrylates and N-aminoalkyl (meth)acrylamides. Examples of these compounds are N,N-dimethylaminoethyl acrylate (DMAEA), DMAEMA, N-(N',N'-dimethylaminoethyl) methacrylamide, N-(N',N'-dimethylaminoethyl) acrylamide, and polymers containing any of the above units.

A U.S. patent was granted to Chancler and Moser concerning an improvement of the dye receptivity of polyolefin materials by coating the materials with a self-curing polymeric binder containing a quaternary ammonium salt.²⁷ Such polymeric coatings were typically produced by the reaction of a salt of DMAEMA, epichlorohydrin, and a lower alkyl methacrylate. An emulsion polymerization technique was employed to produce the coating material.

Crawford, Yamamoto, and Cusano were granted a U.S. patent for the invention of an interpolymer of dialkylaminoalkyl methacrylate and methacrylates containing different alkyl groups.²⁸ Dialkylaminoalkyl methacrylate can be represented by the formula:



where R_1 and R_2 are methyl or ethyl, and n is between 1 and 5. The typical interpolymer consisted of between 1 and 10 wt % of dialkylaminoalkyl methacrylate, between 15 and 30 wt % of 1 to 6 carbon alkyl methacrylate, between 40 and 60 wt % of 10 to 14 carbon alkyl methacrylate, and between 15 and 30 wt % of 16 to 20 carbon alkyl methacrylate. The MW of this interpolymer was between 0.05 and 1 megadalton as determined by membrane osmometry. The limiting viscosity number (LVN) of this polymer was between 0.1 and 2.5 dL/g in benzene at 77 °C. The main application of this interpolymer was as a polymeric additive in mineral lubricating oil compositions.

Lewis and Haggard were granted a U.S. patent concerning the anionic polymerization of methacrylate monomers such as MMA, EMA, nBMA, iBMA, and DMAEMA.²⁹ An anionic polymerization method was employed because of the MW and MW distribution (MWD) regulation property of this method. The resulting polymers had low MWs of up to 3000 daltons and had very narrow MWDs; that is, less than 3 and, in most cases, less than 2.

In a 1979 U.S. patent, Cusano and co-workers of Texaco, Incorporated, described the invention of copolymers comprised of the olefin polymerization product of alkyl methacrylates and a polymerizable monomer containing a basic nitrogen in a side chain.³⁰ The latter included aminoalkyl methacrylate, vinylpyridine, and the like. The polymerization was carried out in a reactor containing the appropriate mixture of monomers, n-dodecylmercaptan (a chain length regulator), and AIBN (an initiator). The MW of the resulting polymers were very low [500-4000 daltons, as determined by vapor pressure osmometry (VPO)]. A similar, nitrogen-containing polymer was patented by Vartanian and Ippolito of Texaco, Incorporated, also in 1979.³¹ This low MW (up to 5000 daltons as determined by VPO), nitrogen-containing polymer was prepared by copolymerization of monomers such as alkyl methacrylate (i.e., DMAEMA), aminoalkyl vinyl ether, or vinylpyridine, with alkyl methacrylate.

In 1979, Yosida, Kumakura, and Kaetsu reported that the radical-induced polymerization of DEAEMA with MMA yielded a linear copolymer, soluble in acid.³² They also reported the synthesis of a copolymer of MAA with MA. The MW of these polymers was not determined, but tablet porosity and drug dissolution properties were determined.

A Nuclear Magnetic Resonance (NMR) spectroscopic study of sequence distribution in poly(MAA-co-DMAEMA) was reported by French researchers, Merle and Merle in 1982.³³ The MAA/DMAEMA copolymer was prepared by either copolymerization of monomers, MAA and DMAEMA, in the presence of a free radical initiator, or by partial hydrolysis of the DMAEMA homopolymer. The authors concluded that the difference in solubility could be caused by the ability of the acid sequences to form insoluble complexes with the amine sequences. In other words, the microstructure of the polymer governed the chemical and physical properties.

Polymers discussed in this section are summarized in Table 4.

