

whereas our value, k_2 , was $5 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$. Chien and Boss²⁵ studied kinetics of autooxidation in polypropylene at 383 K and reported corresponding rate constants of peroxy radicals: for hydrogen abstraction, $1.9 \text{ L mol}^{-1} \text{ s}^{-1}$, and recombination, $3 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$.

Conclusions

In conclusion, we have experimentally tested the applicability of the basic autocatalytic photooxidation mechanism to photooxidation of PnBA using ESR techniques. We find that while peroxy and tertiary alkyl radicals are the major radical intermediates as required by the currently accepted mechanism, there seem to be significant differences in the reaction kinetics of the major intermediates and the mechanism of their formation. The macromolecular peroxy radicals are formed through two separate pathways: oxidation of short-lived intermediate radicals and oxidation of tertiary alkyl radicals. There are at least two different types of tertiary alkyl radicals, one being significantly smaller (and more mobile) than the other. Under the illumination conditions provided in this study, cross-linking by recombination of peroxy radicals is the major degradation pathway, cross-linking of tertiary alkyl radicals becoming important only in oxygen-starved samples.

Acknowledgment. We thank Dr. Robert F. Fedors for many helpful discussions. This paper represents one phase of research performed at the Jet Propulsion Laboratory sponsored by the National Aeronautics and Space Administration under Contract NAS7-918. This research was performed in support of the Flat-Plate Solar Array Project, Reliability Encapsulation Task, sponsored by the Department of Energy.

Registry No. Poly(*n*-butyl acrylate) (homopolymer), 9003-49-0.

References and Notes

- (1) Liang, R. H.; Tsay, F. D.; Gupta, A. *Macromolecules* **1982**, *15*, 974.
- (2) Scott, G. *ACS Symp. Ser.* **1976**, *25*, 340.
- (3) Chakraborty, K. B.; Scott, G. *Polymer* **1977**, *18*, 98.
- (4) Ghaffar, A.; Scott, A.; Scott, G. *Eur. Polym. J.* **1977**, *13*, 89.
- (5) Sitek, F.; Guillet, J. E. *J. Polym. Sci., Symp. Ser.* **1976**, *57*, 343.
- (6) Somersall, A. C.; Guillet, J. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*, 60.
- (7) Bolland, J. L. *Q. Rev., Chem. Soc.* **1949**, *3*, 1.
- (8) Carlsson, D. J.; Garton, A.; Wiles, D. M. In *Developments in Polymer Stabilization 1*; Scott, G., Ed.; Applied Science: Barking, UK; **1979**; p 219.
- (9) Carlsson, D. J.; Wiles, D. M. *J. Macromol. Sci., Rev. Macromol. Chem.* **1976**, *C14*, 65.
- (10) Szocs, F.; Rostasova, O. J. *J. Appl. Polym. Sci.* **1974**, *18*, 2529.
- (11) Abraham, R. J.; Whiffen, D. H. *Trans. Faraday Soc.* **1958**, *54*, 1291.
- (12) Lykos, P. G. *J. Chem. Phys.* **1960**, *32*, 625.
- (13) Ogawa, S. *J. Phys. Soc. Jpn.* **1960**, *16*, 1488.
- (14) Symons, M. C. R. *J. Chem. Soc.* **1963**, 1186.
- (15) Fischer, H. *J. Polym. Sci., Part B* **1964**, *2*, 529.
- (16) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper and Row: New York, **1967**; pp 83-85.
- (17) Moriuchi, S.; Nakamura, M.; Shimada, S.; Kashiwabara, H.; Sohma, J. *Polymer* **1970**, *11*, 630.
- (18) Suryanarayana, D.; Kevan, L.; Schlick, S. *J. Am. Chem. Soc.* **1982**, *104*, 668.
- (19) Gerrard, W. *Solubility of Gases and Liquids, A Graphic Approach*; Plenum: New York, **1976**; p 73.
- (20) One can convert the mole ratio solubility of oxygen, 0.002, into appropriate units of Henry coefficient for PnBA and obtain $\gamma = 2.22 \times 10^{-5} \text{ mol L}^{-1} \text{ torr}^{-1}$. This value is in good agreement with the value cited by Denisov²² for the case of petroleum.
- (21) Dickinson, H. R.; Rogers, C. E.; Simha, R. "Polymers in Solar Energy Utilization"; ACS Symposium Series 220; American Chemical Society: Washington, DC, **1983**; pp 275-292.
- (22) Denisov, E. T. *Dev. Polym. Stab.* **1982**, *5*, 23.
- (23) Denisov, E. T. *Vysokomol. Soedin., Ser. A* **1977**, *19*, 2513.
- (24) Somersall, A. C.; Guillet, J. E. Annual Report, 1981, DOE/JPL-955591-82/1, "Modeling of Photodegradation in Solar Cell Modules of Substrate and Superstrate Design made with Ethylene-Vinyl Acetate as Pottant Material".
- (25) Chien, J. C. W.; Boss, C. R. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 3091.

