Surface Depletion of End Groups in Amine-Terminated Poly(dimethylsiloxane)

C. J. Jalbert, J. T. Koberstein,* R. Balaji,[1] and Q. Bhatia[2]

Institute of Materials Science and Department of Chemical Engineering, University of Connecticut, Storrs, Connecticut 06269-3136

L. Salvati, Jr.[3]

Perkin-Elmer Physical Electronics, Edison, New Jersey 08818

I. Yilgor

Goldschmidt Chemical Company, Hopewell, Virginia 23860

Received September 10, 1993; Revised Manuscript Received January 25, 1994•

ABSTRACT: The depletion of alkylamine terminal groups at the vacuum–polymer interface is measured for α,ω-difunctional poly(dimethylsiloxane) oligomers by X-ray photoelectron spectroscopy. The driving force for this depletion is the high relative surface energy of the amine terminal groups compared to that of the low surface energy poly(dimethylsiloxane) backbone. The degree of surface end group depletion, within the maximum sampling depth probed (ca. 7 nm), is found to be on the order of 40% for a 960 molecular weight oligomer and decreases slightly with an increase in the oligomer molecular weight. Angle-dependent measurements are applied to determine end-group concentration depth profiles. End-group depletion is largest at the shallowest sampling depths and decays rapidly toward the bulk. The decay profiles cannot be explained by simple monotonic decay functions, consistent with the expected effects of connectivity between the end groups and the chain backbone, but the data are insufficient to prove whether the profiles are oscillatory in nature, as expected from theoretical considerations.

Introduction

The segregation of mixtures at surfaces and interfaces is a general phenomenon known to occur for essentially all multiconstituent polymer systems. The thermodynamic driving force for segregation is the difference in surface energies of the various constituents as is embodied in the classical Gibbs adsorption isotherm.[4] The component of lowest surface energy is driven to the surface in order to decrease the overall surface and free energies of the system. The degree to which the component can adsorb at the surface is determined by a balance between the resultant surface energy reduction and the increase in chemical potential associated with the demixing required to create the excess surface concentration.

The balance of energies is most easily treated for the case of miscible binary polymer blends and solutions, where the results of experimental studies on surface segregation[5-9] are in qualitative agreement with theoretical treatments[10-12] of these systems.

Surface segregation becomes constrained for copolymers as a result of the fact that the different constituents are linked together by covalent bonds and cannot simply separate from each other. The configurational constraint caused by this linkage is best understood for symmetric disordered block copolymers, where reasonable accord is found between theory[13] and experiment.[14] The situation is far more complex for random copolymers[15] due to the effects of the comonomer sequence distribution and for microphase-separated block copolymers,[16-18] wherein nonequilibrium effects and surface topologies become important.

We have recently studied the influence of chain end constituents on the surface properties of homopolymers. In essentially all cases, the end group of a polymer chain can be treated as a chemically and energetically distinct component. For this reason, most homopolymers may be considered as a type of triblock copolymer where the end groups act as short copolymer end blocks. In our previous work,[19] we demonstrated that the molecular weight dependence of surface tension for α,ω-difunctionally terminated poly(dimethylsiloxanes) was related to the difference in surface energies between the chain backbone and the end group but could not be fully reproduced by simple group additivity arguments. Group contribution calculations suggested that low-energy amine end groups were preferentially adsorbed at the surface, while high-energy amine end groups were depleted from the surface. In this paper and papers to follow,[20,21] we present the results of experimental characterization of the spatial distribution of end groups at the free surfaces of homopolymers.

Materials and Experimental Section

Propylamine- and pentylamine-terminated poly(dimethylsiloxane) homopolymers were synthesized by an equilibrium polymerization technique.[22] This method ensures a functionality of two amine groups per chain and leads to molecular weight distributions that follow the most probable distribution. The materials employed in this study have been characterized previously[19] by gel permeation chromatography, vapor phase osmometry, and end-group titration. The polydispersity indices were all in the range of 1.5–2.0. The number-average molecular weights of the five samples studied were 960, 1130, 1970, 2740, and 7800.

