Macromolecules **1996,** *29,* 3991−3995

A Method To Assess the Average Molecular Weight for Surface Soft Segments in Poly[(dimethylsiloxane)−urea]s

Tai Ho*,†

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061-0212

Kenneth J. Wynne*

Physical Sciences S&T Division, Office of Naval Research, Arlington, Virginia 22217-5660, and Materials Chemistry Branch, Naval Research Laboratory, Washington, D.C. 20375-5320

Received August 31, 1995⊗

ABSTRACT: A gauge has been devised to measure the average molecular weight for surface soft segments in poly[(dimethylsiloxane)−urea]s. This quantity, M_s, is defined analogously to the number-average molecular weight, M_n. Information on the weight fraction of each segment at the surface, which can be measured by techniques such as electron spectroscopy for chemical analysis, is required for the calculation of M_s. The use of this quantity is illustrated by calculating the M_s for a series of copolymers containing soft segments of broad molecular weight distribution. The limitation of this method with respect to the average molecular weight of the soft segments and possible remedies are discussed.

Introduction

α,ω-Organofunctionally end-capped polysiloxanes are usually prepared by equilibration reactions.[1] The resulting materials have broad molecular weight distributions and most often are used as intermediates in the preparation of various copolymers. In the past few years, we have prepared a series of poly(siloxane−urea−urethane)s based on aminopropyl-end-capped poly(dimethylsiloxane)s (PDMS), isophorone diisocyanate (IPDI), and 1,4-benzenedimethanol (BDM).[2] These materials have been characterized by thermal, mechanical, and surface analyses. ESCA analysis of these copolymers revealed a surface layer with enhanced PDMS content.[3] This was explained by the minimum interfacial energy argument, as the surface energy of the PDMS soft segments is lower than that of the urea−urethane hard segments. ESCA analysis also showed the presence of the hard segments at the region within 1 nm of the interface of the copolymer and the air. Distribution of the hard segments in the surface region is energetically unfavorable. The occurrence of those surface hard segments most likely is because they are tethered to neighboring soft segments. The soft and hard segments are covalently bonded.

If a surface soft segment is short, the neighboring hard segments will be relatively close to the surface, while for a long soft segment, the neighboring hard segments will be relatively far from the surface. Therefore, assuming no segregation by length for the soft segments at the surface, an increase in the proportion of short chains in the soft segment population will lead to an increase in the fraction of hard segments near the surface. On the other hand, a short soft segment is less likely to be found at the surface than a long soft segment, as the per segment reduction in interfacial energy is larger for the latter; thus, the constructive effects of a higher proportion of short chains on the fraction of surface hard segments are offset by the detrimental effects of soft segment segregation. These conflicting considerations lead to the two questions this work addresses. Is the molecular weight distribution for the PDMS soft segments at the surface the same as the distribution in the bulk? And how can surface molecular weight be quantified? In this paper, results from copolymers consisting of soft segments of broad molecular weight distribution are discussed. Investigation on the same phenomena in copolymers consisting of narrowly distributed soft segments is in progress.

Experimental Section

Materials. Isophorone diisocyanate (IPDI, 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethylcyclohexane, a mixture of isomers), was purchased from Aldrich Chemicals. 3-Aminopropyl-end-capped dimethylsiloxane prepolymers, tegomer A-Si series, were kindly provided by Dr. İ. Yilgör of Goldschmidt Chemical Corp., Hopewell, VA. The nominal molecular weights for tegomers A-Si 2120, 2320, and 2920 are 1000, 2400, and 10 000, respectively.