Table 4. Summary of Polymerization and Properties of Alkylamino-alkyl (Meth)Acrylates/Alkyl (Meth)Acrylate Polymers

Acrylate Monomer	Comonomer(s)	Polymerization Method	Physical Properties			Literature cited
			MW (MD)	Solvent	Other	
DMAEMA	VA,AA,MAA, AN,MAN,AM, MAM,styrene, ethylene, acrylates, & methacrylate	solution	0.1 &>	---	quaternization	19
DEAEA, DEAEMA	styrene, AN, alkyl acrylates	emulsion (free radical)	---	---	---	20
DEAEMA, tBAEMA, DEAEMA-co-tBAEMA	---	photo-polymerization	---	---	H-bonding	21
tBAEMA, DMAEMA, other alkyl acrylate	---	solution, bulk-emulsion	---	---	Tg, thermal expansion	22
tBAEMA	AA,MAA,MA, EA,MMA,EMA, etc.	solution, (free radical)	---	toluene, xylene, etc.	linear	24
tBAEMA, DMAEMA	polyamide	---	---	---	cross-linked	25
DMAEMA	epichlorohydrin, lower alkyl methacrylate	emulsion	---	---	coating	27
DMAEMA, DEAEMA, Dalkyl-AEMA's	alkyl methacrylate	---	0.05-1	---	LVN	28
DMAEMA, alkyl MA's	---	anionic	up to 0.003	---	MWD	29
amino-alkyl-MA's	vinyl pyridine	free radical	0.0005 to 0.004	---	VPO	30

Table 4. Summary of Polymerization and Properties of Alkylaminoalkyl (Meth)Acrylates/Alkyl (Meth)Acrylate Polymers (continued)

Acrylate Monomer	Comonomer(s)	Polymerization Method	Physical Properties			Literature cited
			MW (MD)	Solvent	Other	
DMAEMA, alkylMA	vinyl pyridine, aminoalkyl vinyl ether	---	up to 0.005	---	VPO	31
DEAEMA MA	MMA MAA	---	---	---	linear, tablet porosity	32
DMAEMA	MAA	free radical	---	---	hydrolysis	33

2.3 Polymers of Alkylaminoalkyl (Meth)Acrylates with Other Vinyl Monomers.

In a 1954 U.S. patent, Harney described the preparation of copolymers from DMAEMA and other vinyl comonomers such as AN or styrene.³⁴ DMAEMA was used in its quaternary ammonium salt form. For example, the copolymer of DMAEMA/AN was prepared by solution polymerization in water in the presence of ammonium persulfate, the initiator. The polymer obtained was soluble in dimethyl formamide (DMF).

Daniel was granted a U.S. patent concerning polymers containing hydrophobic units as well as hydrophilic units.³⁵ Monomers containing a hydrophilic group included aminoalkyl (meth)acrylates, aminoalkyl acrylamides, vinylpyridines, and the like. The monomers containing a hydrophobic group included vinyl compounds with an aromatic side chain, such as styrene and its derivatives, and alkyl (meth)acrylates in which the alkyl group contained more than 6 and up to 18 or more carbons. The polymerization methods employed were bulk, solution, and emulsion polymerization methods depending on which was more appropriate. The initiators used were AIBN, BP, and other free radical initiators. The MWs of the resulting copolymers were within the range of 50,000 to 500,000 daltons.

A U.S. patent was granted to Suen and Schiller for the invention of cationic polyelectrolyte polymers derived from the polymerization of aminoalkyl acrylates, aminoalkyl acrylamides, or other amine containing monomers.³⁶ Common comonomers such as styrene, ethylene, VA, AN, MA, and EMA, and the resulting copolymers were applied as flocculants for sewage treatment.