On Blends of Poly(vinylidene fluoride) and Poly(vinyl fluoride)

Gaetano Guerra,[†] Frank E. Karasz,* and William J. MacKnight

Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. Received March 17, 1986

ABSTRACT: Experimental evidence indicating immiscibility of the homopolymers poly(vinylidene fluoride) and poly(vinyl fluoride), both in the crystalline and amorphous phases, is presented. The X-ray analysis of the blended samples reveals patterns that are relatively insensitive to blend composition and that are similar to those found in previous studies. However, corresponding differential scanning calorimetry scans show well-defined and separate melting peaks of the component homopolymers, indicating immiscibility in the crystalline phase. In addition, the dynamic mechanical analysis indicates that the main relaxations of the two pure homopolymers are still present in the blend spectrum, implying also an immiscibility of the amorphous phase.

Introduction

The phenomenon of isomorphism between vinylidene fluoride (VF₂) and vinyl fluoride (VF) monomeric units was first discussed in 1965.¹ The very high degree of crystallinity observed for any composition ratio in the

corresponding random copolymers seems to be a strong argument in favor of cocrystallization.¹

Isomorphism between VF₂ and VF monomeric units has also been suggested for blends of the respective homopolymers of poly(vinylidene fluoride) (PVF₂) and poly(vinyl fluoride) (PVF).¹⁻³ In fact, X-ray analyses of the blends revealed the presence of high crystallinity for any composition ratio and consisted only of an intense crystalline peak¹⁻³ in the range of Bragg spacing d between 4

[†] Permanent address: Dipartimento di Chimica, Università di Napoli, Naples 80134, Italy.

and 5 Å. This type of pattern is characteristic of the crystalline modifications of PVF₂ in which the chains are in all-trans (β) or mostly trans (γ) conformation^{4,5} as well as of the crystal structure of PVF (also trans conformation of the chains).⁶ It was held that further indications of cocrystallization were the presence of single melting temperatures, determined by polarization microscopy,^{1,3} and the absence of the more usual α -form of PVF₂ in the blends.¹

Subsequent publications presented evidence that cocrystallization of the PVF₂ and PVF homopolymers may not occur, but in these studies the blends were subjected to different treatments. In one case⁷ the PVF₂ component was crystallized in the α -form, i.e., the crystalline structure presenting TGTG conformation;⁴ in another case the complex melting behavior of PVF₂ suggested the presence of more than one crystalline form, but no X-ray analysis was reported.⁸ Recent reviews⁹⁻¹¹ present the above data and affirm the occurrence of cocrystallization of the homopolymers.

At present there is little information concerning the miscibility of the two homopolymers in the amorphous phase. In two studies^{3,12} the glass transition temperatures (T_g) of the blends were determined from the temperature dependence of the elastic modulus. The presence of a glass transition falling between the T_g 's of the two component homopolymers suggested that the blend was miscible. However, the T_g 's of the pure components used to arrive at this conclusion are not in agreement with more recent, detailed analyses. In particular the T_g of pure PVF₂ has been reported as -120 °C, while a value in the range -30 to -40 °C is now generally accepted.¹³⁻¹⁶

In another paper⁸ the T_g 's of samples quenched in the amorphous state were determined by differential scanning calorimetry. Miscibility for a 50/50 wt % blend was again suggested by the presence of a single glass transition.

In this study the questions of the presence or absence of cocrystallization of PVF₂ and PVF homopolymers and of the miscibility of the amorphous phase of the two homopolymers are investigated with X-ray diffraction and differential scanning calorimetry (DSC) and dynamic mechanical analyses.

Experimental Section

The PVF homopolymer ($M_w = 1.26 \times 10^5$, determined by GPC, $M_n = 3.9 \times 10^4$, determined by viscometry) was supplied by Scientific Polymer Products, Inc. The PVF₂ homopolymer ($M_w = 6.0 \times 10^4$) was supplied by Polysciences. No further information regarding the origin of these samples was available.