Surface chemical compositions and concentration gradients were determined by X-ray photoelectron spectroscopy (XPS) and angle-dependent X-ray photoelectron spectroscopy (ADXPS) measurements performed at the Perkin-Elmer Physical Electronics Laboratory in Edison, NJ, using a Perkin-Elmer Model PHI 5800 spectrophotometer. The source was monochromatic 300-W Mg Kα X-rays, and the detector was of the hemispherical position-sensitive type with pass energies of 178.95 eV for survey spectra and 71.55 eV for multiplex spectra. Vacuum was maintained below 2×10^{-8} Torr for all experiments. Two sets of experiments were performed. In the first set, preliminary

* To whom correspondence should be addressed.
• Abstract published in *Advance ACS Abstracts*, March 1, 1994.

0024-9297/94/2227-2409$04.50/0

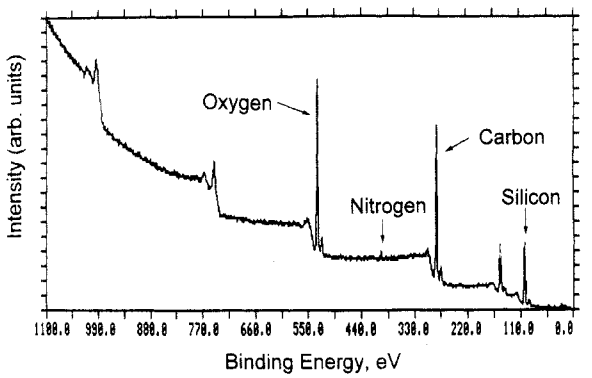

Figure 1. XPS survey spectrum of 960 molecular weight diaminopentyl-terminated PDMS.

Table 1. Surface Composition and Percentage Surface Depletion of Nitrogen End Groups in Aminoalkyl-Terminated PDMS Oligomers (Normal Takeoff Angle XPS Results Neglecting Hydrogen Atoms)

	atomic % nitrogen		
M_n	by XPS	from stoichiometry	% nitrogen depletion
960	2.1 ± 0.3	3.67	43 ± 8
1130	1.8 ± 0.3	3.19	43 ± 9
1970	1.2 ± 0.2	1.85	35 ± 11
2740	0.9 ± 0.2	1.33	32 ± 15
7800	0.4 ± 0.1	0.48	17 ± 21

ADXPS measurements were taken at takeoff angles of 20, 30, 60, and 90° without applying corrections for the photoelectron sensitivity. In the second set, more extensive ADXPS measurements were taken at angles of 10, 15, 20, 30, 60, and 90° and for longer counting times to provide higher precision. Corrections for the machine work function and the photoelectron sensitivity factors were applied to the second data set using the standard PHI software. The two sets of data are generally in good agreement, and selected results from both data sets are reported herein. The carbon 1s photoelectron spectrum at 285 eV was used to calibrate the binding energy.

Samples were prepared by manually coating the liquid polymers onto sapphire substrates followed by gravity draining of the excess under vacuum for several hours followed by vacuum annealing at room temperature for 24–30 h. All experiments were performed at ambient temperature in the XPS, a condition for which all specimens are in the melt state.

Results and Discussion

The XPS survey spectrum of an aminoalkyl-terminated PDMS (Figure 1) is relatively simple. The nitrogen 1s signal originates only from the aminoalkyl end groups, while the oxygen 1s and silicon 2p signals are associated only with the repeat unit of the chain backbone. The carbon 1s signal arises primarily from the pendant methyl groups on the silicone chain backbone, with a small contribution from the methylene units in the aminoalkyl end group. The corrected ratio of the silicon to nitrogen signals therefore serves as a measure of the concentration ratio of the backbone to the end group in the surface region. Alternatively, the atomic composition of the surface region may be calculated.

