REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
Unclassified	
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE	Unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
	AFOSR·TR· 8 7 - 0 5 3 0

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION
J. E. Mark University of Cincinnati		AFOSR/NC

6c. ADDRESS (City, State and ZIP Code)	7b. ADDRESS (City, State and ZIP Code)
Dept. of Chemistry, ML #172 Univ. of Cincinnati Cincinnati, OH 45221	Building 410 Bolling AFB, DC 20332-6448

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
AFOSR	NC	Grant AFOSR 83-0027

8c. ADDRESS (City, State and ZIP Code)	10. SOURCE OF FUNDING NOS.			
AFOSR/NC Bolling AFB, Washington, DC 20332	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT NO.
	61102F	2303	A3	

11. TITLE (Include Security Classification) Unclassified
Conformational Analysis of Some Poly-
silanes, and the Precipitation...Networks

12. PERSONAL AUTHOR(S)
Mark, J. E.

13a. TYPE OF REPORT	13b. TIME COVERED FROM Nov.'85 TO Nov.'86	14. DATE OF REPORT (Yr., Mo., Day) January 16, 1987	15. PAGE COUNT 10

16. SUPPLEMENTARY NOTATION

Science of Ceramic Chemical Processing, published by John Wiley & Sons (1986), pp. 435-443

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB. GR.	Conformational analysis ; In situ precipitations, Polysilanes ; Silica fillers, Preferred rotational states, Elastomer reinforcement.

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This review summarizes conformational energy calculations on two polysilanes, and newly developed methods for precipitating reinforcing ceramic fillers in elastomeric materials.

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3 FEB 1989
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20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☒ DTIC USERS ☐	Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE NUMBER (Include Area Code)	22c. OFFICE SYMBOL
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DD FORM 1473, 83 APR   EDITION OF 1 JAN 73 IS OBSOLETE.   UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE

HIGH-PERFORMANCE POLYMERIC MATERIALS

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Final Report, November 1, 1982 - October 31, 1987

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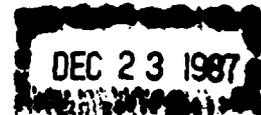
Air Force Office of Scientific Research

December 11, 1987

FOREWORD

Accession For		
NTIS GRA&I	☒	
DTIC TAB	☐	
Unannounced	☐	
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By		
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A. RESEARCH OBJECTIVES AND ACCOMPLISHMENTS

The first primary objective was to obtain an understanding of the properties of relatively stiff polymer chains, and to provide guidance on how these properties can be exploited to obtain high-performance polymeric materials. More specifically, one goal was to use semi-empirical and quantum-mechanical methods to obtain information on the physical properties of rigid-rod benzobisoxazole (PBO), benzobisthiazole (PBT), and structurally related polymers. These materials are of importance to the Air Force because of their high mechanical strength and excellent thermal stability. Such calculations involve energy calculations on both intramolecular (conformational) effects and interchain interactions for the polymers in both the unprotonated and protonated states. Of particular interest is the extent to which the various ring structures in the chains deviate from coplanarity, and how these deviations affect the ordering of the chains in the crystalline state. A related feature is the protonation of these chains, which occurs in the strongly acidic media used as solvents, and its effect on structure and deviations from coplanarity.

One specific study (21)[*] involved conformational energy calculations on two polymers (AAPBO and ABPBO) related to PBO. Another (32) addressed chain packing in a ladder polymer (BBL),

[*]Reference numbers correspond to those in the attached Cumulative List of Publications.

and a less stiff but structurally related polymer (BBB). Good agreement with experimental structural studies was obtained, and the geometry optimization technique was tested on a series of small molecules (16). All of the results obtained on these aspects of the program are summarized in several more general review articles (7,35,43).

Some theoretical and experimental investigations were also carried out on more tractable random-coil polymers in order to evaluate the theoretical methods and to obtain more insight into the properties of the structurally related rigid-rod polymers. These studies specifically involved some polysilanes (6,31,38,47), polygermanes (47), polysiloxanes (9), ethylene-based polyesters (34), and an enzyme inhibitor (DAMP) (2,4).

Electronic band structure calculations were explored with regard to the types of cond ctivity which may be of interest for electronic applications of the rigid-rod polymers and related materials. Similar calculations were also carried out on relatively small molecules having structural features in common with the PBO and PBT polymers. Specific systems studied were PBO (1), two PBO-related polymers (AAPBO and ABPBO) (27), PBT (1,3), two PBT-related polymers (AAPBT and ABPBT) (36), substituted polyacetylenes (14), doped trans-polyacetylene (15), two polyynes (17), iridium carbonyl chloride chains (5), and a bis(oxalato)platinate complex (33). Several polymers were found to have relatively small band gaps, and could therefore be of considerable practical importance. Much of this work is summarized in two review articles (41,45).

In collaboration with Professor William J. Welsh (U. Missouri-St. Louis) and Mr. Henry Kurtz (Memphis State U.), theoretical studies of nonlinear optical effects in small molecules and polymers have been initiated. The goals of this project are: 1) to apply existing methodologies to calculate hyperpolarizabilities of small molecules and polymer subunits and 2) to develop new, more accurate methods for the calculation of such hyperpolarizabilities.

Another series of investigations explored the idea of precipitating fillers into elastomers. The goal was to provide reinforcement of these materials. Also, since the hydrolysis reactions used are very similar to those used in the new sol-gel-ceramics technology, advantageous connections between these two disciplines could be obtained.

In one series of studies, silica-type fillers were precipitated into unimodal and bimodal siloxane polymers after the curing process (11-13,22,29,37,39,42). It was found that the precipitation could also be carried out during the curing process (18,19), or before it (25). Good reinforcement was observed for these elastomers, and for some thermosets (20) as well. Titania particles (29) and iron oxide particles (40) also gave good reinforcement. In some cases extraction procedures gave even larger increases in mechanical properties, and thus even better reinforcement (10).

