Macromolecules **1994,** *27,* 6589-6593

New Miscible Polymer Blends of Propylene–Carbon Monoxide Alternating Copolymer with Poly(methyl methacrylate)

Frank Y. Xu and James C. W. Chien*

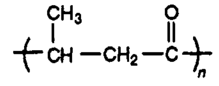
Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Received June 5, 1994; Revised Manuscript Received August 10, 1994[⊗]

ABSTRACT: Propylene–carbon monoxide (P–CO) alternating copolymer was blended with poly(methyl methacrylate) (PMMA) by solution precipitation. Various aspects of blend behaviors were studied by using differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), dynamic dielectric thermal analysis (DETA), Fourier transform infrared (FTIR) spectroscopy, and solid-state cross-polarization magic angle spinning (CP-MAS) NMR. The blends exhibited single T_g's at all compositions, which is an indication of miscibility on the scale of 100 Å. In addition to the α-relaxation (glass transition), the β-relaxation of P–CO was detected by DETA at -65 °C. The IR absorptions of the carbonyl groups of P–CO and PMMA were located at 1706 and 1730 cm^{-1}, respectively. The intensities of both bands were normalized by correcting concentration variation; their ratio changed with blend composition, consistent with some specific interactions involving one or both carbonyl groups. The solid-state NMR proton spin–lattice relaxations in both the laboratory and rotating frame were single-exponential processes. The result showed intimate mixing between P–CO and PMMA on a scale of <30 Å.

Introduction

Both amorphous and semicrystalline propylene–carbon monoxide (P–CO) alternating copolymers (ACP) have been synthesized by us and other groups.[1-7] The ACP has the general structure of a polyketone,



$$\left(\overset{CH_3}{\overset{|}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} \right)_n$$

P–CO along with ethylene–carbon monoxide copolymer has the potential of being used as a photodegradable material.[8] We have now blended amorphous P–CO with poly(methyl methacrylate) (PMMA) to improve the impact strength of PMMA. The blends were found to be miscible at all composition. Several techniques (DSC, DMTA, DETA, FTIR, and solid-state NMR) have been used to provide a broad data base for this new blend system.

Experimental Section

Materials. The alternating copolymer was prepared by polymerization of propylene and CO catalyzed by $(Ph_2P(CH_2)_3PPh_2)Pd^{2+}\cdot 2BF_4^-$ as described previously.[3,6] The copolymerization conditions for propylene–CO are as follows: catalyst (0.02 mmol), methanol (1 mL), 1,2-dichloroethane as solvent (150 mL), 80 psig propylene, 720 psig CO, at 0–20 °C for 24 h. A 300-mL Paar reactor was dried and purged with argon, and then the catalyst, methanol, and solvent were cannulated into it. Propylene and carbon monoxide were introduced in turn. The mixture was cooled to the polymerization temperature. At the end of a copolymerization the unreacted monomers were vented, and the copolymer was purified by precipitation with methanol and dried in vacuo at ambient temperature for 24 h. The number-average molecular weight of the copolymer is around 20 000. The complete characterization of this copolymer was described elsewhere.[6] PMMA was purchased from Scientific Polymer Products, Inc., with the number-average weight of 35 000 (catalog no. 037A). The blends were prepared by dissolving the appropriate amounts of each polymer in chloroform and stirring for 3 days, followed by precipitation into a large excess of hexane. The resulting mixture was then repeatedly washed and subsequently dried in vacuo at 50 °C for 2 days. No evidence of any solvent residue was seen from TGA measurement. Some film samples for FTIR analysis were prepared by slow solvent casting from chloroform. All blend films were clear and transparent.

Blend Characterization. Differential scanning calorimetry (DSC) was performed on a DuPont 2000 thermoanalysis system with a 20 °C/min heating rate. T_g's were taken as the midpoint of heat capacity increment from the second scan. Dynamic mechanical thermal analysis (DMTA) was done on a Polymer Laboratories DMTA MKI model. A GenRad/689M Digibridge controlled by a Polymer Laboratories DETA system I was used for the dynamic dielectric thermal analysis (DETA). Cloud-point determinations were performed by using a programmable hot stage in conjunction with a simple He–Ne laser light scattering device.