Barabas and Fein were granted a U.K. patent for the invention of a copolymer of alkylaminoalkyl acrylate or methacrylate (5-80 mole %) with VP (20-95 mole %).³⁷ The alkylaminoalkyl acrylates included N,N-dimethyl-aminoethyl acrylate (DMAEA), N,N-dimethylaminobutyl acrylate, DEAEA,

N,N-diethylaminoethyl acrylate, and N,N-di-t-butylaminoethyl acrylate. The alkylaminoalkyl methacrylates included DMAEMA, N,N-dimethylaminobutyl methacrylate, N,N-diethylaminobutyl methacrylate, N,N-methylethylaminoethyl methacrylate, and N,N-di-t-butylaminoethyl methacrylate (DtBAEMA). The polymerization technique employed was solution polymerization in water in the presence of a free radical initiator such as t-butylperoxypivalate. The temperature of polymerization ranged from 50 to 100 °C, and the resulting polymers had MWs of 0.015 to 1 megadalton.

Polymers discussed in this section are summarized in Table 5.

Table 5. Summary of the Polymers from Aminoalkyl (Meth)Acrylates and Other Vinyl Monomers

Acrylate Monomer	Comonomer(s)	Polymerization Method	Physical Properties			Literature cited
			MW (MD)	Solvent	Other	
DMAEMA	AN, styrene	solution (free radical)	---	DMF	---	34
amino-alkyl meth-acrylate	styrene and styrene derivatives	bulk, solution, emulsion	0.05 to 0.5	---	---	35
amino-alkyl meth-acrylate	styrene, ethylene, VA, AN	---	---	---	---	36
DMAEA, DEAEA, DMAEMA, DEAEMA, DtBAEMA	VP	solution (free radical)	0.015 to 1.0	water	linear	37

3. POLYMERS OF 1-VINYL-2-PYRROLIDONE OR (METH)ACRYLIC ACID

3.1 Foreign Literature.

In 1966, Rohm and Haas Company received a Netherlands patent for the invention of copolymers of VP with acrylates.³⁸ The linear polymers were prepared by free radical polymerization and were soluble in organic media. The MWs of these polymers were not determined but their thermal stabilities were measured.

Later, Jasiuski and Fein reported the production of VP-alkyl acrylamide-AA terpolymers by an emulsion polymerization technique.³⁹ From the viscosity measurements, the MWs of these polymers ranged up to 2 megadaltons.

Barabanov and Sannikov of the Union of Soviet Socialist Republics (USSR) reported the results of their investigation of copolymers of MMA and MAA in a 1972 article entitled, "Relaxation Time of Gegenions in Nonaqueous Polyelectrolyte Solutions."⁴⁰ This study used an apparatus that measured conductivities in a high-strength field using DMF and acetone as solvents. The results indicated that copolymers of different composition showed different electrolytic capabilities. Despite the differences in the behavior of the copolymer solutions, the results of this study (i.e., the relaxation time) indicated that these systems appear to be specially bonded gegenions.

As discussed in section 2.2 Barabas and Fein, in a British patent, reported on the solution polymerization of VP with acrylate or methacrylate monomer. This yielded linear, water-soluble polymers with MWs of 0.015-1 megadalton.³⁷ They also reported the preparation of terpolymers of VP, (meth)acrylates, and other vinyl or vinylidene monomers such as alkyl vinyl ethers, where alkyl was methyl, ethyl, or octyl; acrylic and methacrylic acids; aromatic vinyl monomers such as styrene or alpha-methyl styrene; halogen containing monomers such as vinyl chloride or vinylidene chloride; AN and its derivatives; AM and its derivatives; and other common monomers such as VA.

In 1976, Savel'tsev and co-workers were granted a Soviet patent that documented the invention of copolymers of alkyl methacrylates with MAA.⁴¹ The polymers were linear, water soluble, and used in herbicidal products.

In 1978, Carton and co-workers reported the preparation of poly(MAA) by ultraviolet (UV) irradiation.⁴² The resulting polymer was linear and soluble in methanol and a mixture of water and 2-chloroethanol. The MW of this polymer was approximately 0.033 megadalton. These researchers also reported the production of poly(2-hydroxyethyl methacrylate), which was linear and soluble in 2-methoxyethanol and a mixture of water and 2-chloroethanol. The MW of this polymer was approximately 0.225 megadalton. Density, viscosity, preferential solvation behavior, and specific refractive index were measured.