It may also be possible to introduce some deformability into the filler particles by carrying along some hydrocarbon groups from the material being hydrolyzed (24,28). Magnetic filler

particles have the advantage that they can be manipulated with an external magnetic field (23).

Particle sizes and particle size distributions have been studied by electron microscopy and small-angle x-ray scattering (8,30). Correlation of this information with hydrolysis conditions and mechanical properties is providing valuable guidance for the exploitation of these materials.

The major results obtained in these reinforcement studies are summarized in a series of review articles (26,31,46).

It is also possible to use compositions and hydrolysis conditions that make the silica the continuous phase, and the polymer the dispersed phase (44). Such polymer-modified ceramics could have extremely attractive properties, for example reduced brittleness.

B. CUMULATIVE LIST OF PUBLICATIONS

1. Calculations of the Electronic Band Structures for Some Rigid Benzobisoxazole and Benzobisthiazole Polymers, D. Bhaumik and J. E. Mark, J. Polym. Sci., Polym. Phys. Ed., 21, 1111 (1983).

2. CNDO/2 Molecular Orbital Calculations on the Antifolate DAMP and Some of its Analogues, W. J. Welsh, J. E. Mark, V. Cody, and S. F. Zakrzewski, in "Chemistry and Biology of Pteridines: Pteridines and Folic Acid Derivatives", ed. by J. A. Blair, W. de Gruyter Pub. Co., Berlin, 1983.

3. A Theoretical Investigation of Chain Packing and Electronic Band Structure of the Rigid-Rod Polymer Trans-(p-Phenylene Benzobisthiazole) in the Crystalline State, D. Bhaumik and J. E. Mark, J. Polym. Sci. Polym. Phys. Ed., 21, 2543 (1983).

4. CNDO/2 Molecular Orbital Calculations on the Antifolate DAMP and Some Related Species: Structural Geometries, Ring Distortions, Charge Distributions, and Conformational Characteristics, W. J. Welsh, V. Cody, J. E. Mark, and S. F. Zakrzewski, Cancer Biochem., Biophys., 7, 27 (1983).

5. Band Structures, Geometry, and Partial Oxidation of Iridium Carbonyl Chloride Chains, D. Bhaumik and J. E. Mark, Synthetic Metals, 6, 29 (1983).

6. Conformational Analysis and Solid State ^{29}Si NMR Spectroscopy of Some Polysilanes, W. J. Welsh, J. Ackerman, and J. E. Mark, Polym. Preprints Div. of Polym. Chem., Inc., ACS, 24(1), 131 (1983).

7. Theoretical Investigations on Some Rigid-Rod Polymers Used as High Performance Materials, W. J. Welsh, D. Bhaumik, H. H. Jaffe', and J. E. Mark, Polym. Eng. Sci., 24, 218 (1984).

8. Particle Sizes of Reinforcing Silica Precipitated Into Elastomeric Networks, Y.-P. Ning, M.-Y. Tang, C.-Y. Jiang, J. E. Mark, and W. C. Roth, J. Appl. Polym. Sci., 29, 3209 (1984).

9. Dipole Moments of Some Poly(Dimethylsiloxane) Linear Chains and Cyclics, E. Riande and J. E. Mark, Eur. Polym. J., 20, 517 (1984).

10. Treatment of Filler-Reinforced Silicone Elastomers to Maximize Increases in Ultimate Strength, Y.-P. Ning and J. E. Mark, Polym. Bulletin, 12, 407 (1984).

11. Effects of Ethylamine Catalyst Concentration in the Precipitation of Reinforcing Silica Filler in an Elastomeric Network, J. E. Mark and Y.-P. Ning Polym. Bulletin, 12, 413 (1984).

12. The Effect of Relative Humidity on the Hydrolytic Precipitation of Silica Into an Elastomeric Network, C.-Y. Jiang and J. E. Mark, Colloid Polym. Sci., 262, 758 (1984).

13. The Effects of Various Catalysts in the In-Situ Precipitation of Reinforcing Silica in Polydimet /lsiloxane Networks, C.-Y. Jiang and J. E. Mark, Makromol. (ie, 185, 2609 (1984).

14. Theoretical Studies of th. Electronic Propeties of Substituted Polyacetylenes, K. C. Metzger and W. J. Welsh, Polym. Preprints, Div. of Polym. Chem., Inc., ACS, 25(1), 195 (1984).

-6-

15. A Theoretical Investigation of the Electronic Band Structure in Doped _Trans_-Polyacetylene, D. Bhaumik and J. E. Mark, _Polym. Preprints_, _Div. of Polym. Chem._, _Inc._, _ACS_, **25(2)**, 266 (1984).

16. Geometry Optimization Using Symmetry Coordinates, H. Kondo, W. J. Welsh, H. H. Jaffe', and H. Y. Lee, _J. Comp. Chem._, **5**, 84 (1984).

17. Theoretical Studies in Electrical Conductivity in Polyynes, K. C. Metzger and W. J. Welsh, _Polym. Preprints_, _Div. of Polym. Chem._, _Inc._, _ACS_, **25(2)**, 270 (1984).

18. Elastomeric Properties of Bimodal Networks Prepared by a Simultaneous Curing-Filling Technique, M.-Y. Tang and J. E. Mark, _Polym. Eng. Sci._, **25**, 29 (1985).

19. Simultaneous Curing and Filling of Elastomers, J. E. Mark, C.-Y. Jiang, and M.-Y. Tang, _Macromolecules_, **17**, 2613 (1984).

