Poly(dimethylsiloxane)/Nylon-6 Block Copolymers: Molecular Mobility at the Interface

Uchu Mukai,[†,‡] **Karen K. Gleason,**[§] **Ali S. Argon,**[‖] **and Robert E. Cohen***[,§]

Program in Polymer Science and Technology and Departments of Materials Science and Engineering, of Chemical Engineering, and of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received February 8, 1995; Revised Manuscript Received April 28, 1995[⊗]

ABSTRACT: The molecular mobility at the interface of poly(dimethylsiloxane) [PDMS]/nylon-6 block copolymers was investigated using dynamic mechanical analysis (DMA) and solid-state deuterium NMR. Using DMA, T_g depression of the nylon matrix was observed with increasing PDMS content, and the mechanical loss peaks were broadened to lower temperature. When the room-temperature line spectra of solid-state deuterium NMR were compared for nylon-6 homopolymer and PDMS/nylon-6 diblock copolymer, a clear difference was observed; a peak associated with highly mobile nylon was observed in the block copolymer spectrum. This high mobility peak was observed even at −50 °C. Using a selectively deuterated triblock copolymer, the origin of this peak was shown to arise from a shell of softened nylon in the vicinity of PDMS domains. This softening effect was lost at −80 °C where PDMS domains can crystallize. This softened shell is not only from the compositionally mixed interfacial zone but also from a fraction of the pure nylon region surrounding the interfacial zone.

Introduction

A series of previous publications has addressed the synthesis,[1−3] molecular organization,[4,5] morphology,[6−9] and gas transport properties[10] of a variety of diblock copolymers in which at least one of the blocks was capable of crystallizing. Of these various semicrystalline copolymer systems, the poly(dimethylsiloxane) [PDMS]/nylon-6 diblocks were selected[2,6,11] for a detailed investigation of mechanical behavior, owing to the widespread commercial and academic interest[12] in rubber-toughened nylon materials. In the course of the program of mechanical experiments it became apparent that a full explanation of the observed deformation and toughness of the PDMS/nylon-6 diblock copolymers, and their blends with nylon-6 homopolymer, would require an understanding of the nature of the nylon in the shell of material bordering the PDMS domains. To explain our observed mechanical properties, details of which will be reported elsewhere,[13] it was postulated that this nylon shell must have unusually high levels of mobility; during deformation, these "soft" zones percolate through the specimen, thereby imparting favorable levels of toughness to the material.

There is prior work in the literature to support the general nature of our hypothesis. For example, in crystallizable polymers, including nylon-6 homopolymer, the existence of two types of amorphous material is proposed by some researchers. Raman spectra,[14,15] ^{1}H broad-line NMR,[16,17] ^{13}C solid-state NMR,[18−20] and dielectric spectroscopy[21] have been employed in these studies. The two regions were categorized as conventional amorphous and rigid amorphous; the latter locates at the interface between amorphous and crystalline material. At the interface, there are necessarily changes in density and chain mobility. These changes from the disordered amorphous state to the ordered crystalline state occur gradually. As a result, there exists an interface region as a transition zone between amorphous and crystalline material wherein the mobility of the molecules is restricted compared with that in the fully amorphous region.[22]

In amorphous diblock copolymers, the chain mobility of a given block sequence at the interface is highly influenced by the mobility of the coblock. Recently, Samulski and co-workers[23,24] reported on chain mobility of poly(styrene-*b*-isoprene) with deuterium NMR and dynamic infrared linear dichroism (DIRLD). Their experiments showed clearly that the portion of the polystyrene block that is close to the junction with polyisoprene is affected by the highly mobile polyisoprene chain and remains flexible even below its nominal T_g. On the other hand, the portion of the polyisoprene molecule near the interface showed less mobility than that far from the interface because of the influence of polystyrene chains.

In our own work on PDMS/nylon-6 diblock copolymers, observations[25] of shifts in the locations of T_g, unaccountably low modulus values, and the aforementioned higher than expected levels of toughness pointed indirectly to a soft nylon shell surrounding the PDMS domains. The purpose of this paper is to verify the existence of the soft nylon shell via dynamic mechanical thermal analysis and through the use of specially synthesized, deuterium-labeled polymers in solid-state ^{2}H NMR experiments.