Homogeneous mixtures of PVF₂ and PVF homopolymers were obtained by dissolving 1.0 g of a 50/50 wt % polymer mixture in 15 mL of *N,N*'-dimethylformamide (DMF) at about 120–130 °C. The hot solutions were stirred for about 2 h and then slowly poured with stirring into 150 mL of a methanol–water mixture (50/50 (v/v)). The precipitated powder was filtered, washed with methanol, and dried to constant weight at 50 °C. In control experiments the individual homopolymers were subjected to the same treatment.

Samples for dynamic mechanical analyses were prepared by compression molding of the precipitated powders at 210 °C, followed by quenching in a dry ice–methanol bath. The samples obtained were about 1 mm thick and 8 mm wide.

Wide-angle X-ray diffraction patterns were obtained with a D-500 Siemens diffractometer with nickel-filtered Cu K α radiation.

Normalized DSC scans were obtained with a Perkin-Elmer DSC-4 differential scanning calorimeter with sample sizes of approximately 10 mg. All the thermal treatments described were performed in this apparatus.

The dynamic mechanical analyses were carried out in a Polymer Laboratories DMTA apparatus at a frequency of 10 Hz and a heating rate of 2 °C/min.

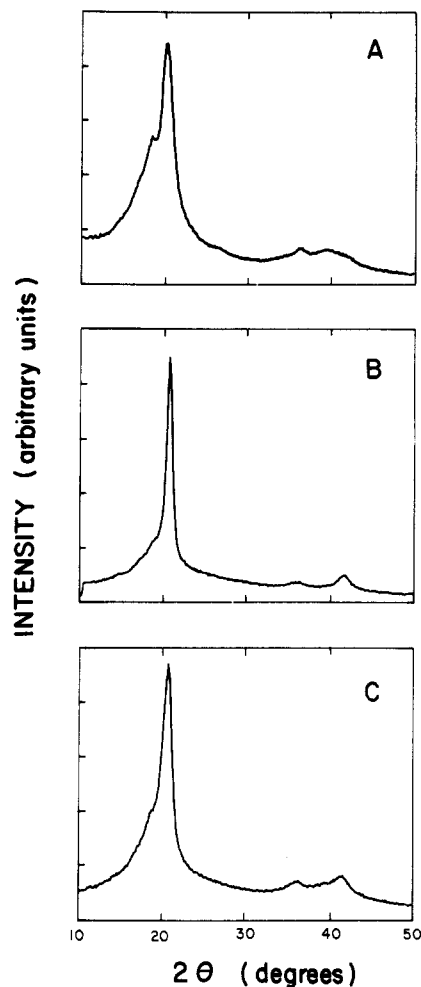


Figure 1. X-ray diffraction patterns of samples precipitated from DMF (see Experimental Section): (A) PVF₂, (B) PVF, (C) 50/50 wt % PVF₂/PVF blend.

Results and Discussion

The X-ray diffraction patterns of pure PVF₂ and PVF and of the 50/50 wt % PVF₂/PVF blend treated as described above are shown in Figure 1. It is apparent that these patterns are very similar; as previously described^{1,3} the only intense crystalline peak is one with a Bragg spacing, d , ranging from 4.28 (Figure 1B) to 4.39 Å (Figure 1A), which is present in all samples.

Pure PVF₂ crystallizes mainly in the γ -form and not in the β -form; in fact the most intense reflection is located at $d = 4.39$ Å for the γ -form and at $d = 4.27$ Å for the β -form.⁴ Two weaker reflections are also present at $d = 4.80$ Å and $d = 2.48$ Å ($2\theta = 18.5^\circ$ and 36.2°), respectively, both typical of the γ -form.^{5,17} The presence of the γ -form of PVF₂ was also pointed out in films cast from DMF solutions.³ In agreement with previous studies⁶ the X-ray diffraction pattern of PVF studied here presents two broad reflections at $d = 2.5$ Å and $d = 2.17$ Å, ($2\theta = 36^\circ$ and 41.5°), respectively, in addition to the main peak.

The X-ray diffraction pattern of the blend (Figure 1C) presents to a good approximation a summation of the patterns of the pure components (Figure 1, parts A and B); in fact, in addition to the main peak centered at $2\theta = 20.6^\circ$ and a broad reflection at $2\theta = 36^\circ$, the reflections at $2\theta = 18.5^\circ$ and $2\theta = 41.5^\circ$, which characterize the patterns of Figure 1, parts A and B, respectively, are also present.