The experimental atomic percentages of nitrogen in the surface region (for a 90° photoelectron takeoff angle and neglecting hydrogen) are compared to calculated percentages (from the known stoichiometry of the molecule assuming a random distribution of end groups) for PDMS homopolymers of various molecular weights in Table 1. In all cases, the experimental percentages fall below the stoichiometric values, indicating depletion of chain ends, or an excess of chain backbone, at the vacuum–homopolymer melt interface. This result corroborates our previous surface tension measurements which suggested the occurrence of surface depletion of the amine terminal groups. The driving force for this depletion is the high relative surface energy of the amine terminal groups (32.8 dyn/cm) compared to that of the low surface energy poly(dimethylsiloxane) backbone (20.4 dyn/cm), as has been discussed thoroughly in our previous paper.[19]

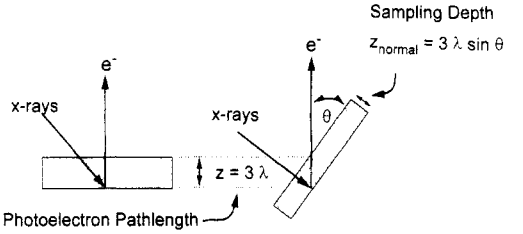

Figure 2. Schematic representation of the ADXPS geometry and the effect of the photoelectron takeoff angle on the sampling depth.

The discrepancy between the experimental and calculated values appears largest for the lowest molecular weight homopolymer and decreases as the molecular weight increases. When the measurement errors are properly accounted for, however, the percentage depletion of amine groups in the probed surface region (see Table 1) exhibits only a slight decrease with molecular weight. This trend is also qualitatively consistent with the previous surface tension experiments, where the discrepancy between measured surface tension and surface tension calculated from group contribution methods increased as the molecular weight decreased. The precision of the results becomes limiting at high molecular weights due to the low concentration of end groups present and the relatively poor photoelectron yield for nitrogen.

The data for normal takeoff angles reflect a weighted average of the surface concentration gradient integrated over the photoelectron escape depth and are only qualitatively representative of the degree of surface segregation. Characterization of the integral composition depth profile can be accomplished with ADXPS measurements,[23] in which the photoelectron takeoff angle is varied systematically. The angle-dependent signal $S_j(\theta)$ for a particular core level photoelectron, j, is given by

$$S_j(\theta) = K_j(\theta)\left[\int_0^\infty n_j(z)\, e^{-z/(\lambda_j \sin\theta)}\, dz\right] \quad (1)$$

where $n_j(z)$ is the atomic composition as a function of the depth, z; $K_j(\theta)$ is a calibrated constant dependent upon the takeoff angle (θ), the machine function, and the sensitivity factor; and λ_j is the photoelectron mean free path. A schematic representation of the ADXPS geometry is illustrated in Figure 2. At normal detector incidence, about 95% of the photoelectrons reaching the detector emanate from depths of 3λ or less into the material. If the detector is tilted by an angle θ from the surface, the component of the sampling depth in the direction normal to the sample surface decreases to a value given by 3λ sin θ. The photoelectron mean free path for typical polymers has been estimated to be 2.3 ± 0.3 nm.[24,25] The ADXPS experiment therefore measures an integral depth profile of the surface composition over a range of approximately 0.7–7 nm, illustrating the high surface sensitivity afforded by the technique.

As a check on the performance of the instrument, we first report results for the oxygen (1s):silicon (2p) and carbon (1s):silicon (2p) ratios as a function of the photoelectron takeoff angle (the effective sampling depth increases with θ). These signals all originate primarily from the polymer backbone and thus should be indepen-

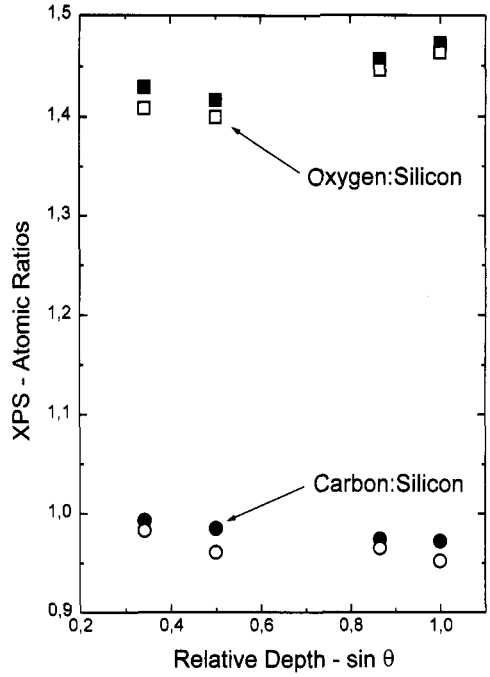

Figure 3. XPS atomic composition ratios as a function of the relative sampling depth for 2740 molecular weight diaminopentyl-terminated PDMS. The filled and unfilled symbols denote results obtained independently and illustrate the reproducibility.