Experimental Section

Synthesis. 3,3,7,7-Tetradeuterated ϵ-caprolactam (CPL) was synthesized. First, deuterated cyclohexanone (2,2,6,6-d_4, 98%; Cambridge Isotope Inc.) was transformed into deuterated cyclohexanone oxime. As a next step, deuterated cyclohexanone oxime was transformed into deuterated ϵ-caprolactam (3,3,7,7-d_4) via a Beckmann rearrangement reaction. Some references are available regarding these two-step reactions.[26−30] Crude ϵ-caprolactam was recrystallized from hot cyclohexane for further purification. At each step, the synthesized chemical was analyzed with solution-state ^{1}H NMR.

Three types of deuterated polymers were anionically synthesized: deuterated nylon-6 homopolymer, a diblock copolymer, PDMS/deuterated nylon-6, and a special triblock copolymer, PDMS/deuterated nylon-6/nylon-6, in which a deuterium

---

[†] Present address: Bridgestone Corp., Kodairashi, Tokyo, Japan.

[‡] Program in Polymer Science and Technology and Department of Materials Science and Engineering.

[§] Department of Chemical Engineering.

[‖] Department of Mechanical Engineering.

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1995.

0024-9297/95/2228-4899$09.00/0

Table 1. Molecular Characteristics of the Samples

sample	initial PDMS M_n ($\times 10^3$)	PDMS (wt %)	d-nylon (wt %)	unlabeled nylon (wt %)	PDMS Mn ($\times 10^3$)	nylon-6 M_n ($\times 10^3$)
dNY6			100			
PDMS/dNY6	19.5	41.3	58.7			
PDMS/dNY6/NY6	19.5	68.0	15.1	16.9		
PDMS/NY6	19.5	28.6		71.4	15.2[a]	39.1[a]
NY6				100		11.2

[a] The block molecular weights were estimated using the method described by Veith.[2,6]

labeled nylon sequence is the midblock. For nylon-6 homopolymer polymerization, *N*-acetylcaprolactam (Aldrich) was used as an initiator. In the reactor (20-mL flask), 1.5 g of deuterated CPL was dried at 130 °C for 30 min with a vacuum and charged with argon gas. Then the initiator was added (ca. 0.02 g) and dried under the same conditions. Finally 1.0 × 10^{-4} mol of the catalyst[2,11] $LiAlH_2(OBu)_2$ was added, and the reaction mixture was held for 1.5 h at 130 °C. This polymer was named "dNY6", for deuterated nylon-6 homopolymer.

For diblock copolymer synthesis, extensive details are provided elsewhere.[2,6,11,25] The initial molecular weight of PDMS synthesized anionically in THF was 19 500 with low polydispersity (~1.01). By using this PDMS as a macromonomer,[2] the labeled diblock copolymer, PDMS/dNY6, was synthesized. The triblock copolymer, PDMS/dNY6/NY6, was synthesized by injecting a large excess of hot dried CPL at the appropriate stage during the diblock copolymerization process mentioned above. A PDMS/NY6 unlabeled diblock copolymer was also synthesized for use in the dynamic mechanical experiments. The composition ratios of block copolymers were confirmed with solution-state ^1H NMR. Results of molecular characterizations and stoichiometric analysis appear in Table 1.

Dynamic mechanical properties were observed with a DMS-200 (Seiko dynamic mechanical rheology station). tan δ, E', and E'' were measured in the range of −130 to +150 °C at a heating rate of 2 °C/min. The strain amplitude was in the range between 0.1 and 0.2%. The frequency of the mechanical oscillation was 1 Hz.

NMR spectra were recorded on a home-built spectrometer at a ^2H Larmor frequency of 41.3282 MHz using a Doty Scientific probe. The temperature was controlled with a Lakeshore temperature controller (DRC-91CA). Subambient temperatures were obtained by cooling the sample tube with cold dry nitrogen gas. As a standard sample, deuterated water (Cambridge Isotope Inc.; 98%) was used for room temperature measurement and deuterated toluene (Cambridge Isotope Inc.; 98%) was used for low-temperature measurements.

Deuterium NMR spectra were obtained using a modified quadrupole echo technique, [$\pi/4-\tau_1-\pi/4-\tau_1-$acquisition], described by Spiess et al.[31] A τ_1 delay of 70 μs was employed in order to minimize line-shape distortions which can result from using other than $\pi/2$ pulses. The quadrature-detected echoes were digitized at 1 μs/point for a total of 2048 points for subsequent Fourier transformation. The line shapes were corrected to account for the finite spectral bandwidth of the radio-frequency excitation pulses[32] and also contain 1 kHz of broadening. Spin−lattice relaxation experiments were performed using a range of delay times from 0.1 to 60 s.