20. Impact Resistance of Unfilled and Filled Bimodal Thermosets of Poly(dimethylsiloxane), M.-Y. Tang, A. Letton, and J. E. Mark, _Colloid Polym. Sci._, **262**, 990 (1984).

21. Molecular Orbital Conformational Energy Calculations of the Aromatic Heterocyclic Poly(5,5'-Bibenzoxazole-2,2'-Diyl-1,4-Phenylene) and Poly(2,5-Benzoxazole), W. J. Welsh, and J. E. Mark, _Polym. Eng. Sci._, **25**, 965 (1985).

22. Bimodal Networks and Networks Reinforced by the In-Situ Precipitation of Silica, J. E. Mark, _Brit. Polym. J._, **17**, 144 (1985).

23. Effects of a Magnetic Field Applied During the Curing of a Polymer Loaded with Magnetic Filler, Z. Rigbi and J. E. Mark, *J. Polym. Sci.*, *Polym. Phys. Ed.*, **23**, 1267 (1985).

24. Hydrolysis of Several Ethylethoxysilanes to Yield Deformable Filler Particles, Y.-P. Ning, Z. Rigbi and J. E. Mark, *Polym. Bulletin*, **13**, 155 (1985).

25. Precipitation of Reinforcing Filler Into Poly(Dimethyl-siloxane) Prior to Its End Linking Into Elastomeric Networks, Y.-P. Ning and J. E. Mark, *J. Appl. Polym. Sci.*, **30**, 3519 (1985).

26. Molecular Aspects of Rubberlike Elasticity, J. E. Mark, *Acc. Chem. Res.*, **18**, 202 (1985).

27. A Theoretical Study of Conformations and Electronic Band Structures for Two Benzoxazole Polymers, K. Nayak and J. E. Mark, *Makromol. Chemie*, **186**, 2153 (1985).

28. Reinforcing Effects from Silica-Type Fillers Containing Hydrocarbon Groups, J. E. Mark and G. S. Sur, *Polym. Bulletin*, **14**, 325 (1985).

29. Elastomeric Networks Cross Linked by Silica or Titania Fillers, G. S. Sur and J. E. Mark, *Eur. Polym. J.*, 21, 1051 (1985).

30. Electron Microscopy of Elastomers Containing In-Situ Precipitated Silica, J. E. Mark, Y.-P. Ning, C.-Y. Jiang, M.-Y. Tang, and W. C. Roth, *Polymer*, **26**, 2069 (1985).

31. Conformational Analysis of Some Polysilanes and the Precipitation of Reinforcing Silica Into Elastomeric Networks, J. E. Mark, in "Science of Ceramic Chemical

Processing", ed. by L. L. Hench and D. R. Ulrich, Wiley, New York, 1986.

32. Chain Packing in Two Aromatic Heterocyclic Polymers, One of Which Has a Ladder Structure, K. Nayak and J. E. Mark, Makromol. Chemie, **187**, 1547 (1986).

33. Band Structure Analysis of a Bis(oxalato)platinate Complex, K. Nayak, D. Bhaumik, and J. E. Mark, Synthetic Metals, **14**, 309 (1986).

34. Odd-Even Variations in the Melting Points of some Ethylene Polyesters, D. Bhaumik and J. E. Mark, Makromol. Chemie, **187**, 1329 (1986).

35. Theoretical Studies of Liquid-Crystalline Rodlike Polymers Used as High-Performance Materials, W. J. Welsh and J. E. Mark, Chemical Design Automation News, **1(6)**, 2 (1986).

36. Conformational and Electronic Band Structure Analysis of a New Type of High Performance Polybenzothiazole Polymers, K. Nayak, J. Mat. Sci., **21**, 2232 (1986).

37. Comparisons Among Some Tetra-Alkoxysilanes in the Hydrolytic Precipitation of Silica into Elastomeric Networks, G. S. Sur and J. E. Mark, Makromol. Chemie, **187**, 2861 (1986).

38. Conformational Energies and Unperturbed Chain Dimensions of Polysilane and Polydimethylsilylene, W. J. Welsh, L. DeBolt, and J. E. Mark, Macromolecules, **19**, 2978 (1986).

39. Ethylamine and Ammonia as Catalysts in the In-Situ Precipitation of Silica in Silicone Networks, Y.-P. Ning and J. E. Mark, Polym. Eng. Sci., **26**, 167 (1986).

40. Precipitation of Iron Oxide Filler Particles Into an

Elastomer, S. Liu and J. E. Mark, <u>Polym. Bulletin</u>, 18, 33 (1987).

41. Theoretical Studies of Electrical Conductivity in Polymers, W. J. Welsh, <u>Chemical Design Automation News</u>, 2(2), 4 (1987).

42. Reinforcement of a Non-Crystallizable Elastomer by the In-Situ Precipitation of Silica, S. J. Clarson and J. E. Mark, <u>Polym. Comm.</u>, 28, 249 (1987).

43. Conformational Characteristics of Some Liquid-Crystalline Aromatic Heterocyclic Polymers Useable as High-Performance Materials, W. J. Welsh, in "Current Topics in Polymer Science Vol. 1", ed by R. M. Ottenbrite, L. A. Utracki, and S. Inoue, Hanser Publishers, New York, 1987.

44. Polymer-Modified Silica Glasses. I. Control of Hardness, J. E. Mark and C.-C. Sun, <u>Polym. Bulletin</u>, 18, 259 (1987).

45. Band-Structure Calculations on Polymeric Chains, W. J. Welsh, in "Polymers for High Technology", ed. by M. J. Bowden and S. R. Turner, Am. Chem. Soc., Washington, DC, 1987.

46. In-Situ Generation of Ceramic Particles in Elastomeric Matrices, J. E. Mark, in "Ultrastructure Processing of Ceramics, Glasses, and Composites", ed. by J. D. Mackenzie and D. R. Ulrich, Wiley New York, 1988.