The DSC scans at 20 °C/min for the samples whose X-ray patterns are shown in Figure 1 are presented in Figure 2. The pure homopolymers display melting en-

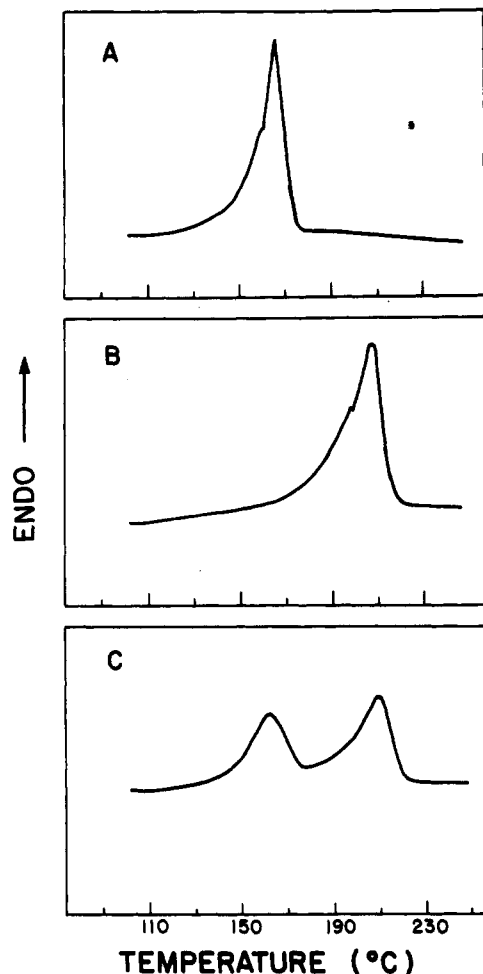


Figure 2. DSC scans at 20 °C/min of samples precipitated from DMF: (A) PVF₂, (B) PVF, (C) 50/50 wt % PVF₂/PVF blend.

dothems at substantially different temperatures: the peaks are at 164.5 and 208 °C for PVF₂ and PVF, respectively. The 50/50 wt % blend shows two well-defined melting endotherms at nearly the same temperatures as those of the pure components. Two distinct endotherms are also present also for much lower heating rates (down to 0.5 °C/min).

The results presented above are independent of the concentration of the polymers in the DMF solution and of the composition of the blends. The data indicate unequivocally that cocrystallization of PVF₂ and PVF does not occur under these conditions, at least for the samples used in this study.

The X-ray diffraction pattern of the 50/50 wt % blend after annealing at 185 °C for 10 min (i.e., above the melting temperature of PVF₂) and cooling to room temperature is presented in Figure 3. It is apparent that the pattern changes substantially because of the presence of the α -form of PVF₂. In particular, the shoulder at $2\theta = 20^\circ$ ($d = 4.4$ Å) and the broad reflection at $2\theta = 26.5^\circ$ ($d = 3.35$ Å) are indicative of the presence of the α -form.⁴ Hence, the γ -structure does not appear to be stabilized by the presence of the PVF homopolymer as previously suggested^{1,2} but seems to be due merely to the solvent history of the samples employed in these and earlier investigations. Specifically, in this study the γ -structure is produced by crystallization from DMF.^{3,18}

The results of our experiments allow a simple interpretation of the report that the α -form of PVF₂ occurs in blends with PVF prepared by precipitation from DMF solutions;⁷ in that study the samples were treated at 200

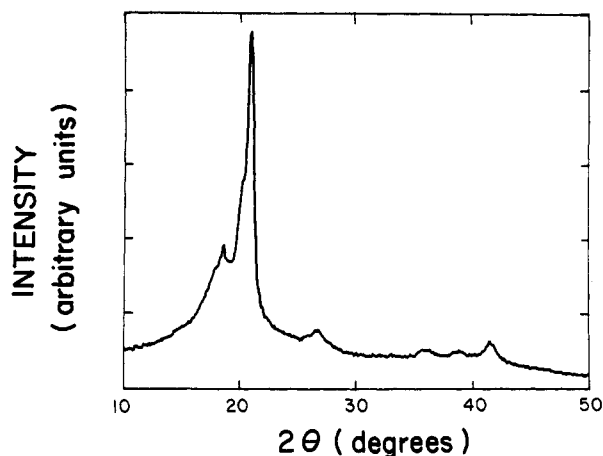


Figure 3. X-ray diffraction pattern of the 50/50 wt % PVF₂/PVF blend after annealing at 185 °C for 10 min.