Very low MW (900-4,500 daltons) phosphine group containing pyrrolidone polymers were prepared by Achiha, Shiba, and Ishizuka in 1979.⁴³ These linear polymers, which were insoluble in organic media, were characterized by infrared (IR) spectroscopy, refractive index, and elemental analysis.

Bronnsack prepared VP-containing polymers that can be applied to hair-care products.⁴⁴ These polymers were soluble in water, low MW alcohols, glycerin, sorbitol, DMF, and benzyl alcohol.

Russian researchers Meyiya, Nesterova, and Nikolayev reported the synthesis and properties of copolymers containing AA.⁴⁵ Copolymers VA-co-AA and MMA-co-AA were synthesized with different blocking (that is, different distribution of chemical links in the polymers) by using different monomer ratios and different solvents. A subsequent study of the properties of these copolymers showed that the "more blocked" copolymers had higher resistance to moisture and acid. Using poly(MMA-co-AA) films of different compositions, the relationship between the rate of swelling and the composition of the

polymer film was studied. This study showed that the increase in the AA content of the poly(MMA-co-AA) led to an increase of the film swelling rate and to a reduction in the activation energy of the process. This study, coupled with the knowledge of the relationship between the rate of swelling and the film thickness, enabled the authors to select copolymers of different compositions for use as coatings that can provide a predicted time of decomposition for use in controlled release medicines. The copolymers of MMA and AA provided reliable protection of encapsulated medical preparations against the action of gastric juices, which are acidic at a pH of around 1, and swelled in an environment similar to the human intestinal tract, which is basic at a pH >8, thus freeing the medicine. By changing the AA content of the copolymer, the rate of swelling can be controlled to that which is directly proportional to the rate of the medicine release.

Related research on polymers containing VP was reported in the USSR. Both graft and linear copolymers of VP with MAA were obtained by Nurgalieva and co-workers.⁴⁶ The investigation of a comparative study of properties in graft and random copolymers of VP with MAA resulted in polymers that were insoluble in water but that were soluble in methanol, DMF, and amines. These polymers were characterized for viscosity, potentiometric titration, sorption isotherms, swelling heat, and composition of copolymers by indicator titration of carboxylic acid.

Lorenz and co-workers were granted a European patent for the synthesis of vinylcaprolactam-VP-alkyl acrylate terpolymers by solution polymerization.⁴⁷ The resulting linear polymers were soluble in water and low MW alcohols.

Zonova, Shakhovskaya, and Kryazhev reported on the rheological properties of dispersions of poly(MMA-co-MAA) copolymers in phthalic esters in 1982.⁴⁸ The copolymers, containing about 12% MAA, were prepared by emulsion polymerization and resulted in MWs of 0.87-1.58 megadaltons. The study showed that the rheological properties of poly(MMA-co-MAA) copolymer dispersions in esters of phthalic acid during heating or storage for a prolonged period were influenced not only by the molecular characteristics but also, to a significant degree, by the morphological characteristics of the samples.

The polymers discussed above are summarized in Table 6.

3.2 U.S. Literature.

In 1966, a U.S. patent was granted to Brown for an interpolymer of N-alkyl acrylamides, acrylic esters, and/or VP.⁴⁹ The polymerization was initiated by a free radical in solution, and the resulting polymer was linear. This polymer was soluble in acetone and MEK. Viscosity measurements and tensile tests were performed.

Blumstein and co-workers reported the successful conversion of poly(MAA) to poly(MMA) through methylation with 1-methyl-3-p-tolyltriazene (MTT) instead of with the more common methylating agent, diazomethane.⁵⁰

They also converted poly(MMA) into poly(MAA) by hydrolysis in concentrated sulfuric acid. The authors found that the tacticity of the polymers was not affected by methylation using MTT.