47. AM1 and MNDO/2 Molecular Orbital Conformational Energy Calculations on Model Compounds of Simple Polysilanes and Polygermanes, W. D. Johnson and W. J. Welsh, Proceedings of "Silicon-Based Polymer Science Workshop", Polymer Division, ACS, Makaha, Hawaii, November 1987.

C. PROFESSIONAL PERSONNEL

1. Dr. J. E. Mark, Senior Investigator; Distinguished Research Professor of Chemistry and Director of the Polymer Research Center, The University of Cincinnati.

2. Dr. W. J. Welsh, previously Postdoctoral Fellow and Adjunct Professor, The University of Cincinnati, and Assistant Professor, College of Mount St. Joseph. Presently Associate Professor, University of Missouri at St. Louis.

3. Dr. D. Bhaumik, previously Postdoctoral Fellow, The University of Cincinnati. Presently Computer Scientist, Evans and Sutherland Co.

4. Dr. K. Nayak, previously Graduate Student, The University of Cincinnati. Presently Postdoctoral Fellow, University of Texas at Arlington.

5. Dr. H. H. Jaffé, Professor of Chemistry, The University of Cincinnati.

6. Mr. Y.-P. Ning, M.-Y. Tang, C.-Y. Jiang, S. Liu, and C.-C. Sun, Visiting Scholars, the University of Cincinnati.

7. Dr. G. S. Sur, Postdoctoral Fellow, the University of Cincinnati.

8. Mr. K. Metzger, previously Graduate Student, the University of Cincinnati.

9. Dr. A. Letton, previously Graduate Student, the University of Cincinnati. Presently Research Scientist, Dow Chemical Co.

10. Dr. L. DeBolt, previously Graduate Student, the University of Cincinnati. Presently Research Chemist, Sherwin Williams Co.

11. Dr. Z. Rigbi, Visiting Professor, University of Cincinnati.

12. Dr. S. J. Clarson, Postdoctoral Fellow, the University of Cincinnati.

13. Mr. W. D. Johnson, Graduate Student, the University of Missouri at St. Louis.

D. INTERACTIONS

Essentially all of this material was presented in talks at National Meetings of the American Chemical Society and American Physical Society, at Gordon Research Conferences, and at various International Conferences. Numerous talks were also given at other universities and at industrial and government research laboratories. All of the work on the rigid-rod polymers has been presented and discussed in detail at various Reviews of the Air Force Ordered Polymers Program, organized by Dr. T. E. Helminiak and held approximately annually at the Wright-Patterson Air Force Base in Ohio.

J. E. Mark

December 11, 1987

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CONFORMATIONAL ANALYSIS OF SOME POLYSILANES, AND THE PRECIPITATION OF REINFORCING SILICA INTO ELASTOMERIC POLY(DIMETHYLSILOXANE) NETWORKS

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INTRODUCTION

The polysilanes [—SiRR'—] are a new class of semi-inorganic polymers with fascinating properties and considerable promise in a variety of applications. For example, some members of this series can be cast into transparent films. spun into fibers, and converted into silicon carbide at high temperatures.[1,2] They can also be used as photoinitiators,[3] resists in UV lithography,[2,4] p-type semiconductors when properly doped,[2] and as reinforcing media in ceramics when converted *in situ* into β-SiC fibers.[5]

Relatively little is known about the conformational characteristics of the polysilanes from either an experimental or theoretical point of view. although some work is in progress.[6,7] For this reason, conformational energies were calculated for two of the simpler polysilanes. Information thus obtained can

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be used to predict the regular conformations in which the polymers should crystallize,[8] and the equilibrium flexibility of the chains in the undiluted amorphous state and in solution.[8]

The structurally related polysiloxanes [—SiRR'O—] have long been known and extensively studied.[8] The dimethyl polymer has been of particular interest because of its unusual flexibility. This property is exploited, for example, in the use of the crosslinked polymer as an elastomeric material[9,10] in low-temperature applications. These elastomers, however, unlike their competitors such as natural rubber and butyl rubber, cannot undergo strain-induced crystallization.[11,12] They are therefore inherently weak and require reinforcement with a high surface area filler in practically all applications.[9] Blending such fillers into (highly viscous) polymers prior to crosslinking can be very difficult and filler agglomeration is almost impossible to avoid. For these reasons it could be highly advantageous to generate such filler *in situ*, for example, by the hydrolysis of silicates sufficiently nonpolar to dissolve in typical elastomers such as poly-(dimethylsiloxane) (PDMS). Such techniques have now been developed, and the results obtained should transcend the area of elastomer reinforcement, giving information useful as well in the area of sol–gel–ceramics technology.[13]

CONFORMATIONAL ANALYSIS OF SOME POLYSILANES

Computational Details

The first polymer of interest was polysilane (PSL) itself, [—SiH$_2$—], and the specific sequence investigated is shown in Fig. 47.1.[7] The length l of the Si—Si skeletal bonds is 0.234 nm, which is considerably larger than the 0.153-nm length of the C—C bonds in the hydrocarbon analogue, polyethylene (PE) [—CH$_2$CH$_2$—].[8] This should reduce repulsive interactions in polysilanes, but could be partially offset by the increased length of the Si—H bond relative to the C—H bond (0.148 versus 0.110 nm). Skeletal bond angles in PSL are approximately tetrahedral, as they are in PE.[8] Rotational states are *trans* (T), *gauche*
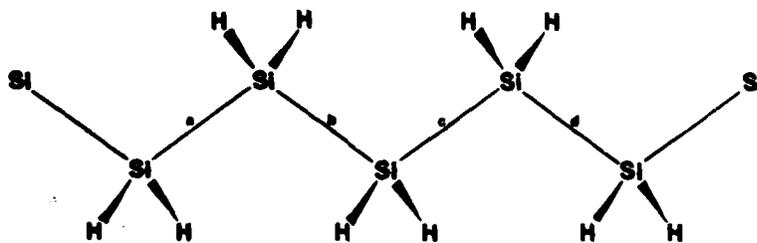