Polymerization. In a typical run, a measured amount of IPDI was dissolved in tetrahydrofuran (THF) in a 3-necked flask by stirring under nitrogen, and then a stoichiometric amount of PDMS prepolymer was added dropwise to the solution; at this point the total of the reactants amounted to about 15% by weight of the solution. The reaction was carried out at room temperature for 2 h and then at 50 °C for 15 h to ensure completion. The product was poured into a glass petri dish, and solvent was removed by drying in the hood for 5−8 h and then in a vacuum oven at 60 °C for at least 1 day. In this analysis, we chose to use copolymers prepared without chain extenders to minimize complications introduced by aggregation of the hard segments. The size of each hard segment[4] is small relative to the average size of the soft segments, and there was no aggregation of the hard segments detected by differential scanning calorimetry (DSC).[2]

Gel Permeation Chromatography (GPC). The equipment consisted of a Hewlett-Packard Series 1050 pump and two Altex μ-spherogel columns (size 10^3 and 10^4 Å, respectively) connected in series. The solvent was THF. Polymer contents in the effluent of the columns were detected with a Wyatt/Optilab 903 interferometric refractometer, and the average molecular weights were determined using polystyrene standards as references.

NMR Spectroscopy. All NMR spectra were acquired on a Bruker AMX 400 spectrometer operating at 400.13 MHz for

---

† Correspondence should be addressed to: Code 6120, Naval Research Laboratory, Washington, DC 20375-5320.

⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1996.

S0024-9297(95)01302-7 CCC: $12.00

Table 1. Average Molecular Weights for the Prepolymers and Copolymers

	$M_w \times 10^{-3\ a}$	$M_n \times 10^{-3\ a}$	$M_n \times 10^{-3\ b}$	$M_n \times 10^{-3\ b}$
tegomer A-Si 2120	0.91	0.49	0.93	0.81
tegomer A-Si 2320	2.60	0.89	2.55	2.23
tegomer A-Si 2920	17.3	6.20	10.7	9.36
PDMS1K−1P	16.7	12.0	na	na
PDMS2.4K−1P	65.0	30.7	na	na
PDMS10K−1P	109	54.5	na	na

[a] By GPC. [b] By NMR. [c] 0.875 times values by NMR (see text for details). na, not measured.

Table 2. Angle-Resolved ESCA Data on Three Copolymers

	PDMS, wt %				
	$\theta = 10°$	$\theta = 15°$	$\theta = 30°$	$\theta = 90°$	bulk[a]
		As Cast			
PDMS1K−IP	93.6 ± 1.3	90.6 ± 2.3	86.8 ± 2.2	83.5 ± 1.3	0.688
PDMS2.4K−IP	96.8 ± 0.8	94.4 ± 1.0	92.4 ± 0.2	90.6 ± 0.3	0.800
PDMS10K−IP	98.9 ± 0.7	98.5 ± 0.5	97.7 ± 0.1	97.0 ± 0.6	0.965
		Annealed at 120 °C for 15 min			
PDMS1K−IP	93.7 ± 0.2	90.8 ± 0.8	87.3 ± 0.5	84.0 ± 0.6	0.688
PDMS2.4K−IP	97.1 ± 0.5	95.4 ± 1.0	92.5 ± 0.4	91.3 ± 0.4	0.800
PDMS10K−IP	99.9 ± 0.1	99.5 ± 0.2	98.5 ± 0.7	97.1 ± 0.2	0.965

[a] Calculated by eq 1.

^1H acquisition. Solutions of tegomers were prepared in $CDCl_3$ (Cambridge Isotope Laboratories), and the residual protonated solvent was used as the secondary reference to TMS.

Nomenclature. The copolymers are designated in the following manner, illustrated for PDMS1K−IP, where PDMS1K identifies the nominal molecular weight of the soft segment and IP the diisocyanate (IPDI).