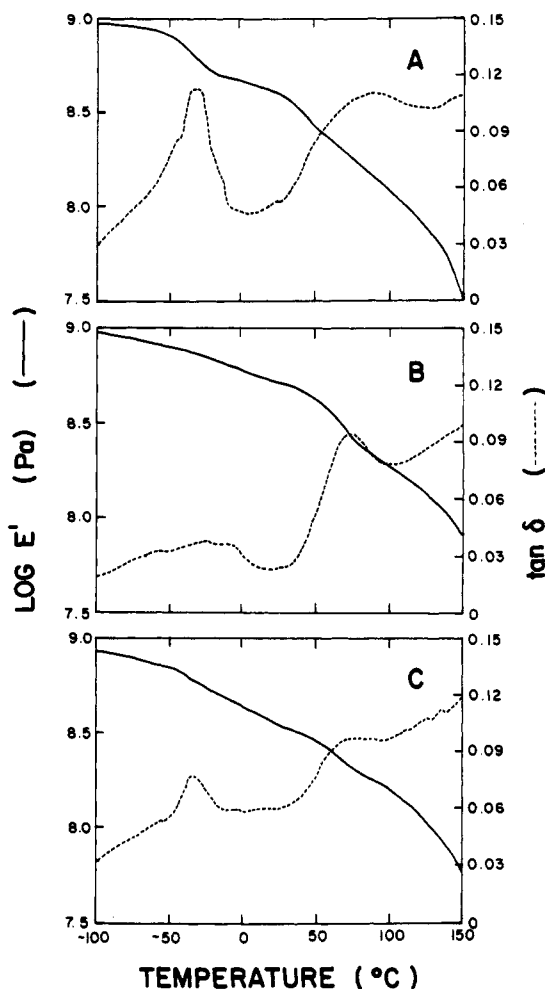


Figure 4. Dynamic modulus (E') and loss tangent ($\tan \delta$) at 10 Hz: (A) PVF₂, (B) PVF, (C) 50/50 wt % PVF₂/PVF blend.

°C for 30 min before the analysis so that the PVF₂ component of the mixture has been melted and crystallized in the α -form upon cooling.

To study the miscibility of the component polymers in the amorphous phase, we attempted to obtain completely amorphous samples as in ref 8, but all quenching procedures that were attempted produced highly crystalline samples. The high degree of crystallinity in the samples interfered with the unequivocal determination of the glass transition temperatures by DSC. However, the dynamic mechanical analysis of the pure homopolymers and of the 50/50 wt % blend, molded as described in the Experi-

mental Section, are shown in Figure 4 and are more revealing. PVF₂ (Figure 4A) displays a main relaxation (β) at -35 °C as well as the broad α relaxation at ≈ 90 °C.^{13,16,19} PVF (Figure 4B) displays a main relaxation at 70 °C in addition to another very broad relaxation at -15 °C in good agreement with data presented in the literature.^{13,19} The pattern of the 50/50 wt % blend (Figure 4C) displays a well-defined relaxation at -35 °C and a very broad relaxation between 60 and 95 °C. The patterns shown in Figure 4 taken as a whole indicate that the PVF₂ and PVF homopolymers used here are also immiscible in the amorphous phase.

Acknowledgment. We thank Prof. G. Allegra of the University of Milan and Prof. P. Corradini of the University of Naples for useful discussions. This work was supported by AFOSR 84-0101. G.G. thanks the Consiglio Nazionale delle Ricerche for support.

Registry No. PVF₂ (homopolymer), 24937-79-9; PVF (homopolymer), 24981-14-4.