Figure 47.1   Sketch of the polysilane chain.[*] Conformational energies are calculated as a function of the rotation angles about skeletal bonds *b* and *c*.

positive (G^+), and *gauche* negative (G^-), and are expected to occur in the vicinity of the symmetric locations specified by the rotational angles $\phi = 0°$, $120°$, and $-120°$, respectively. The second polymer was poly(dimethylsilylene) (PDMSL) $[-Si(CH_3)_2-]$, shown in Fig. 47.2[7] The model for it was similar to that for PSL, but with the rotational angles of the methyl side groups representing additional variables.

Distances between all pairs of atoms were calculated in the usual manner,[7,8] as a function of the skeletal and side-chain rotational angles. Conformational energies were then calculated from these distances using empirical potential energy functions, and a torsional contribution corresponding to a barrier height of 0.4 kcal/mole (which is considerably smaller than that for PE, 2.8 kcal/mole).[8] Entire contour maps of the energy against rotational angles were obtained, and then used to calculate configurational partition functions and to average the energies and rotational angles about the minima. In this way, configurational statistical weights were refined to include a preexponential or entropy factor. The statistical weights were then used in a matrix multiplication scheme to calculate values of the *characteristic ratio* $\langle r^2 \rangle_0 / nl^2$, where $\langle r^2 \rangle_0$ is the chain dimension as unperturbed by excluded volume effects[14] and n is the number of skeletal bonds. This ratio is much used as an inverse measure of equilibrium chain flexibility.[8]

Results for Polysilane

Polysilane was found to show a preference for pairs of *gauche* states of the same sign $(G^\pm G^\pm)$ over the corresponding *trans* states (TT) by ca. 0.5 kcal/mole, in contrast to the analogous *n*-alkanes which prefer TT over $G^\pm G^\pm$ by ca. 1.0 kcal/mole.[8] Even $G^\pm G^\mp$ states, commonly found to be prohibitively repulsive for most polymers, were preferred over the TT states by 0.4 kcal/mole.[7] The predicted crystalline state conformation could thus be described as helical, of a pitch similar to that shown by polyoxymethylene $[-CH_2O-]$. It is thus quite different from the PE preferred form, which is the planar, all-*trans*, zig-zag
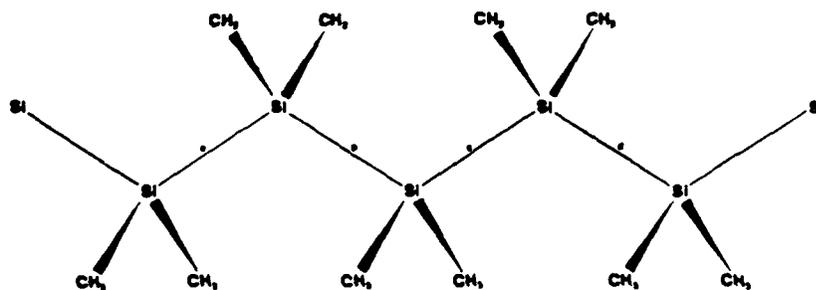

Figure 47.2   Sketch of the poly(dimethylsilylene) chain.

conformation. The same conclusion was reached in an earlier theoretical study of this chain[6] which focused exclusively on discrete minima. As can be seen from Fig. 47.3, nearly all regions of configurational space were within 2 kcal/ mole of the minima, indicating considerable chain flexibility. This was confirmed by the unusually low value, 4.0, calculated for the characteristic ratio. The value for PE is approximately 7.5.

Results for Poly(Dimethylsilylene)

Previous calculations[6] on this polymer indicated the $G^{\pm}G^{\pm}$ conformation again preferred. The present results,[7] however, indicate $G^{\pm}G^{\pm}$ and $TG^{\pm}$ (or $G^{\pm}T$) conformations to have essentially the same energies (0.08 versus 0.00 kcal/ mole). If the energy difference is indeed this small, the conformation actually adopted by the chain upon crystallization would probably be determined by differences in chain packing energies.

Location of $G^{\pm}$ states at angles that minimize the energy would place them at $\pm 95°$. This revision in the direction of the T state, and the diminished number
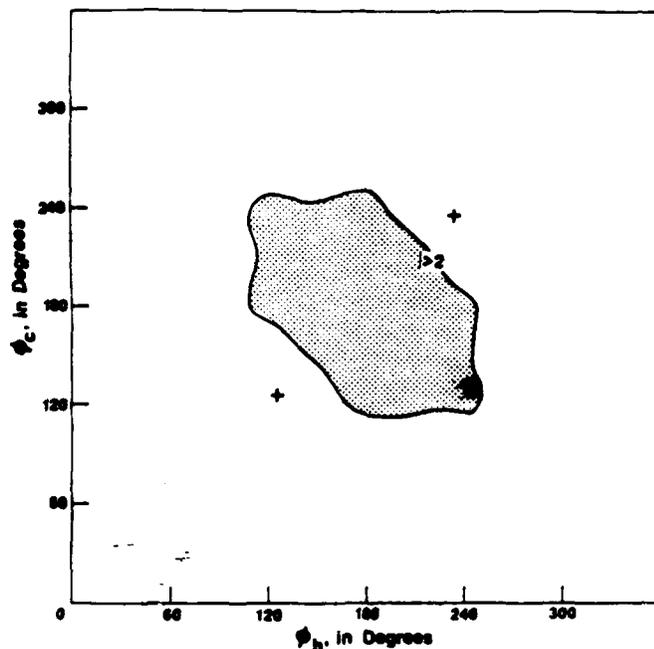

Figure 47.3 Conformational energy map for the polysilane segment giving the energy, in kcal/ mole relative to the conformational energy minima designated by " + " on the map. The energy contours are shown as a function of the rotational angles ϕ_b and ϕ_c.[7] The shaded region corresponds to energies greater than 2 kcal/mole above the minima.

of compact $G^{\pm}$ states should increase the characteristic ratio to the vicinity of 15. This would make the PDMSL chain considerably less flexible than both PSL and PE.