Table 6. Properties of Polymers Containing VP or MAA

Acrylate Monomer	Comonomer(s)	Physical Properties				Literature cited
		MW (MD)	Solvent	Configuration	Other	
VP	acrylates	---	organic solvents	linear	thermal stability	38
VP	alkyl acrylamide, AA	up to 2.0	organic solvents	graft	viscosity	39
MAA	MMA	---	DMF acetone	---	conductivity, relaxation time	40
VP	---	0.015 to 1.0	water	linear	viscosity, pH	37
MAA	methacrylate	---	water	linear	---	41
MAA	---	0.033	methanol, water/2-chloroethanol	---	initiated by UV radiation, density, viscosity, dialysis	42
VP	acrylates	0.0009 to 0.0045	water	linear	IR, refractive index, elemental analysis	43
VP	---	---	water, low MW alcohols, DMF, sorbitol	---	---	44
AA	VA, MMA	---	---	---	rate of swelling	45
VP	MAA	---	methanol, DMF, formamide, amines	graft & linear	viscosity, potentiometric titration, sorption isotherms, titration of carboxylic groups, swelling heat	46

Table 6. Properties of Polymers Containing VP or MAA (continued)

Acrylate Monomer	Comonomer(s)	Physical Properties				Literature cited
		MW (MD)	Solvent	Configuration	Other	
VP	vinyl caprolactam, alkylacrylate	---	water, low MW alcohols	linear	tackiness, moisture content	47
MAA	MMA	0.087 to 1.58	---	---	emulsion polymerization, rheological properties	48

Barabas and Grosser reported the preparation of a tetrapolymer by solution polymerization which consisted of 50-80 parts VP, 6-20 parts AM, 4-20 parts MAM, and 5-20 parts N-alkylaminoalkyl acrylate or methacrylate.⁵¹ An inorganic free radical initiator, tetrapotassium peroxy diphosphate, was used. The polymer obtained was water soluble and was reported to be applicable as a flocculant.

Radic and Gargallo published their results of the copolymerization of aromatic methacrylates with VP in 1978.^{52,53} The solution polymerization, with free radical initiation, yielded linear polymers that were soluble in organic media such as benzene or chloroform. Viscosities were measured, and the reactivity ratios were determined by IR and elemental analysis.

Japanese scientists, Yokota and co-workers, published the results of a ¹³C NMR study of polymers containing VP in *Macromolecules*.⁵⁴ These polymers [a homopolymer of VP, copolymers of VP and MMA, and poly(hydroxyethyl methacrylate)] were prepared by free radical initiation and were covalently cross-linked.

Homo- and copolymers of MAA and their derivatives, prepared by solution polymerization, were reported by Lewis in a U.S. patent.⁵⁵ The resulting polymers, prepared by anionic initiation, were linear and had MWs from 400-10,000 daltons. These polymers were soluble in organic media such as toluene or xylene and had cross-linkable functional groups. The MWs of these polymers were determined by Size Exclusion Chromatography (SEC).

The synthesis of copolymers of VP with some unsaturated carbonyl compounds was reported by Gross in a U.S. patent.⁵⁶ The monomer units in the polymers were as follows: (1) 0 to 90% of at least 2 acrylate monomers, (2) 0 to 95% of a vinyl monomer such as styrene, AN, or vinyl chloride, (3) 0.5 to 5% of VP, and (4) 2 to 15% of an unsaturated compound from the group of AA, MAA, formic acid, itaconic acid, maleic acid, and maleic anhydride. The emulsion polymerization of this monomer mixture yielded a linear polymer

that was soluble in ethylene glycol monoethyl ether and ethylene glycol monobutyl ether.

Poly(VP) with a MW of 1.69 megadaltons, poly(AA), and poly(DMAEMA) were synthesized by Roy-Chowdhury.⁵⁷ These linear polymers were prepared by solution polymerization and were soluble in methanol and 1,4-dioxane. Viscosities and adiabatic compressibilities of these polymers were determined.

The polymers discussed above are summarized in Table 7.