Electron Spectroscopy for Chemical Analysis (ESCA). Angle-dependent ESCA experiments were performed on a Perkin-Elmer Physical Electronic Model 5300 ESCA with a hemispherical analyzer and a single channel detector as described previously.[3] Films were cast from 0.5−1.0 wt % solutions in THF. Estimated film thickness was 50 μm. The experimental data were treated with a deconvolution procedure to give the concentration depth profiles for the hard segments in the surface region.[3]

Results and Discussion

Characterization of the Polymers. The average molecular weights of the various PDMS prepolymers and the poly[(dimethylsiloxane)−urea] copolymers have been determined by GPC and ^1H-NMR.[2] The values are summarized in Table 1. Angle-resolved ESCA data on solvent-cast films of the three copolymers have also been reported previously,[3] and the data are listed in Table 2. There is a significant discrepancy between the M_n values measured by GPC and NMR for the PDMS prepolymers. The value obtained by NMR is about 2 times as large as the value obtained by GPC. These results are quite similar to those reported by Fleischer and co-workers.[5] In that work GPC measurements were performed with toluene as the solvent, the PDMS oligomers were derivatized with phenol isocyanate, and the GPC results were compared with M_n values obtained by end group titration.

The principal source of error for data obtained by NMR and end group titration is the uncertainty of the functionality of the molecules. It has been reported that PDMS oligomers prepared by equilibration reactions contain about 10−15 wt % of cyclic species.[1] In the present work GPC measurements were performed with THF as the solvent, and the order of the refractive indices for the solvent, the cyclic species, and the linear species is such that the peaks for the cyclic species and the linear species are opposite in sign. The ratio of the area under the cyclic and linear peaks agrees with the estimate of 10−15 wt % of cyclic species in the mixture. Therefore, the M_n obtained by NMR is 10−15% too high.

The error in data obtained by GPC has several sources. The breakdown of the assumption that hydrodynamic volume in solution determines the retention characteristics in the oligomer range has been examined recently.[6] It was concluded that the type of the substituents on the main chain has strong effects on the retention characteristics, and using polystyrenes as the standards leads to a 20% *over* estimate in molecular weight for polyisobutylene and polyethylene in the oligomer range (<5000). The adsorbing of polar functional groups in the columns leading to changes in the retention patterns has been suggested.[7] However, since for a given set of columns the adsorption is a complicated function of the functional group, the composition of the soft segment, the length of the neighboring soft segment, the solvent, and so on, the net effect of this proposition is not clear. A third source of error is a strong dependence of the refractive index on the molecular weight which distorts the GPC traces. Refractive index (RI) detectors are commonly used in GPC. One of the underlying principles of RI detectors is that the specific increment in refractive index (dn/dc) for the dilute solution is independent of the molecular weight of the solute. For PDMS oligomers this is not true. The refractive indices (n_D^{23}) for tegomers A-Si 2120, 2320, and 2920 are 1.418, 1.409, and 1.405, respectively. Since the refractive index for THF (n_D^{20}) is 0.407, it is clear that dn/dc for a dilute solution of PDMS in THF is molecular weight dependent and decreases with increasing molecular weight. As a result, molecules of lower molecular weights are overrepresented in the GPC trace compared with molecules of higher molecular weights, and the M_n determined by GPC is too low. The true values for M_w and M_n can be determined if the relation between dn/dc and molecular weight is established.

On the basis of the above considerations, it is believed that the true M_n is best represented by 0.875 times the value determined by NMR; thus M_n values for tegomers A-Si 2120, 2320, and 2920 are 810, 2230, and 9360, respectively.

Quantification of Surface Molecular Weight. We use the same concept defining the number-average molecular weight in the bulk to quantify the surface molecular weight, i.e., the total mass in a defined volume is divided by the total number of chain ends to give the average molecular weight.