The spin−lattice relaxation of the nylon matrix displayed multiexponential behavior. In the block copolymers at room temperature and at −50 °C, three relaxations, rigid (crystalline) nylon, amorphous nylon, and the soft nylon zones, were assumed. In the case of nylon-6 homopolymer, two relaxation zones, crystalline nylon and amorphous nylon, were assumed.

Results and Discussion

As pointed out previously,[2,6] a PDMS backbiting reaction can occur during the anionic polymerization of the nylon block (Table 1). Although methods to minimize this undesirable reaction were developed,[2] the molecular weight of the PDMS block is a little smaller than the initial value. The molecular weight of the nylon block of PDMS/NY6 is much larger than that of the nylon-6 homopolymer that was used in blends. Therefore, as reported by many researchers regarding the blend between a diblock copolymer and a homopolymer,[33-37] clear microphase separation occurred in blending and no macrophase separation was observed.[25]

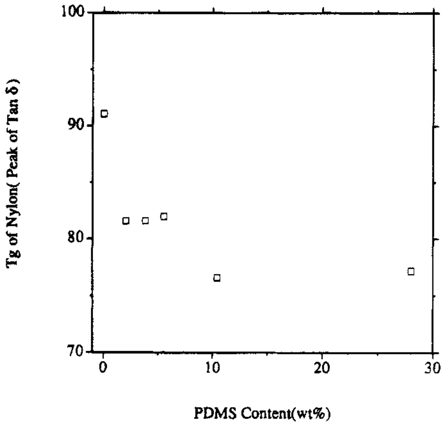


Figure 1. Nylon T_g vs PDMS content. Various values of PDMS wt % were obtained by blending[25] diblock PDMS/NY6 with various amounts of NY6 homopolymer.

Figure 1, showing the temperature of the tan δ peak of α-relaxation of nylon matrix versus PDMS weight fraction, demonstrates the decrease in nylon T_g with increasing PDMS content. Compared with the value of a nylon-6 homopolymer, the T_g of the diblock copolymer, PDMS/NY6, decreased by 15 °C. The value of the T_g of the nylon-6 homopolymer is close to the values reported for almost perfectly dried nylon-6 by some researchers.[38-43] We observed no water absorption peak,[44] typically seen in nylons near −70 °C, in any of the materials used in this study. We therefore cannot attribute the observed T_g reduction to water absorption. The decrease of T_g is expected to arise from the significant fraction of nylon which resides around the small (ca. 200 Å diameter) PDMS domains of these materials. The mobility of this nylon fraction is influenced by the proximity of the highly mobile PDMS chains.

The baseline of E'' was not constant in the range of the α-relaxation. To calculate the breadth of E'' transitions, the values of E'' were first modified to compensate for the changing baseline. The change of the breadth of these corrected E'' peaks is demonstrated in Figure 2. In results not shown here, it was also determined that the breadth of the E'' peak of nylon-6 homopolymer decreased as crystallinity decreased.[25] On the other hand, when the diblock copolymer was added into nylon-6 homopolymer, the breadth of E'' increases, even though crystallinity decreased somewhat. These opposing phenomena demonstrate that the relaxation mechanism introduced by the addition of PDMS/nylon-6 diblock copolymer is different from that due to crystallinity reduction. Specifically, we are proposing that nylon chains connected to PDMS chains have higher

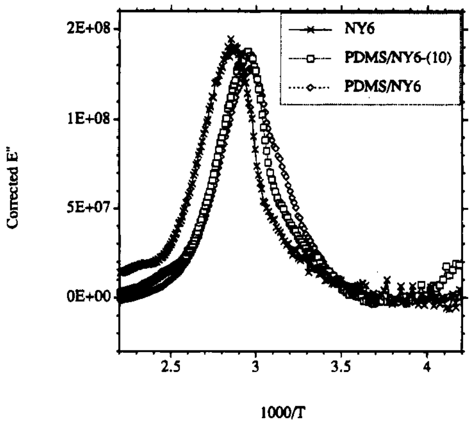


Figure 2. Baseline-modified E'' transitions as a function of $1/T$.