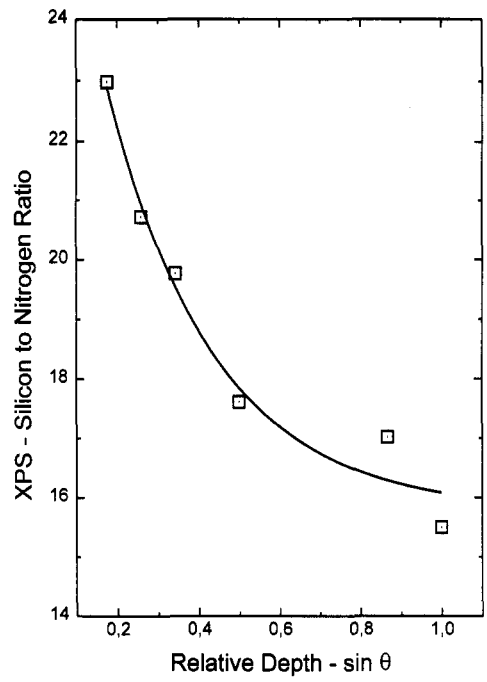

Figure 4. Corrected integral composition depth profile for 960 molecular weight diaminopentyl-terminated PDMS. The line illustrates a monotonic exponential decay profile.

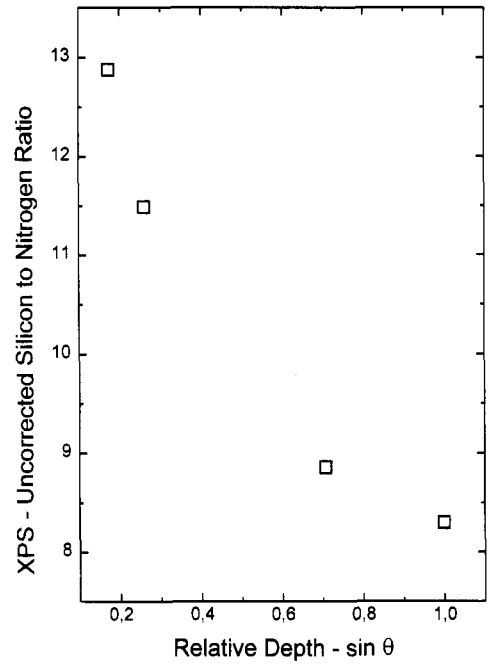

Figure 5. Uncorrected integral composition depth profile for 1130 molecular weight diaminopropyl-terminated PDMS.

dent of the sampling depth. The results for aminopentyl-terminated PDMS of molecular weight 2740 (Figure 3) are indeed independent of takeoff angle, indicating that the instrument is functioning properly and furthermore demonstrating that adsorbed amounts of adventitious carbon- or oxygen-containing species are insignificant. The figure includes the results of two separate analyses carried out several months apart on samples that were prepared independently. The agreement between the two sets of data demonstrates the high absolute reproducibility attained in these particular experiments (on the order of ±3% for these atoms and for this low molecular weight). Similar results (not shown) have been obtained for the other low molecular weight materials studied.

The results for the silicon (2p):nitrogen (1s) ratios (Figures 4–8) differ markedly, demonstrating an excess of the silicone backbone and corresponding depletion of amine end groups (i.e., depletion of nitrogen) at the surface. In all cases the experimental silicon-to-nitrogen (Si/N) ratios exceed the calculated stoichiometric values at low sampling depths and gradually fall toward those values as the sampling depth increases. Note that, since this is an integral depth profile, the profile will not reach the exact stoichiometric value for the bulk if there is surface segregation. The reason for this behavior can easily be understood from inspection of (1).

At the shallowest sampling depths, the ratio is found to exceed the stoichiometric value by factors as large as 4 for the lowest molecular weight examined. The corrected data (Figures 4, 6, and 7) can be compared directly to the calculated stoichiometric ratios of 5.5, 12.5, and 17.5, respectively, for the 960, 1970, and 2740 molecular weight oligomers. The data for shallow sampling depths are subject to the largest errors, however, due to effects such as surface roughness, so that we have not attempted any quantitative analysis of the molecular weight dependence of the surface segregation phenomenon.