All solid-state NMR measurements were taken on an IBM 200 AF spectrometer equipped with an IBM solid accessory and a Doty CP-MAS probe. Samples were generally spun at 4.0–4.5 kHz and cross-polarized at 50 kHz (6 and 5 μs 90° pulses for ^1H and ^{13}C, respectively). The Hartmann–Hahn match was adjusted prior to every run using a di-*tert*-butylbenzene standard. The proton spin–lattice relaxation time in the rotating frame, $T_{1\rho}^{H}$, was measured through the change in cross-polarized carbon signal intensities after a variable ^1H spin-lock time, τ.[9] The proton spin–lattice relaxation time in the laboratory frame, T_1^H, was determined via an inversion–recovery pulse sequence in a cross-polarization transfer experiment.[10] Quadrature detection and phase alternation were used throughout.

Results and Discussion

Thermal Analysis. The second scans of the DSC traces for pure PMMA, pure P–CO, and 50:50 blend are shown in Figure 1. The glass transition temperatures for pure P–CO and PMMA are 22 and 109 °C, respectively. Because the T_g's for the pure components are sufficiently separated, the T_g's of the blends can be used as an indicator for miscibility. Like the 50:50 blend, blends with different compositions all exhibited single-T_g behavior. Figure 2 shows a plot of T_g versus weight fraction of PMMA for a series of PMMA/P–CO blends. The dashed line represents the simple additive behavior of the two components by weight. The experimental results showed a concave deviation from the dashed line. The composition variation of T_g can be described satisfactorily by the Gordon–

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1994.

0024-9297/94/2227-6589$04.50/0

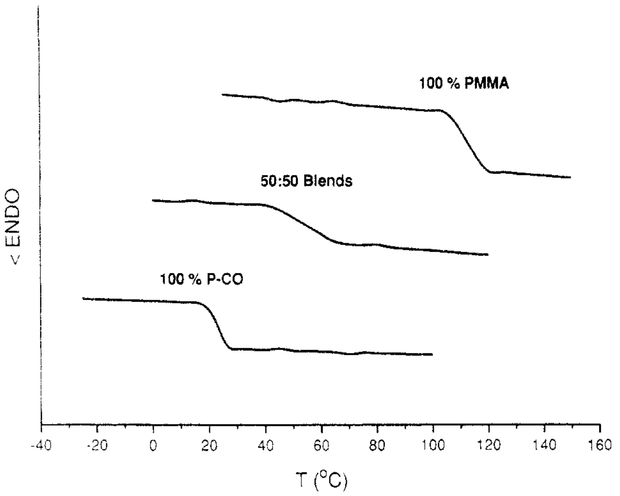


Figure 1. Second scan of DSC trace for pure PMMA, pure P–CO, and a 50:50 wt:wt blend of PMMA and P–CO.

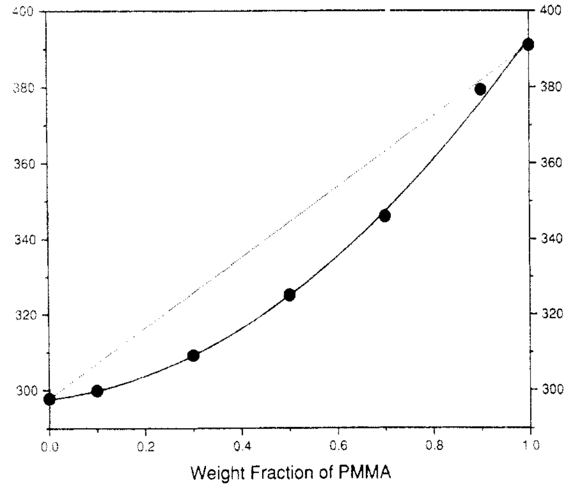


Figure 2. T_g as a function of PMMA weight fraction in the PMMA/P–CO blends. The dashed line represents the simple additive behavior of the two components by weight. The experimental results are in filled circles.

Taylor equation:[11]

$$T_{g,b} = \frac{T_{g,1} + (KT_{g,2} - T_{g,1})W_2}{1 + (K - 1)W_2} \qquad (1)$$

where $T_{g,1}$, $T_{g,2}$, W_1, and W_2 are the component glass transition temperatures and weight fractions. The fitting parameter K is equal to 0.46. Therefore, the blends are miscible according to the T_g variation.

Cloud-point measurement was performed by using a simple laser scattering device to monitor scattered intensity as a function of temperature. No lower critical solution temperature (LCST) was found for all the blends up to 320 °C, where P–CO alternating copolymer begins to degrade. The results of the cloud-point measurements indicate the blends are miscible.