Table 7. Properties of Polymers from VP or MAA Published in U.S. Literature

Acrylate Monomer	Comonomer(s)	Polymerization Method	Physical Properties			Literature cited
			MW (MD)	Solvent	Other	
VP	N-alkylacrylamides, acrylates	solution	---	acetone, MEK	linear, viscosity, tensile test	49
MAA	---	---	---	benzene, DMF	linear, methylation	50
VP	AM, MAM, N-alkylaminoacrylates	---	---	water	---	51
VP	aromatic methacrylates	solution	---	benzene, chloroform	linear, viscosity, IR, reactivity ratios	52,53
VP	MMA	free radical	---	---	cross-linked, ¹³ C NMR	54
methacrylates	---	anionic	0.0004 to 0.01	toluene, xylene	linear, MWD by SEC, cross-linkable functional groups	55

Table 7. Properties of Polymers from VP or MAA Published in U.S. Literature (continued)

Acrylate Monomer	Comonomer(s)	Polymerization Method	Physical Properties			Literature cited
			MW (MD)	Solvent	Other	
VP	acrylate, AA, vinyl monomers such as styrene, vinyl chloride, etc.	emulsion	---	ethylene glycol monoethyl ether	linear, viscosity	56
VP	---	solution	1.69	water, methanol, dioxane	linear, viscosity, adiabatic compressibility	57
AA DMAEMA	---	---	---	methanol, dioxane	linear, viscosity, adiabatic compressibility	57

4. CONCLUSION

Polymers prepared from acrylates and methacrylates are practically and theoretically important because they can be polymerized by various methods (bulk, solution, emulsion, or suspension polymerization) through various mechanisms (free-radical or anionic initiation) to yield a wide variety of products.

These polymers are especially important when the monomers are modified to contain pendant amino groups. The resulting polymers are thus polyelectrolytes, which improves their solubility in both water and various organic solvents.

Various other hydrophilic or electrolytic polymers can be obtained by copolymerization with VP, AA, or MAA. Products from these monomers possess a wide range of commercial applications; for example, these polymers are used as additives for motor oils, additives for cosmetics, and as coatings.

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APPENDIX A

DATA BASE LITERATURE REVIEW STRATEGIES APPLICABLE TO POLYMER RESEARCH: DETERMINATION OF HOMOPOLYMER AND COPOLYMER CHEMICAL ABSTRACT SERVICE (CAS) NUMBERS THROUGH DIALOG INFORMATION SERVICES, INC.

During the development of new polymer materials, available literature must be reviewed to determine if there has been documentation of specific polymer/solvent interactions and polymer physical properties. At other times, the literature must be reviewed to determine whether proposed copolymer compositions or similar materials have been previously produced and if they are commercially available. If these proposed homopolymers or copolymers have already been developed, a further review of the literature must be conducted to determine their specific polymer/solvent properties and physical properties. If other, similar, materials have been developed, the appropriate literature for these materials may also be reviewed because it may be possible to estimate polymer/solvent properties and physical properties for the polymers of interest.

DIALOG Information Services, Incorporated, provides a computer search system for several chemical information data bases, including Chemical Abstracts (from 1967 to present), Chemname, Chemsis, Chemzero. There is a search technique for those compounds for which the CAS number is readily available. However, for homopolymers or unique copolymers, the CAS number must first be determined.

The CAS number of the homopolymer or copolymer can be determined through DIALOG, followed by a subsequent literature search. The strategy used to determine a homopolymer or copolymer CAS number starting with a monomer structure is as follows:

a. Determine the CAS number of the monomer. If this is not readily available, it can be determined through DIALOG or hard copy references (Registry of the Toxic Effects of Chemical Substances, etc.). The search for the monomer CAS number requires only the molecular formula or one or more proposed names or synonyms.

b. Perform the DIALOG search using the CAS number of the monomer as a Registered Component (RC); for example, RC = monomer CAS number. This lists all compounds that have this monomer as a component.

c. Specify that the monomer must be polymerized and that the formula given is the full term. This is signified by bracketing the molecular formula followed by a postscript X/FF. For example, for polyethylene, MF = C2H2) X/FF. Including the specification that the number of components (NC) only equals one is required to determine the homopolymer CAS number from the monomer CAS number (i.e., NC = 01).

This mode of search provides the CAS number of the homopolymer containing only a single monomer. If desired, stereospecific polymers can be deleted through the use of an appropriate command option. However, this

will most often not be necessary since the number of stereospecific combinations is limited to only three for polymers: atactic, isotactic, and syndiotactic.