The signal from the amine end groups diminishes rapidly as the molecular weight increases, due to the relatively poor photoelectron yield for nitrogen and the low overall end-group concentration. The measurement errors for the nitrogen signal are therefore significantly larger than those discussed earlier for the carbon, silicon, and oxygen signals and will become even larger as the molecular weight increases. The poor reproducibility at high molecular weight (± about 50% on an absolute basis for the 7800 molecular weight material, see, e.g., Figure 8) therefore limits our investigation to molecular weights less than about 10 000.

The surface segregation of end groups is constrained by the covalent bond linking them to the chain backbone. A depletion of the end groups at the surface is then necessarily accompanied by an excess of end groups at slightly larger depths. Computer simulations on polymer melts confined between two plates,[26] for example, show that the end-group concentration profiles are periodic, wherein the magnitude of the concentration fluctuations

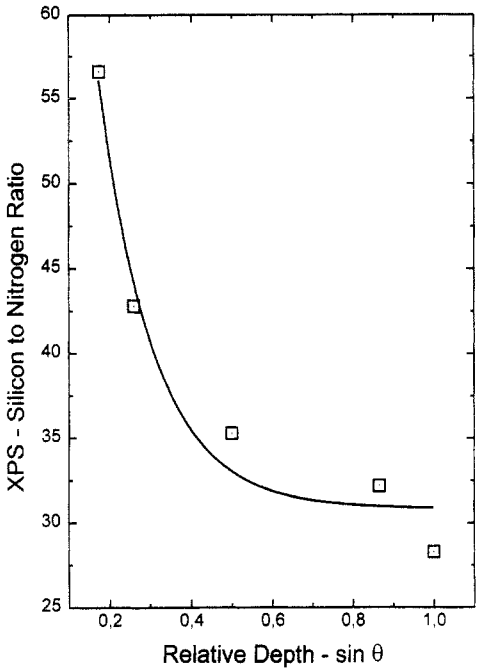

Figure 6. Corrected integral composition depth profile for 1970 molecular weight diaminopropyl-terminated PDMS. The line illustrates a monotonic exponential decay profile.

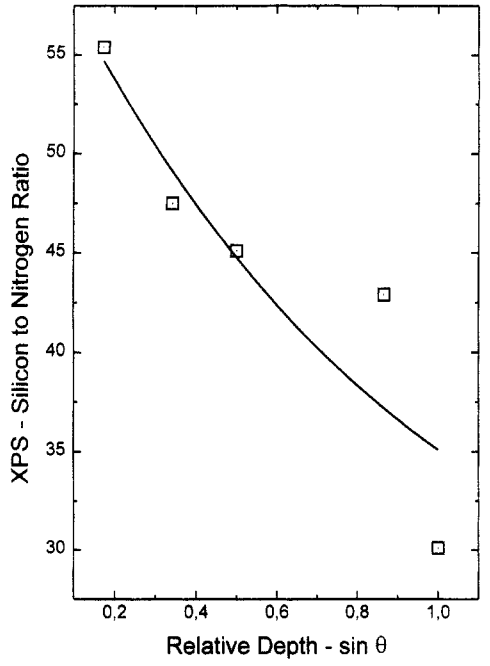

Figure 7. Corrected integral composition depth profile for 2740 molecular weight diaminopentyl-terminated PDMS.

damps out as the depth increases. Similar damped periodic concentration depth profiles have been predicted for block copolymers in the disordered state.[13] In these systems, the block copolymer sequence of lower surface energy adsorbs preferentially at the surface. Experimental results have confirmed the occurrence of damped periodic concentration profiles for such systems.[14]

The molecular architecture of our difunctionally terminated homopolymers is equivalent to that of a triblock copolymer with very short end blocks. It might be expected then to find periodic concentration depth profiles in our materials. In addition, the chain connectivity between the end group and the chain backbone requires that surface depletion must be accompanied by an excess of end groups somewhere deeper in the material.