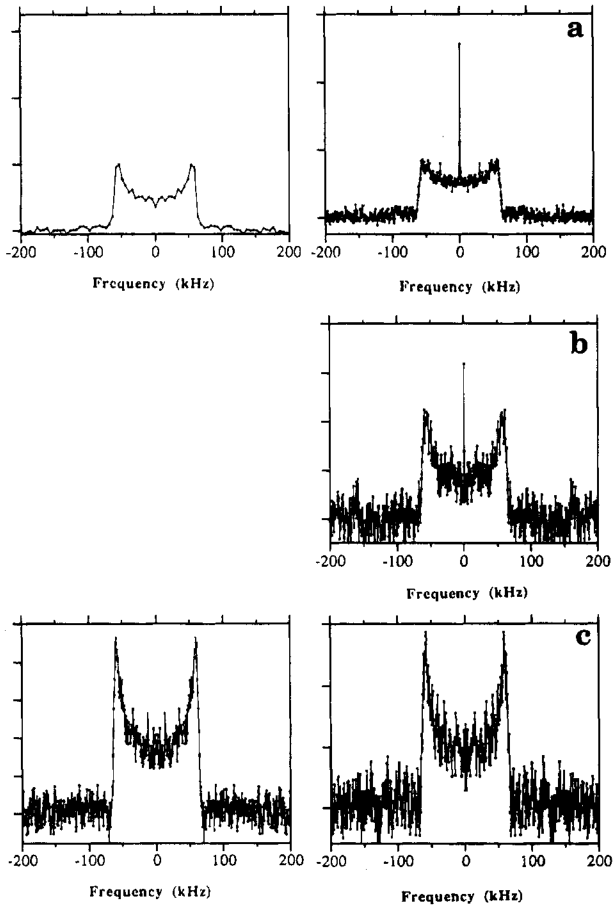


Figure 3. Comparison of the fully relaxed line spectra between dNY6 (left) and PDMS/dNY6 (right) at (a) room temperature, (b) −50 °C, and (c) −80 °C.

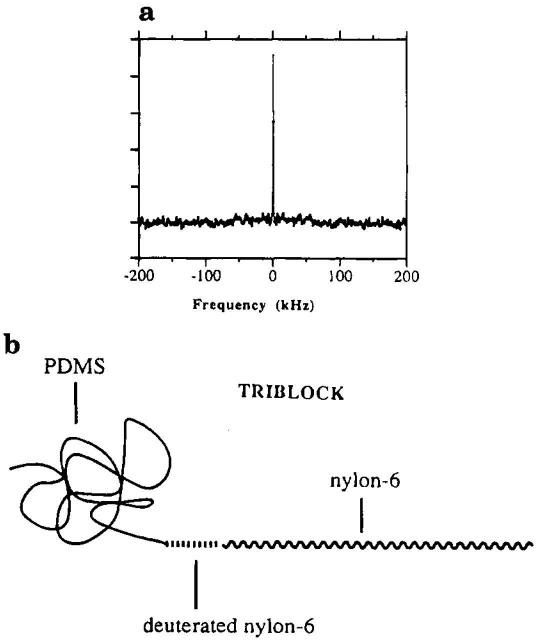


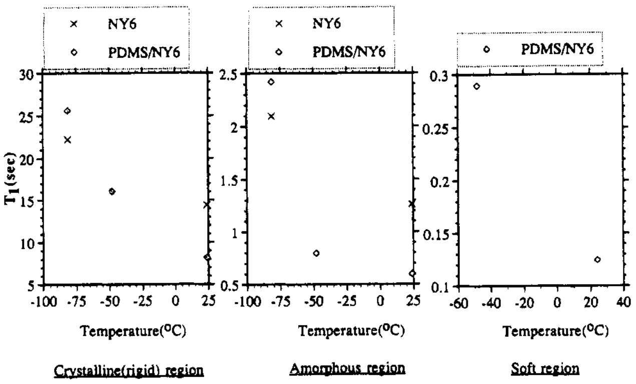
Figure 4. (a) A fully relaxed line spectrum of PDMS/dNY6/NY6 triblock copolymer. (b) Schematic representation of the molecular architecture of this polymer.

mobility than conventional amorphous nylon chains. The suggestion of higher mobility is reinforced by the systematic broadening of the E'' peak on the low-temperature side of the transition. Plots[25] of tan δ vs temperature for these and other diblock/nylon-6 compositions also support this proposition.