PRECIPITATION OF REINFORCING SILICA INTO ELASTOMERIC NETWORKS

Some Experimental Details

Silica may be prepared by the hydrolysis

$$Si(OC_2H_5)_4 + 2H_2O \rightarrow SiO_2 + 4C_2H_5OH \tag{1}$$
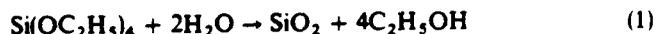
of tetraethylorthosilicate (TEOS), in the presence of any of a variety of catalysts. There are three techniques by which silica thus precipitated can be used to reinforce an elastomeric material. First, an already cured network, for example, prepared from PDMS, may be swollen in TEOS and the TEOS hydrolyzed in situ.[15-20] Alternatively, hydroxyl-terminated PDMS may be mixed with TEOS, which then serves simultaneously to tetrafunctionally end link the PDMS into a network structure and to act as a source of SiO_2 upon hydrolysis.[21-23] Finally, TEOS mixed with vinyl-terminated PDMS can be hydrolyzed to give a SiO_2-filled polymer capable of subsequent end linking by means of a multifunctional silane.[24]

Precipitation Rates

The rates of the precipitation reaction were studied through plots of weight percent filler against time. Typical results for the $C_2H_5NH_2$-catalyzed system within an already cross linked PDMS elastomer are shown in Fig. 47.4.[19] Although the rates increase with catalyst concentration,[20] as expected, they are seen to vary in a complex manner. One complication is the deswelling of the network due to migration of TEOS and the by-product ethanol to the surrounding aqueous solution. The loss of TEOS should be smaller in the case of the more dilute $C_2H_5NH_2$ solution (since it is more hydrophilic), and this would explain the relatively simple monotonic form of the corresponding precipitation curves. In the case of the more concentrated $C_2H_5NH_2$ solutions the curves level off, because of the TEOS migration, and then turn downward. presumably because of loss of colloidal silica. At constant time, less filler is precipitated in the case of the networks having the larger value of the molecular weight between crosslinks, and this is probably due to larger losses of TEOS and silica from the larger "pores" in these networks in the highly swollen state.[19]

Mechanical Properties of the Filled Elastomers

The elastomeric properties of primary interest here are the nominal stress $f^* \equiv f/A^*$ (where f is the equilibrium elastic force and A^* the undeformed
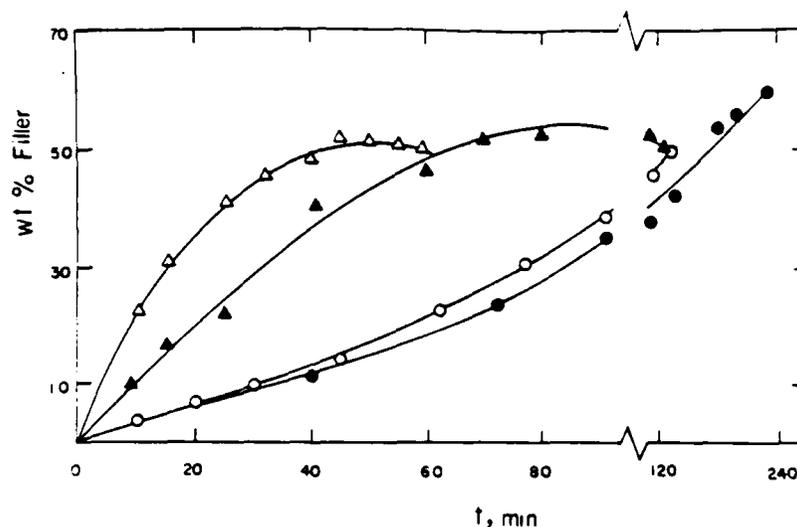
Figure 47.4 Weight percent filler precipitated as a function of time.[19] The circles locate the results for 2.0 wt% ethylamine and the triangles the results for 25.0 wt%; the open symbols are for networks having a molecular weight between crosslinks of 8.0 × 10³ g/mole, and the filled symbols 21.3 × 10³ g/mole.

cross-sectional area), and the reduced stress or modulus[25] $[f^*] \equiv f^*/(\alpha - \alpha^{-2})$ (where $\alpha = L/L_i$ is the elongation or relative length of the sample).

Typical stress–strain isotherms obtained on the *in situ* filled PDMS networks are given in Fig. 47.5. The data show[25] the dependence of the reduced stress on reciprocal elongation. The presence and efficacy of the filler are demonstrated by the large increases in modulus, with marked upturns at the higher elongations. Figure 47.6 shows the data of Fig. 47.5 plotted in such a way that the area under each stress–strain curve corresponds to the energy E_r of rupture, which is the standard measure of elastomer toughness. Increase in % filler decreases the maximum extensibility α_r but increases the ultimate strength f_r^*. The latter effect predominates and E_r increases accordingly. In some cases, extremely large levels of reinforcement are obtained. Such networks behave nearly as thermosets, with some brittleness (small α_r), but with extraordinarily large values of the modulus $[f^*]$.[19]