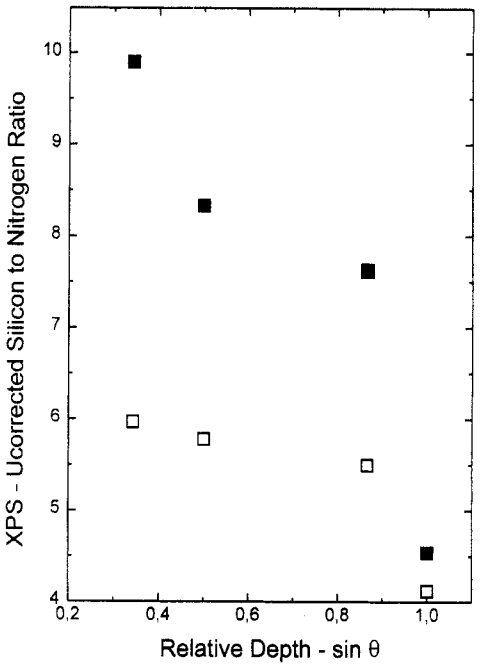

Figure 8. Uncorrected integral composition depth profile for 7800 molecular weight diaminopropyl-terminated PDMS. The open and filled symbols denote two data sets taken independently and illustrate the reproducibility of the experiments.

In order to examine whether our data exhibits the characteristics of a damped periodic concentration profile, we have, in Figures 4, 6, and 7, fit the experimental integral depth profiles (for the purpose of illustration only) with a single-exponential decay function. This type of profile decays monotonically, as does the exponential concentration depth profile predicted by mean-field theory for surface segregation in a number of types of polymer mixtures.[8,12] The experimental data in all cases would be expected to oscillate about the monotonic decay profile if it were of a damped oscillatory nature.

The concentration profiles shown in Figures 4, 6, and 7 all have shapes similar to that in Figure 8: first, at shallow depths, there is a rapid decrease in Si/N; this is followed by more or less a plateau at intermediate depths, and finally there is again a rapid decrease in the ratio at the largest relative depths. The shapes of the concentration depth profiles are much more reproducible than are their absolute magnitudes. This is clearly illustrated in Figure 8. Although the reproducibility in magnitude in poor, the shapes of the two profiles shown in the figure are unmistakably similar. These profiles are clearly inconsistent with simple monotonic decay behavior (indicated by the solid lines in the figures). In the first three of these samples (i.e., those with the greatest precision and largest number of takeoff angles) the Si/N ratio data fall considerably above the monotonic profiles for relative depths in the range of 0.6–0.8, which is consistent with what might be expected for an oscillatory profile. Unfortunately, the precision of the data is insufficient to prove the existence of oscillations. We can therefore only conclude that the data cannot be explained by simple monotonic decay profiles and may be consistent with the existence of oscillatory profiles.

There are three basic factors which limit our ability to resolve the question as to whether oscillatory composition depth profiles are present in these materials: first, the errors in the data are intrinsically high due to the low end-group concentration and low photoelectron yield of nitrogen; second, an integral profile is measured; that is, the experimental profile is a Laplace transform of the true

profile; and third, our samples have an intrinsically broad molecular weight distribution. The latter two factors lead to a broadening of the observed profile that compromises the observation of any oscillations.

Since, at present, there exists no theory to directly predict the functional form for end-group concentration depth profiles, even for monodisperse materials, it is difficult to extract the true concentration depth profile from the experimental integral depth profile. Efforts to apply direct transformation methods to perform the Laplace inversion required for this purpose [see (1)] have not been successful. We therefore cannot present any "true" concentration depth profiles or quantitative estimates of decay lengths at this time.

Theoretical efforts are underway to simulate end-group concentration depth profiles for end-functional homopolymers, and the results of investigations of end-group distributions for narrow molecular weight distribution end-functional polystyrenes will be reported shortly.[20,21] These latter data more clearly demonstrate the damped periodic nature of end-group surface concentration profiles for end-functional homopolymers.