The fully relaxed deuterium NMR line spectra of dNY6 (deuterated nylon-6 homopolymer) and PDMS/dNY6 (PDMS-deuterated nylon-6 diblock) at various temperatures are shown in Figure 3. In the absence of chain motion, the deuterium line shape is a result of the angle between the C−D vector and magnetic field, which results in a Pake pattern[45] with singularities located at ca. ±60 kHz. On the other hand, when the chain mobility is very high compared with the correlation time,[46] the shape of the spectrum becomes one sharp peak at the center. At room temperature, dNY6 essentially shows a rigid Pake pattern, a result which is reasonable because the glass transition temperature of nylon-6 homopolymer is much above room temperature. On the other hand, in PDMS/NY6 at room temperature a sharp peak from a mobile region is superimposed on the rigid Pake pattern. Even at −50 °C, about 100 °C below the glass transition temperature of nylon-6 homopolymer, the mobile central peak could still be observed in PDMS/dNY6. This means that very flexible nylon molecules exist in PDMS/dNY6 even at temperatures much below the T_g of the nylon-6 homopolymer. At −80 °C, no sharp central peak was observed in either sample and the shapes of the line spectra are almost identical for dNY6 and PDMS/dNY6. The mobility of nylon molecules is almost identical in the diblock copolymer and in the homopolymer at this very low temperature. The maximal rate of PDMS crystallization is expected[47] to occur around −80 °C; at this temperature the mobility-enhancing influence of PDMS molecules on nylon molecules is lost because the chain mobility of PDMS domains drops as a result of the crystal formation. The molecules of nylon are frozen in both polymers.

A fully relaxed spectrum of PDMS/dNY6/NY6 triblock copolymer at room temperature is shown in Figure 4. For the triblock, the sharp central peak is larger relative to the rigid Pake pattern as compared to the spectrum of PDMS/NY6. This result clarifies the location of the flexible nylon molecules. These flexible molecules are from the portions of the nylon-6 matrix in the vicinity of the PDMS domains.

The changes of the spin−lattice relaxation time constants with temperature in various regions of the nylon matrix are shown in Figure 5 and Table 2. At room temperature, both rigid (crystalline) nylon and amorphous nylon have shorter relaxation times in the diblock copolymer than in nylon-6 homopolymer. At −80 °C, however, this difference disappears for the same reason mentioned above.



Crystalline(rigid) region

Amorphous region

Soft region

Figure 5. Spin–lattice relaxation time in three regions.

Table 2. Spin–Lattice Relaxation Times of Nylon-6 Homopolymer (dNY6) and Diblock Copolymer (PDMS/dNY6) at Various Temperatures

		T_1 (s)		
temp (°C)	sample	crystal	amorphous	soft
20	dNY6	14.4	1.3	
	PDMS/dNY6	8.2	0.6	0.1
−50	PDMS/dNY6	16.1	0.8	0.1
−80	dNY6	22.3	2.1	
	PDMS/dNY6	25.7	2.4	

The set of the experiments above clearly verifies a nylon region with enhanced molecular mobility. The origin of this region is envisioned in at least two ways: One is that mobile nylon lies within a compositionally mixed interfacial region, which exists in essentially all block copolymer systems; the other possibility is that the extra mobility is imparted to the nylon even beyond the mixed interfacial zone by the highly flexible PDMS molecules. To clarify this point, it is necessary to estimate the interfacial thickness for the PDMS/nylon system.

There are many theoretical approaches to quantify the nature of the interfaces in block copolymers and polymer blends.[48] In general, the interfacial tension, γ, scales with a fractional power of the segmental interaction parameter, χ, and the interfacial thickness, d varies inversely with γ. Here we choose to follow predictions of Helfand's lattice theory[49] which indicates that d is proportional to $\chi^{-1/2}$. Adopting the commonly employed relationship[50] between χ and the square of the difference between solubility parameters, δ, of the dissimilar segments in the diblock copolymer results in the interfacial thickness, d, being inversely proportional to $|\delta_A - \delta_B|$. Thus, d for the nylon/PDMS system can be estimated if the solubility parameters are known and if interfacial thickness and solubility parameters are known for another system. The polystyrene/polybutadiene diblock copolymer interface has been carefully characterized previously in our laboratory by small-angle neutron scattering;[51] a value of $d_{SB} = 15$ Å was obtained.