The mechanical relaxation behavior of the blends was first studied by DMTA. The tan δ is plotted against temperature in Figure 3 for pure PMMA and a 30:70 PMMA/P–CO blend. The pure PMMA exhibited both α- and β-relaxation at 125 and 30 °C, respectively, under a frequency of 1 Hz. The β-relaxation of PMMA was generally assigned to the rotation of the $COOCH_3$ side group;[12] it was suppressed in the blend probably due to the broadened distribution of the relaxation times. The DMTA spectrum of the blend shows a single T_g without the observation of the β-relaxation of the P–CO copolymer. The possible β-relaxation of the P–CO copolymer can be attributed to the vibration or flipping movement of the carbonyl group; such motion may not affect the mechanical modulus significantly. However, the carbonyl group always exhibits a strong dielectric loss peak in the dynamic dielectric measurement. The DETA measurements at 1 kHz (Figure 4) showed a strong dielectric loss at −60 °C for the pure P–CO copolymer. Therefore, we can conclude that the β-relaxation is due to the motion of the carbonyl group in the P–CO ACP.

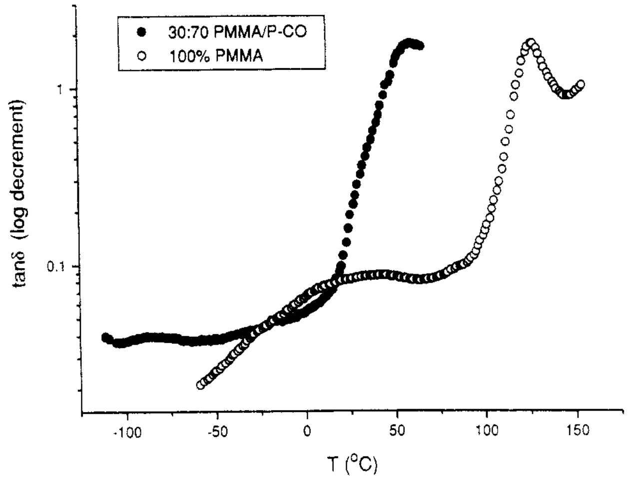


Figure 3. DMTA measurement at 1 Hz. tan δ is plotted versus temperature for pure PMMA and 30:70 PMMA/P–CO blend.

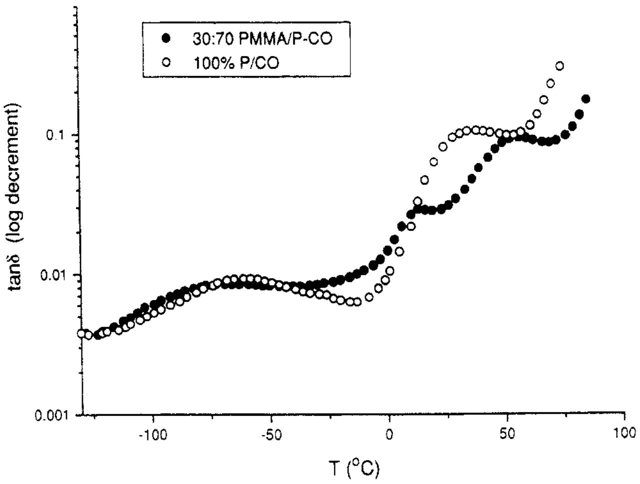


Figure 4. DETA measurement at 1 kHz. tan δ is plotted versus temperature for pure P–CO and 30:70 PMMA/P–CO blend.

FTIR Spectroscopy. FTIR studies were performed for blends of different composition. The IR spectra of the carbonyl group stretching region are shown in Figure 5. The carbonyl groups of PMMA and P–CO absorbs radiation at 1730 and 1707 cm^{-1}, respectively. The most important characteristic band parameters measured in IR spectroscopy are frequency (energy) and intensity (polar character). Both intensity change and frequency shift provide information on possible specific interactions in polymer blends.[13] As a tool for the discrimination of structural elements, the IR intensities are significantly more sensitive to small changes in structure or bond environment than are the IR frequencies.[14] In the PMMA/P–CO blends, no significant frequency shifts were observed for the two carbonyl bands. The intensity changes, however, were very obvious.