Summary

X-ray photoelectron spectroscopy has been applied to characterize surface segregation effects in diaminoalkyl-terminated poly(dimethylsiloxane) oligomers. In all cases, the amine terminal groups are depleted from the surface due to their relatively high surface energy compared to that of the low-energy poly(dimethylsiloxane) backbone, confirming our previous interpretation of surface tension data.[19] The relative degree of end-group depletion (i.e., compared to the stoichiometric end-group concentration) is largest for the lowest molecular weight and decreases weakly with an increase in the molecular weight. Surface composition depth profiles determined by angle-dependent measurements show that depletion is a maximum at the shallowest sampling depths and decays rapidly into the bulk. The end-group concentration depth profiles cannot be explained by simple monotonic decay profiles, but the data are insufficient to established whether these profiles are oscillatory in nature as is expected from theoretical considerations.

Acknowledgment. Partial support for this research was provided by a grant from the Office of Naval Research and by a grant from the National Science Foundation Polymer Program (DMR-8818232).

References and Notes

(1) Present address: Tredegan Film Products, 3400 Fort Harrison Rd., Terre Haute, IN 47808.
(2) Present address: General Electric Co., Selkirk, NY 12158.
(3) Present address: Abbot Laboratories, 1 Abbot Park Rd., Department 45, North Chicago, IL 60064.
(4) Jaycock, M. J.; Parfitt, G. D. *Chemistry of Interfaces*; Ellis Horwood, Ltd.: Chichester, U.K., 1981.
(5) Bhatia, Q. S.; Pan, D. H.; Koberstein, J. T. *Macromolecules* **1988**, *21*, 2166.
(6) LeGrand, D. G.; Gaines, G. L., Jr. *J. Polym. Sci.* **1971**, *C34*, 45.
(7) Gaines, G. L., Jr. *J. Polym. Sci. Polym. Phys. Ed.* **1969**, *7*, 1379.
(8) Ober, R.; Paz, L.; Taupin, C.; Pincus, P.; Boileau, S. *Macromolecules* **1983**, *16*, 50.
(9) di Meglio, J. M.; Ober, R.; Paz, L.; Taupin, C.; Pincus, P.; Boileau, S. S. *J. Phys. (Paris)* **1983**, *44*, 1035.
(10) Poser, C. I.; Sanchez, I. C. *Macromolecules* **1981**, *14*, 361.
(11) Nakanishi, H.; Pincus, P. *J. Chem. Phys.* **1983**, *79*, 977.
(12) Schmidt, I.; Binder, K. *J. Phys. (Paris)* **1985**, *46*, 1631.
(13) Fredrickson, G. *Macromolecules* **1987**, *20*, 2535.
(14) Russell, T. P.; Anastasiadis, S. H.; Satija, S. K.; Majkrzak, C. F. *Mater. Res. Soc. Symp. Proc.* **1990**, *166*, 145.
(15) Thomas, H. R.; O'Malley, J. J. *ACS Symp. Ser.* **1981**, *162*, 319.
(16) Rastogi, A. K.; St. Pierre, L. E. *J. Colloid Interface Sci.* **1971**, *35*, 16.
(17) Dwight, D. W.; McGrath, J. E.; Riffle, J. S.; Smith, S. D.; York, G. A. *J. Electron Spectrosc. Relat. Phenom.* **1990**, *52*, 457.
(18) O'Malley, J. J.; Thomas, H. R.; Lee, G. M. *Macromolecules* **1981**, *14*, 1316.
(19) Jalbert, J.; Koberstein, J. T.; Yilgor, I.; Gallagher, P.; Krukonis, V. *Macromolecules* **1993**, *26*, 3069.
(20) Jalbert, C.; Koberstein, J. T.; Elman, J.; Long, T.; Gunesin, B. *Macromolecules*, in preparation.
(21) Elman, J.; Long, T.; Koberstein, J. T. *Macromolecules*, in preparation.
(22) Yilgor, I.; Riffle, J.; McGrath, J. E. In *Advances in OrganoSiloxane Copolymers*; Springer Verlag: Heidelberg, Germany, 1986.
(23) Fadley, C. S.; Bergstrom, S. A. L. *Phys. Lett.* **1971**, *35A*, 375.
(24) Clark, D. T.; Thomas, H. R. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2843.
(25) Szajman, J.; Liesegang, J.; Jenkin, J. G.; Leckey, R. G. G. *J. Electron Spectrosc. Relat. Phenom.* **1978**, *14*, 247.
(26) Kumar, S. K.; Vacatello, M.; Yoon, D. Y. *Macromolecules* **1990**, *23*, 2189.