Using appropriate values[25] of solubility parameters [$\delta_{N6} = 10$, $\delta_{PDMS} = 7.5$, $\delta_S = 9.1$, $\delta_B = 8.4$, all in (cal/cm^3)$^{1/2}$] results in an estimate of the interfacial thickness of about 4 Å for the nylon/PDMS system. At 4 Å thickness, the compositionally mixed interfacial zone comprises only about 3% of the volume of the diblock copolymer studied here. Crude simulations[25] of line shapes suggest that a percentage of mobile nylon in the range of 25% is necessary to explain the diblock spectrum observed at room temperature (Figure 3). Therefore, we conclude that the region of anomalously mobile nylon arises not only from chains lying in the interfacial zone but also from a roughly 20 Å shell of nylon which is "plasticized" by the transmitted mobility of the spatially neighboring and topologically connected PDMS sequences of the diblock copolymer.

Conclusion

The existence of a soft mobile layer of nylon-6 in a PDMS/nylon-6 diblock copolymer system was demonstrated with DMA and solid-state deuterium NMR. This soft layer exists close to the junction with the PDMS sequences of the copolymer. Very high flexibility of nylon molecules in this region was observed even at temperatures 100 °C below the glass transition temperature of nylon-6 homopolymer. This mobile layer disappeared at −80 °C, the temperature of maximum crystallization rate of PDMS. The dynamics of nylon-6 molecules in the soft layer are highly influenced by PDMS molecules. From the results of the calculation of the interfacial thickness of this polymer composite, it is expected that the origin of this mobile nylon shell is from not only the interfacial zone but also a shell of pure nylon which surrounds the PDMS domains.

Acknowledgment. Bridgestone Corp. is acknowledged for the finanical support of U.M. during his period of study at MIT. A.S.A. and R.E.C. acknowledge support in part by the National Science Foundation, DMR-90-22933, via the MIT Center for Materials Science and Engineering; K.K.G. and R.E.C. acknowledge NSF Grant CTS-9411656.

References and Notes

(1) Drzewinski, M. A.; Cohen, R. E. *J. Polym. Sci., Polym. Chem. Ed.* **1968**, *24*, 2457.
(2) Veith, C. A.; Cohen, R. E. *Makromol. Chem., Macromol. Symp.* **1991**, *43*, 241.
(3) Cazzaniga, L.; Cohen, R. E. *Macromolecules* **1991**, *24*, 5817.
(4) Douzinas, K. C.; Cohen, R. E. *Macromolecules* **1991**, *24*, 4497; **1992**, *25*, 5030.
(5) Cohen, R. E.; Bellare, A.; Drzewinski, M. A. *Macromolecules* **1994**, *27*, 2321.
(6) Veith, C. A.; Cohen, R. E.; Argon, A. S. *Polymer* **1991**, *32*, 1545.
(7) Del Giudice, L.; Cohen, R. E.; Attalla, G.; Bertinotti, F. *J. Appl. Polym. Sci.* **1985**, *30*, 4305.
(8) Cheng, P. L.; Douzinas, K.; Kofinas, P.; Berney, C. V.; Cohen, R. E. *Macromolecules* **1990**, *24*, 324.
(9) Kofinas, P.; Cohen, R. E. *Macromolecules* **1994**, *27*, 3002; **1995**, *28*, 336.
(10) Kofinas, P.; Cohen, R. E. *Polymer* **1994**, *35*, 1229.
(11) Mukai, U. M.S. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1992.
(12) Keskkula, H.; Paul, D. R. In *Nylon Plastics Handbook*; M. I., Kohan, Ed.; Carl Hanser Verlag: München, Germany, 1994.
(13) Mukai, U.; Cohen, R. E.; Argon, A. S. *Polymer*, submitted for publication.
(14) Strobl, G. R.; Hagedorm, W. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1181.
(15) Failla, M.; Alamo, R. G.; Mandelkern, L. *Polym. Testing* **1992**, *11*, 151.
(16) Bergmann, K.; Nawotki, K. *Kolloid Z. Z. Polym.* **1967**, *219*, 132.
(17) Kitamaru, R.; Horii, F. *Adv. Polym. Sci.* **1978**, *26*, 139.
(18) Kitamaru, R.; Horii, F.; Murayama, K. *Macromolecules* **1985**, *19*, 636.
(19) Saito, S.; Moteki, Y.; Nakagawa, M.; Horii, F.; Kitamaru, R. *Macromolecules* **1990**, *23*, 3256.
(20) Hirai, A.; Horii, F.; Kitamaru, R.; Fatou, J. G.; Bello, A. *Macromolecules* **1990**, *23*, 2913.
(21) Cebe, P.; Huo, P. P. *Thermochim. Acta* **1994**, *238*, 229.
(22) Stein, R. S.; Satkowski, M. M.; Noda, I. In *Polymer Solution, Blends, and Interfaces*; Noda, I., Rubingh, D. N., Eds.; Elsevier Science Publishers: Amsterdam, The Netherlands, 1992; pp 109–131.