References and Notes

- (1) Natta, G.; Allegra, G.; Bassi, I. W.; Sianesi, D.; Caporiccio, G.; Torti, E. *J. Polym. Sci., Part A* **1965**, *3*, 4263.
- (2) Doll, W. W.; Lando, J. B. *J. Macromol. Sci., Phys.* **1970**, *B4*, 897.
- (3) Bychkov, R. A.; Gal'perin, Ye. L.; Konkin, A. A. *Vysokomol. Soedin., Ser. A* **1971**, *13*, 1156.
- (4) Hasegawa, R.; Takahashi, Y.; Chatani, Y.; Tadokoro, H. *Polym. J. (Tokyo)* **1972**, *3*, 600.
- (5) Weinhold, S.; Litt, M. H.; Lando, J. B. *J. Polym. Sci., Polym. Lett. Ed.* **1979**, *17*, 585.
- (6) Natta, G.; Bassi, I. W.; Allegra, G. *Acad. Naz. Lincei, Rend. Sci. Fis. Mat. Nat.* **1961**, *31*, 350.
- (7) Lee, H.; Salomon, R. E.; Labes, M. M. *Macromolecules* **1978**, *11*, 171.
- (8) Godovskii, Yu K.; Zharikova, Z. F.; Malinskii, Yu M. *Vysokomol. Soedin Ser. A* **1981**, *23*, 133.
- (9) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer-Polymer Miscibility*; Academic: New York, 1979; Chapter 5.
- (10) Wunderlich, B. *Macromolecular Physics*; Academic: New York, 1976; Vol. 1, Chapter II; 1980; Vol. 3, Chapter VIII.
- (11) Lovinger, A. J. "Poly(vinylidene fluoride)" In *Developments in Crystalline Polymers-1*; Bassett, D. C., Ed.; Applied Science: London and New Jersey, 1982; Chapter 5.
- (12) Zverev, M. P.; Polovikhina, L. A.; Barash, A. N.; Mal'kova, L. P.; Litovchenko, G. D. *Vysokomol. Soedin., Ser. A* **1974**, *16*, 1813.
- (13) Görlitz, M.; Minke, R.; Trautvetter, W.; Weisgerber, G. *Angew. Makromol. Chem.* **1973**, *29/30*, 137.
- (14) Kalfoglou, N. K.; Williams, H. L. *J. Appl. Polym. Sci.* **1973**, *17*, 3367.
- (15) Furukawa, T.; Aiba, J.; Fukada, E. *J. Appl. Phys.* **1979**, *50*, 3615.
- (16) Lovinger, A. J.; Wang, T. A. *Polymer* **1979**, *20*, 725.
- (17) Gal'perin, Ye. L.; Kosmynin, B. P.; Smirnov, V. K. *Vysokomol. Soedin., Ser. A* **1970**, *12*, 1880.
- (18) Gal'perin, Ye. L.; Kosmynin, B. P.; Smirnov, V. K. *Vysokomol. Soedin., Ser. B* **1970**, *12*, 555.
- (19) Enns, J. B.; Simha, R. *J. Macromol. Sci., Phys.* **1977**, *B13*, 11.

Phase Behavior of Amorphous Binary Mixtures of Perdeuterated and Normal 1,4-Polybutadienes

F. S. Bates* and S. B. Dierker

AT&T Bell Laboratories, Murray Hill, New Jersey 07974

G. D. Wignall

National Center for Small Angle Scattering Research, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831. Received February 5, 1986

ABSTRACT: A series of amorphous binary mixtures of normal and perdeuterated 1,4-polybutadienes has been examined by small-angle neutron scattering (SANS). Contrary to the generally held assumption that isotopic polymer mixtures form ideal solutions, we conclusively demonstrate that these mixtures are characterized by an upper critical solution temperature (UCST). This isotope effect derives from a small, measurable difference in segment volume between normal and perdeuterated species. Above the UCST, the SANS results are quantitatively predicted by the mean-field theory of de Gennes for homogeneous binary polymer mixtures. Increasing the degree of polymerization raises the critical temperature, resulting in phase separation. Owing to the combined effects of the close proximity to the consolute point and a small segment-segment interaction parameter ($\chi \approx 10^{-3}$), the phase-separated mixtures exhibit extensive interfacial mixing; Porod analysis of the SANS results reveals an average interfacial thickness of $\langle D \rangle = 250$ Å. Overall, these findings demonstrate that normal and perdeuterated amorphous polymers represent a new class of materials with which to study polymer-polymer phase behavior.

Introduction

The introduction of coherent elastic small-angle neutron scattering (SANS) to the study of macromolecules over a decade ago^{1,2} represents one of the most significant experimental developments in the relatively brief history of polymer science. A recent review article³ outlines the broad range of applications of this technique to the investigation of solution and bulk properties of polymers and polymer mixtures. What most distinguishes SANS from small-angle X-ray scattering (SAXS)⁴ is the unique ability to selectively introduce a scattering length density difference

(contrast) between or within molecules by substituting deuterium for hydrogen. In general, it has been assumed that this method of isotope labeling produces no other perceptible chemical or physical effects in polymer melts.

Isotope substitution leads to numerous alterations in the physical and chemical properties of condensed matter. Perhaps the most universally recognized thermodynamic effects are the differences in melting and boiling temperatures exhibited by isotopically different molecules (or atoms). For example, heavy water boils at 101.4 °C and melts at 3.8 °C,⁵ deuterium (²H₂) melts and boils at 4.5 and