In beginning an analysis of surface molecular weight, we must define a surface volume. The defined volume in this case is a surface layer of a thickness t, where $t = 3(\sin 10°)\lambda$, and λ is the escape depth of the photoelectrons. Since λ for polymers is about 34 Å,[8] t is about 17 Å. The arbitrary surface volume is selected such that data used in our analysis are independent of the model employed to establish the depth profiles for the soft and hard segments. Thus, the volume fraction for each segment within the surface volume is unambiguously determined. In a previous publication, we described a deconvolution procedure to construct surface concentration depth profiles for the two segments from ESCA data.[3] Using those concentration depth profiles, we can calculate the PDMS weight fractions in the surface region of the copolymers. For surface layers as described above, the values for the PDMS weight fraction,

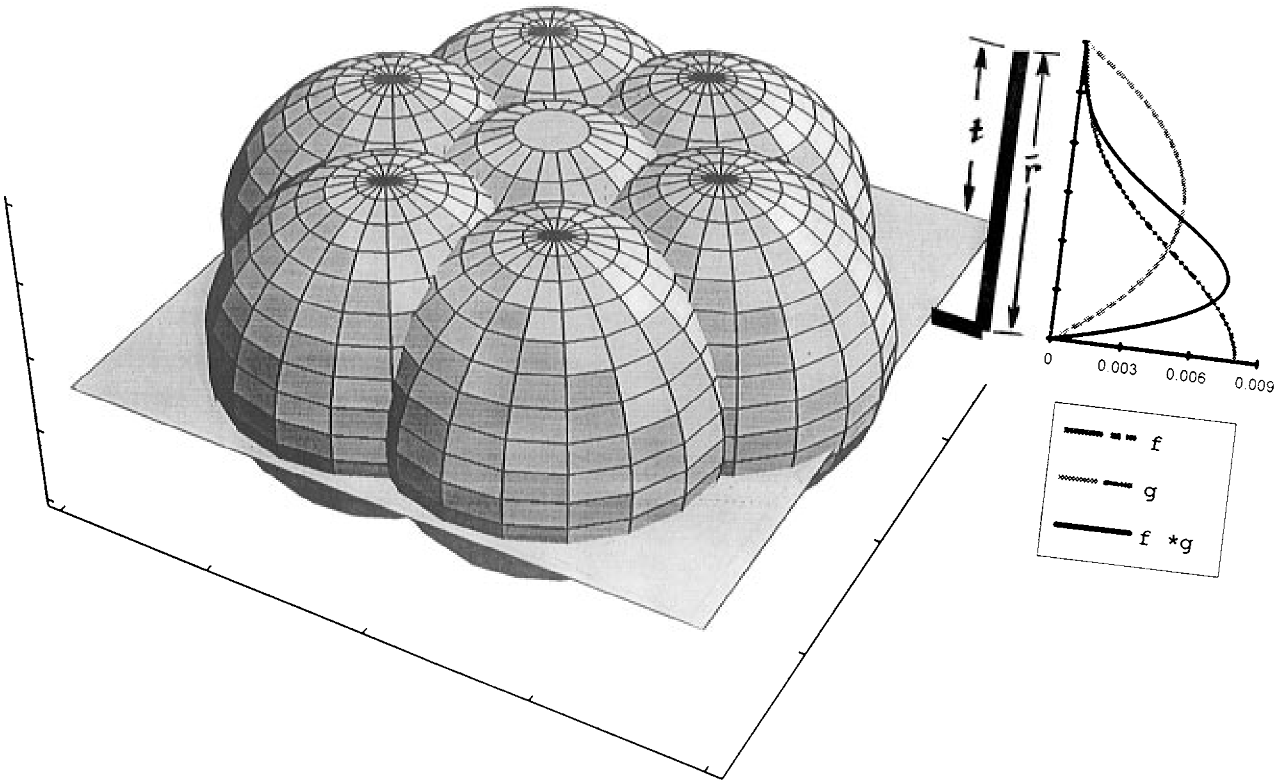

Figure 1. Schematic representation of the assumptions used in the determination of M_s.

Φ_s, are for PDMS1K−IP, 0.90_4 as cast and 0.90_7 after annealing at 120 °C for 15 min; for PDMS2.4K−IP, 0.95_0 as cast and 0.95_6 after annealing; and for PDMS10K−IP, 0.99_0 as cast and 0.99_7 after annealing.