Characterization of the Filler Particles

Transmission electron microscopy,[16] and light scattering and neutron scattering measurements[26] are being used to study the filler particles. As illustration, an electron micrograph for a PDMS elastomer in which TEOS has been hydrolyzed is shown in Fig. 47.7.[16] The existence of filler particles in the network, originally hypothesized on the basis of mechanical properties,[15] is clearly confirmed. The particles have average diameters of approximately 250 Å, which is in the range
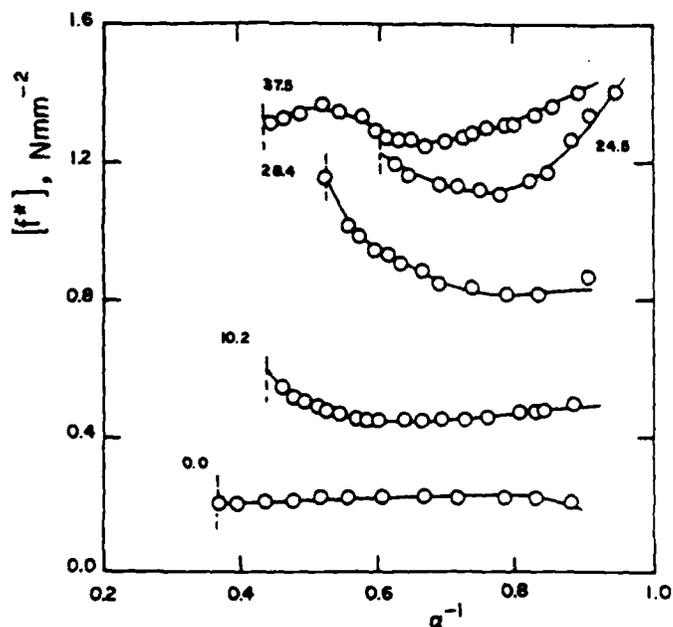
Figure 47.5 The reduced stress as a function of reciprocal elongation, at 25°C, for PDMS networks filled in 2.0 wt% $C_2H_5NH_2$ solution.[19] Each curve is labeled with the wt% filler in the network including results for the unfilled elastomer.

of particle sizes of fillers typically introduced into polymers in the usual blending techniques. The distribution of sizes is relatively narrow, with most values of the diameter falling in the range 200–300 Å.[16]

Strikingly, particles aggregation invariably present in the usual types of filled elastomers is absent. These materials should be useful in characterizing effects of aggregation, and could be of practical importance as well.[16]

Other Novel Filling Techniques

In typical filled systems, anisotropy of mechanical properties can arise only if the filler particles or their agglomerates are asymmetric, since they are then oriented as a result of the flow of the un-crosslinked mix during processing operations. In fact, fibrous fillers are often used for the express purpose of introducing mechanical anisotropy. Recent studies, however, show that even when the particles are spherical, if they are magnetic and the filled elastomer is cured in a magnetic field, then highly anisotropic thermal[27] and mechanical[28] properties can be obtained.

The filler used in one study[28] was an extremely fine commercial magnetic powder (MG-410 Magnaglo) in which the particles are very nearly spherical,
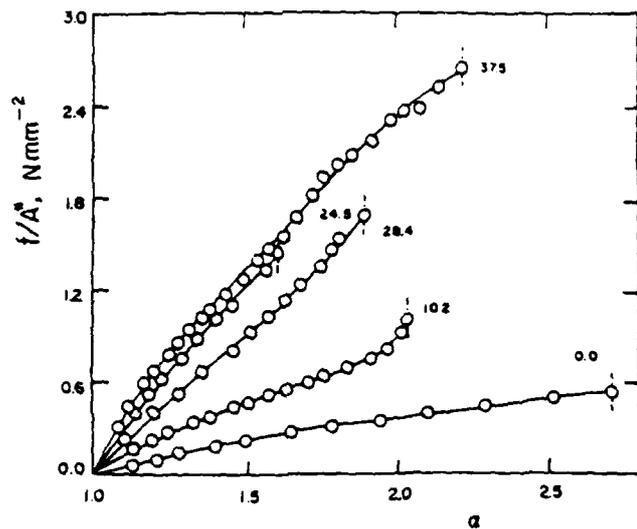
Figure 47.6 Reduced stress as a function of reciprocal elongation for the networks filled in the 50.0 wt% $C_2H_5NH_2$ solution.

Figure 47.7 Transmission electron micrograph (118,800X) for *in-situ* filled PDMS network containing 34.4 wt% filler.[10] The average particle diameter is 250 Å.

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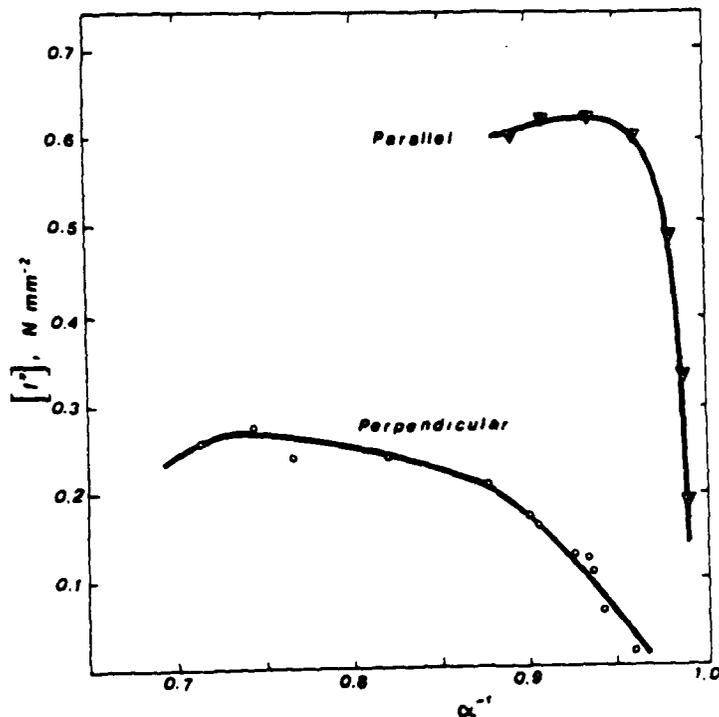
Figure 47.8 Reduced stress shown as a function of reciprocal elongation for magnetic-particle filled PDMS strips cut parallel and perpendicular to the magnetic field imposed during the curing procedure.[28]