(23) Hutchison, J. L.; Samulski, E. T.; Smith, S. D. *Polym. Propr. (Am. Chem. Soc., Div. Polym. Chem.* **1993**, *34* (2), 618.
(24) Smith, D. D.; Noda, I.; Marcott, C.; Dowrey, A. E.; Russel, T. P.; Mayes, A.; Kornfield, J. A.; Chung, C. C.; Samulski, E. T.; Hutchison, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.* **1994**, *35* (1), 596.
(25) Mukai, U. Sc.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1995.
(26) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley & Sons: New York, 1985, Chapter 8.
(27) Hatfield, G. R.; Glans, J. H.; Hammond, W. B. *Macromolecules* **1990**, *23*, 1654.
(28) Powell, D. G.; Sikes, A. M.; Mathias, L. J. *Macromolecules* **1988**, *21*, 1533.
(29) Pearson, D. E.; Stone, R. M. *J. Am. Chem. Soc.* **1961**, *83*, 1715.
(30) Powell, D. G.; Mathias, L. J. *J. Am. Chem. Soc.* **1990**, *112*, 669.
(31) Hentschel, R.; Spiess, H. W. *J. Magn. Reson.* **1979**, *35*, 157.
(32) Fukushima, E.; Roeder, S. B. *Experimental Pulsed NMR*; Addison-Wesley: Reading, MA, 1981.
(33) Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Makromol. Chem., Macromol. Symp.* **1992**, *62*, 75.
(34) Kinning, D. J.; Winey, K. I. Thomas, E. L. *Macromolecules* **1988**, *21*, 3502.
(35) Winey, K. I.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1992**, *25*, 2645.
(36) Löwenhaupt, B.; Hellmann, G. P. *Polymer* **1991**, *32*, 1065.
(37) Cheng, P. L.; Berney, C. V.; Cohen, R. E. *Makromol. Chem.* **1989**, *190*, 589.
(38) Starkweather, H. W., Jr. *J. Appl. Polym. Sci.* **1959**, *5*, 129.
(39) Woodward, A. E.; Crissman, J. M.; Sauer, J. A. *J. Polym. Sci.* **1960**, *30*, 23.
(40) Kolarik, J.; Janacek, J. *J. Polym. Sci., Polym. Chem.* **1967**, *16*, 441.
(41) Papir, Y. S.; Kapur, S.; Robers, C. E.; Baer, E. *J. Polym. Sci., Polym. Phys. Ed.* **1972**, *10*, 1305.
(42) Kettle, G. J. *Polymer* **1977**, *18*, 742.
(43) Le Huy, H. M.; Rault, J. *Polymer* **1994**, *35*, 136.
(44) McCrum, N. G.; Read, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover Publications, Inc.: New York, 1992.
(45) Abragam, A. B. *The Principles of Nuclear Magnetism*; Oxford University Press: Oxford, 1961.
(46) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(47) Andrianov, K. A.; Slonimskii, G. L.; Zhdanov, A. A.; Levin, V. Yu.; Godovski, Yu. K.; Moskalenko, V. A. *J. Polym. Sci., Polym. Chem. Ed.* **1972**, *10*, 1.
(48) Paul, D. R., Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1978; Vol. 1, Chapter 6.
(49) Helfand, E. *J. Chem. Phys.* **1975**, *63*, 2192.
(50) Paul, D. R., Newman, S., Eds.; *Polymer Blends*; Academic Press: New York, 1978; Vol. 1, Chapter 2, p 30.
(51) Bates, F. S.; Berney, C. V.; Cohen, R. E. *Macromolecules* **1983**, *16*, 1101.

MA9501510