In the bulk, the relation among the number-average molecular weight for the soft segments, M_n, the molecular weight of the hard segment (≈222), and the PDMS weight fraction, Φ_b, is described by the following equation:

$$\Phi_b = M_n/(M_n + 222) \qquad (1)$$

Analogously, the average molecular weight for the *surface* soft segments, M_s, and the *surface* PDMS weight fraction, Φ_s, are correlated (eq 2):

$$\Phi_s = \alpha M_s/[\alpha M_s + \beta(222)] \qquad (2)$$

Here, α and β are correction factors used to account for the fact that as molecular weight of the soft segment increases, increasingly larger portion of the soft segment is excluded from the surface volume. We will elaborate on how to determine the values for these two correction factors later. Once values for these factors are determined, M_s can be calculated from eq 2.

Correction Factors. The PDMS soft segments in the bulk are amorphous, and the linear dimension of the volume occupied by each segment is on the order of its root-mean-square end-to-end distance, $\bar{r}$. Flory showed that for PDMS $\bar{r}$ (in Å) and the molecular weight, MW, are correlated through the equation $\bar{r} = 0.73(\mathrm{MW})^{1/2}$.[9] We assume the configuration of a soft segment at the surface does not differ very much from that in the bulk, and *the space occupied by a surface soft segment can be described as a sphere of diameter* $\bar{r}$. These molecular spheres are not mutually exclusive. It can be shown from density data that extensive mutual overlap is the rule.

We further assume that the surface layer consists of the upper portion of a single layer of laterally overlapping spheres, as depicted in Figure 1. The model is valid when $\bar{r}$ calculated from M_s is significantly larger than the thickness of the surface layer. It breaks down when $\bar{r}$ approaches $1.5t$ because vertical overlap of spheres becomes increasingly necessary for volume filling in the defined surface volume. The correction factor for the soft segment, α, in eq 2, is the volume fraction of each sphere that falls inside the surface layer. This value can be calculated using eq 3:

$$\alpha = \int_0^t g(x)\,\mathrm{d}x \Big/ \int_0^{\bar{r}} g(x)\,\mathrm{d}x = (1/3)\pi h^2[3(\bar{r}/2) - h]/(4/3)\pi(\bar{r}/2)^3 \qquad (3)$$

where $g(x)$, as shown in Figure 1, is the fraction of the sphere that locates at a distance x from the surface and h is the height of the segment of the sphere that falls inside the surface layer; in this case, $h = t$.

To determine the value for the correction factor for the hard segment, β, we use the same assumption on the shape of the soft segments as described above. In addition, we incorporate the fact that the hard segments are less likely to be in the surface layer than the soft segments as reflected in the large excess surface PDMS wt % shown in Table 2. We recognize that there is only one hard segment contained in the sphere occupied by each surface soft segment and assign a probability to each position in the sphere, such that this probability represents the chance of finding the hard segment at that locale. The probability is weighed against proximity to the interface, i.e., the farther from the surface, the higher the value. We use a Gaussian type distribution, eq 4, for this purpose:

$$f(x) = 2\kappa\{n[x/(\bar{r}/3) - 3] - n(-3)\} \qquad (4)$$

where x is the distance from the polymer air interface,

$$\kappa = 1/[n(3) - n(-3)]$$

and

$$n(u) = 1/(2\pi)^{1/2} \int_{-\infty}^{u} \exp(-t^2/2)\, \mathrm{d}t$$

The distribution of f is illustrated in Figure 1. Given $g(x)$ and $f(x)$, the value for β is found by eq 5:

$$\beta = \int_0^t f(x)\, g(x)\, \mathrm{d}x \Big/ \int_0^{\bar{r}} f(x)\, g(x)\, \mathrm{d}x \qquad (5)$$

Average Molecular Weights for Surface Soft Segments. Using surface PDMS weight fraction, Φ_s, determined from ESCA data and solving eqs 2, 3, and 5, we determined the number-average molecular weight for the *surface* soft segments, M_s, for the three copolymers. For PDMS1K−IP, M_s is 1250 as cast and 1270 after annealing, while M_n determined as described above is 810; corresponding values for PDMS2.4K−IP are 1790, 1920, and 2230 and for PDMS10K−IP 4200, 8600, and 9360.