with an average diameter of approximately 10 μm. The particles and benzoyl peroxide were mixed into high molecular weight PDMS, and the mixture was cured in a magnetic field provided by a 580-gauss permanent magnet. (The final product contained about 31.5% by weight of magnetic filler, which corresponds to roughly 6% by volume.) The cured sheet was cut into rectangular strips parallel to and perpendicular to the vector of the magnetic field.

The stress–strain isotherms obtained are shown in Fig. 47.8.[28] They are seen to be very different from those usually obtained, which almost invariably have a constant, positive slope in the region of low to moderate elongation.[25] The isotherms also show the highly anisotropic nature of the reinforcement obtained in the presence of the magnetic field. For example, the maximum value of [f^*] for the strip cut parallel to the field exceeds the corresponding value for the perpendicular strip by a factor of nearly 3.

Another novel technique is the generation of magnetic filler particles by the in situ thermal or photochemical decomposition[29,30] of carbonyl compounds of iron, nickel, or cobalt, with elastomer curing being carried out in a magnetic field.

ACKNOWLEDGMENTS

REFERENCES

1. J. P. Wesson and T. C. Williams. *J. Polym. Sci., Polym. Chem. Ed.* **18**, 959 (1980): **19**, 65 (1981).

2. R. West, L. D. David, P. I. Djurovich, K. L. Stearley, K. S. V. Srinivasan, and H. Yu, *J. Am. Chem. Soc.* **103**, 7352 (1981); P. Trefonas III, P. I. Djurovich, X.-H. Zhang, R. West, R. D. Miller, and D. Hofer. *J. Polym. Sci. Polym. Lett. Ed.* **21**, 819 (1983); P. Trefonas III, R. West, R. D. Miller, and D. Hofer. *J. Polym. Sci. Polym. Lett. Ed.* **21**, 823 (1983).

3. A. R. Wolfe, R. West, and D. G. Peterson, Eighteenth Organosilicon Symposium, April 1984.

4. D. C. Hofer, R. D. Miller, and C. G. Willson. *Proc. SPIE* **469**, 16 (1984).

5. R. West, L. D. David, P. I. Djurovich, H. Yu, and R. Sinclair, *Ceram. Bull.* **62**, 899 (1983).

6. J. R. Damewood, Jr. and R. West, *Macromolecules* **18**, 159 (1985).

7. W. J. Welsh, L. C. DeBolt, J. E. Mark, J. R. Damewood, Jr., and R. West, manuscript in preparation.

8. P. J. Flory. *Statistical Mechanics of Chain Molecules*, Wiley-Interscience, New York, 1969.

9. E. L. Warrick, O. R. Pierce, K. E. Polmanteer, and J. C. Saam, *Rubber Chem. Technol.* **52**, 437 (1979).

10. J. E. Mark, *Adv. Polym. Sci.* **44**, 1 (1982).

11. J. E. Mark, *Polym. Eng. Sci.* **19**, 254 (1979).

12. J. E. Mark, *Polym. Eng. Sci.* **19**, 409 (1979).

13. L. L. Hench and D. R. Ulrich, Eds., *Ultrastructure Processing of Ceramics, Glasses, and Composites*. J. Wiley, New York, 1984.

14. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953.

15. J. E. Mark and S.-J. Pan, *Makromol. Chemie, Rapid Comm.* **3**, 681 (1982).

16. Y.-P. Ning, M.-Y. Tang, C.-Y. Jiang, J. E. Mark, and W. C. Roth, *J. Appl. Polym. Sci.* **29**, 3209 (1984).

17. C.-Y. Jiang and J. E. Mark, *Makromol. Chemie* **185**, 2609 (1984).

18. C.-Y. Jiang and J. E. Mark, *Colloid Polym. Sci.* **262**, 758 (1984).

19. Y.-P. Ning and J. E. Mark, *Polym. Eng. Sci.* **25**, 000 (1985).

20. J. E. Mark and Y.-P. Ning, *Polym. Bulletin* **12**, 413 (1984).

21. M.-Y. Tang and J. E. Mark, *Polym. Eng. Sci.* **25**, 29 (1985).

22. J. E. Mark, C.-Y. Jiang, and M.-Y. Tang, *Macromolecules* **17**, 2613 (1984).

23. M.-Y. Tang, A. Letton, and J. E. Mark, *Coll. Polym. Sci.* **262**, 990 (1984).

24. Y.-P. Ning and J. E. Mark, *J. Appl. Polym. Sci.* **30**, 3519 (1985).

25. J. E. Mark. *Rubber Chem. Technol.* **48**, 495 (1975).

26. D. W. Schaefer, Y.-P. Ning, and J. E. Mark, unpublished results.

27. G. J. L. Griffin, in *Advances in Polymer Friction and Wear*, Vol. 5B, L.-H. Lee, Ed., Plenum Press, New York, 1972.

28. Z. Rigbi and J. E. Mark, *J. Polym. Sci., Polym. Phys. Ed.* **23**, 1267 (1985).

29. T. W. Smith and D. Wychick, *J. Phys. Chem.* **84**, 1621 (1980).

30. S. Reich and E. P. Goldberg, *J. Polym. Sci., Polym. Phys. Ed.* **21**, 869 (1983).