At this point, the CAS number for proposed copolymers can be determined in a manner similar to that used to determine the homopolymer CAS number. Perform the DIALOG search again as described in steps "a" and "b" above using the CAS number of the comonomer as a registered component (i.e., RC = comonomer CAS number). The results of this search will again provide information on all known compounds (including copolymers) that have the comonomer as a component. The CAS numbers for specific copolymer compositions can be determined by use of data base logic to exclusively combine the CAS numbers for the comonomers of interest (i.e., RC = comonomer 1 CAS number AND RC = comonomer 2 CAS number). The identification of commercial trade names and synonyms for this copolymer is often successful with this technique. However, manufacturers are not likely to identify specific product compositions in terms of molar ratios, weight ratios, etc. for comonomer content.

When the CAS numbers for all homopolymers and/or copolymers of interest have been obtained, a full literature search for polymer/solvent and/or polymer physical properties can be conducted through DIALOG. The polymer CAS number is combined with other key words by employing data base logic in the usual manner (conversation with D.C. Smith, Management Information Systems Directorate, U.S. Army Chemical Research, Development and Engineering Center, February 1987).^{1,2}

¹Guide to DIALOG Searching, DIALOG Information Services, Incorporated, Palo Alto, CA, May 1982.

²Chemical Information Seminar-Draft, DIALOG Information Services, Incorporated, Palo Alto, CA, August 1984.

Table A-1. Possible Polymer Search Needs

Given/Known	Desired
Comonomer, monomer	Trade names and manufacturers of homopolymers or copolymers
Specific trade name	Comonomer content (class of polymer available through Material Safety Data Sheets) Manufacturer Uses, properties, etc.
Homopolymer or copolymer	Trade names Manufacturers Uses Properties
Classes	Properties Commercial products/trade names/ manufacturers Uses
Generic trade name	Polymer composition Properties Class

Blank

APPENDIX B

SUMMARY OF PHYSICAL PROPERTY AND CHEMICAL TERMS AND ACRONYMS

	<u>Acronym</u>
MONOMERS:	
<u>Acrylates</u>	
methyl acrylate	MA
ethyl acrylate	EA
isopropyl acrylate	IPA
benzyl acrylate	BzA
<u>Methacrylates</u>	
methyl methacrylate	MMA
ethyl methacrylate	EMA
n-propyl methacrylate	nPMA
isopropyl methacrylate	IPMA
n-butyl methacrylate	nBMA
isobutyl methacrylate	IBMA
t-butyl methacrylate	tBMA
2-ethylhexyl methacrylate	EHMA
<u>Alkylaminoalkyl acrylates</u>	
N,N-dimethylaminoethyl acrylate	DMAEA
N,N-diethylaminoethyl acrylate	DEAEA
<u>Alkylaminoalkyl methacrylates</u>	
N-t-butylaminoethyl methacrylate	tBAEMA
N,N-dimethylaminoethyl methacrylate	DMAEMA
N,N-diethylaminoethyl methacrylate	DEAEMA
N,N-di-t-butylaminoethyl methacrylate	DtBAEMA
<u>Others</u>	
acrylic acid	AA
methacrylic acid	MAA
acrylamide	AM
methacrylamide	MAM
acrylonitrile	AN
methacrylonitrile	MAN
1-vinyl-2-pyrrolidone	VP
vinyl acetate	VA
PHYSICAL PROPERTY TERMS:	
molecular weight	MW
glass transition temperature	Tg
limiting viscosity number	LVN

Acronym

PHYSICAL PROPERTY TERMS (continued):

molecular weight distribution	MWD
vapor pressure osmometry	VPO
size exclusion chromatography	SEC

CHEMICALS:

4-phenyl-1,3-dioxane hydroperoxide	PDHP
benzoyl peroxide	BP
azobisisobutyronitrile	AIBN
lauryl peroxide	LP
methyl ethyl ketone	MEK
dimethyl formamide	DMF
1-methyl-3-p-tolyltriazene	MTT