In calculating M_s, we assume a preferential distribution of the hard segment away from the interface and a spherical shape for the volume occupied by the soft segment. We also calculated M_s under different assumptions, and the results are tabulated in Table 3. The assumption on the shape of the soft segment has only minor effects. As illustrated, if the shape were assumed to be an elongated cylinder, i.e., more rodlike, M_s would decrease. And, it can be inferred that, if the shape were a depressed cylinder, i.e., more disklike, M_s would increase. Without actual knowledge of the shape of the surface segments, a sphere represents a conservative assumption. If the assumption of preferential distribution were lifted, the resulting values for M_s would be at least 2 times larger than the corresponding M_n values listed in Table 1. The distribution of the hard segments is affected by the size of the neighboring soft segments. Although a Gaussian type distribution is suitable for hard segments connected to a short soft segment, as discussed below, it does not properly describe the distribution of hard segments connected to a long soft segment.

Some Limitations of This Analysis. As pointed out in an earlier section, the laterally overlapping sphere model for the surface volume breaks down as $\bar{r}$ approaches 1.5t. This places a lower limit on the surface molecular weight below which the current analysis is less accurate. Since 1.5t is about 25 Å, the lower limit for the M_s is about 900. The calculated values for M_s are above this lower limit for all three copolymers investigated.

The Gaussian type distribution as described in eq 4 becomes less realistic as the molecular weight of the soft segment becomes larger. In the concentration depth profiles for the copolymers reported previously,[3] the hard segment content reaches a maximum at about 34 Å (1λ) from the surface and levels off to the bulk value rapidly, indicating that preferential distribution occurs mostly in a regime <34 Å from the surface. The current treatment assumes the regime of preferential distribution covers the whole molecule, which leads to an underestimate of M_s if the root-mean-square end-to-end distance of the soft segment is larger than 34 Å. The size 34 Å corresponds to a molecule of molecular weight 1900. Accurate assessment of large M_s can be achieved in cases where the molecular weights of the soft segments are narrowly distributed. In these cases, there is no complication caused by segregation of the soft segments by size, and the distribution of the hard segments can be uniquely determined.

Another source of uncertainty in our ESCA measurement is the contribution to the N 1s peak from the free amine group on one end of each chain. The surface energy of the amine end group is higher than that of the neighboring soft segment, which favors depletion of amine end group at the surface. On the other hand, entropic consideration favors enrichment of chain ends at the surface. Jalbert and co-workers[10] studied the distribution of amine end groups in films of oligomers and showed that the end groups are depleted at the surface. Thus, both the free amine end groups and the hard segments show a distribution favoring away from the surface. Furthermore, the effects of the free amine end groups on the analyses of PDMS1K−IP and PDMS2.4K−IP are minimal, as the two copolymers are of reasonably high degree of polymerization. For the present investigation, no corrections for this factor were incorporated.

Table 3. Average Molecular Weights for the Surface Soft Segments[a]

	PDMS1K−IP		PDMS2.4K−IP		PDMS10K−IP	
	as cast	annealed	as cast	annealed	as cast	annealed
Gaussian spherical	1250	1270	1790	1920	4200	8600
Gaussian cylindrical	1080	1100	1520	1620	3600	7100
flat spherical	2100	2180	4250	4800	>20 000	>20 000

[a] Gaussian, the probability of finding the hard segment at a given location is described by eq 4. Spherical, the volume occupied by the soft segment is a sphere, the diameter of which is the root-mean-square end-to-end distance for that segment. Cylindrical, the volume occupied by the soft segment is a cylinder, the height of which is the root-mean-square end-to-end distance for that segment. Flat, the probability of finding the hard segment at any location is the same.

Comparison of Average Molecular Weights of the Soft Segments at the Interface and in the Bulk. Whether there is a significant difference between the molecular weight distributions for the soft segments at the interface and in the bulk cannot be answered with certainty at this moment. In the case of PDMS1K−IP, to which the current method is undoubtedly applicable, M_s is about 1.6 times M_n (1270 vs 810), indicating that a large portion of the shorter soft segments is excluded from the interface. The same conclusion cannot be reached in the cases of PDMS2.4K−IP, where M_s is about 0.9 times M_n (1920 vs 2230), and PDMS10K−IP, where M_s is also about 0.9 times M_n (8600 vs 9360), although, as discussed above, in these cases the M_s is somewhat underestimated.

The definition of M_s suggests that the M_s to M_n ratio should be unity for copolymers consisting of narrowly distributed soft segments. The usefulness of the current method can be improved significantly by incorporating insights gained from experiments using this type of material. In particular, the function that links the preferential distribution of the hard segment with the length of the soft segment can be uniquely determined. Segregation of soft segments by length is not expected, as chains on the short end of the distribution are not very different from chains on the other end in terms of length and energetic considerations. Functionally end-capped PDMS with narrow molecular weight distribution can be prepared.[11] An investigation into the effects of the molecular weight distribution for the soft segment in the bulk on the hard segments contents at the interface is in progress.

Conclusions

The average molecular weight of the soft segments at the surface of poly(siloxane−urea) copolymers can be quantified by M_s, which is defined analogously to M_n. The relative magnitudes of M_s and M_n suggest that segregation of soft segments by length occurs in the case where the M_n for the soft segments is 830, and the shorter soft segments are excluded from the surface. It is not certain whether the same occurs in cases where the M_n values for the soft segments are 2230 and 9360. The current method can be improved by incorporating information regarding the preferential distribution of the hard segments as a function of the length of the soft segment.

Acknowledgment. This research was supported in part by the Office of Naval Research and the Strategic Environmental Research and Development Program (SERDP). ESCA measurements were carried out at the State University of New York at Buffalo by Professor Joseph A. Gardella, Jr., and Dr. Xin Chen. NMR measurements were performed by Dr. Robin A. Nissan of Naval Air Weapons Center, China Lake, CA.

References and Notes

(1) Yilgör, İ.; McGrath, J. E. *Adv. Polym. Sci.* **1988**, *86*, 1.
(2) Ho, T.; Wynne, K. J.; Nissan, R. *Macromolecules* **1993**, *26*, 7029.
(3) Chen, X.; Gardella, J. A., Jr.; Ho, T.; Wynne, K. J. *Macromolecules* **1995**, *28*, 1635.
(4) The isophorone diisocyanate moiety may appear to be too small and too soft to be called the hard segment; nevertheless, since this paper is a continuation of previous publications, namely, refs 2 and 3, where hard segments of various lengths and compositions were investigated, we preserve this denotation for consistency.
(5) Fleischer, C. A.; Koberstein, J. T.; Krukonis, V.; Wetmore, P. A. *Macromolecules* **1993**, *26*, 4172.
(6) Boyd, R. H.; Chance, R. R.; Ver Strate, G. *Macromolecules* **1996**, *29*, 1182.
(7) Elman, J. F.; Lee, D. H.-T.; Koberstein, J. T.; Thompson, P. M. *Langmuir* **1995**, *11* (7), 2761.
(8) Seah, M. P.; Dench, W. A. *Surface Interface Anal.* **1979**, *1*, 2.
(9) Flory, P. J.; Mandelkern, L.; Kinsinger, J. B.; Shultz, W. B. *J. Am. Chem. Soc.* **1952**, *74*, 3364.
(10) Jalbert, C. J.; Kolberstein, J. T.; Balaji, R.; Bhatia, Q.; Salvati, L., Jr.; Yilgor, I. *Macromolecules* **1994**, *27*, 2409.
(11) Lee, C. L.; Johannson, O. K. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 729.

MA9513022