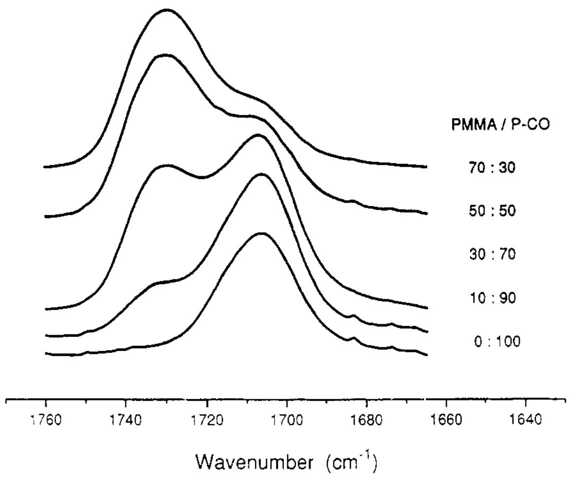


Figure 5. IR spectra of the carbonyl group stretching region for pure Q-CO and blends as indicated. The bands around 1730 and 1707 cm^{-1} are attributed to the carbonyl stretching of PMMA and P-CO, respectively.

The IR intensity, A_s, which is usually referred to an integrated absorbance,[14,15]

$$A_s = \left[\frac{1}{cb}\right] \int_{\text{band}} \ln\left(\frac{I_0}{I}\right) d\nu \qquad (2)$$

where c is the concentration, b is the path length, I_0 is the incident light intensity per unit time, I is the transmitted light intensity per unit time, and ν is the wavenumber. When IR radiation is absorbed by a molecule, the intensity of the absorption depends on the movement of the electronic charges during the molecular vibration. Therefore, the IR intensities should provide information about the electronic charge distributions in molecules and about how the electrons redistribute themselves during molecular vibrations.[14] If we set $A_{s,1}$ and $A_{s,2}$ as the IR intensities of the carbonyl groups for PMMA and P-CO, respectively, the relative IR intensity ratio can be written as

$$\frac{A_{s,1}}{A_{s,2}} = \frac{c_2}{c_1}\,\frac{\text{band area 1}}{\text{band area 2}} \qquad (3)$$

Since the two carbonyl bands were not severely overlapping, deconvolution of them by curve fitting is easily accomplished. Knowing the areas of the two bands and the concentration of the blends, the intensity ratio, $A_{s,1}/A_{s,2}$, was readily calculated. The intensity ratios and bandwidths at half-height of the two carbonyl bands are plotted versus weight fraction of PMMA in Figure 6. The intensity ratio changed significantly from 1.44 for the 10:90 PMMA/P-CO blend to 0.32 for the 90:10 PMMA/P-CO blend. In Figure 6, it can be seen that the composition variation of the intensity ratio is not monotonic. It shows a maximum at ca. 50 wt % PMMA.

The significant effect of blending on the intensity ratio of the carbonyl stretching may imply that some groups in the blends interact favorably with one of the carbonyl groups or that two carbonyl groups interact favorably with each other. The variation of width at half-height also supports this argument.

Solid-State NMR Relaxation. Many examples of the use of the proton spin-lattice relaxation time in the laboratory and rotating frame, T_1^{H} and $T_{1\rho}^{\mathrm{H}}$, and spin diffusion measurements to characterize polymer/polymer miscibility have been reported.[16-26] A single T_g is taken to indicate the miscibility of blends on the scale of 100 Å.

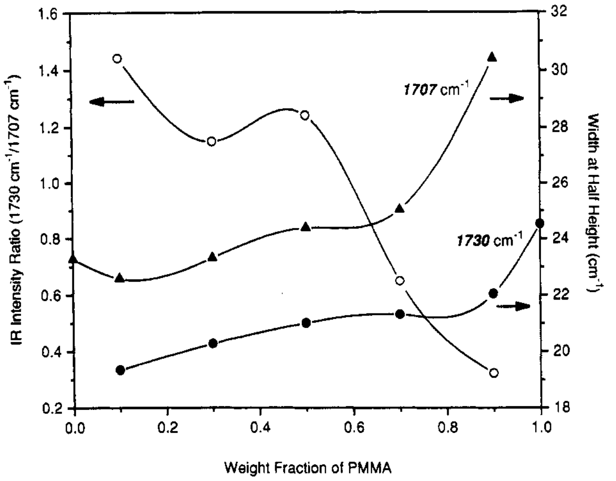


Figure 6. Composition dependence of IR intensity ratio and the width at half-height of the two carbonyl bands at 1730 and 1707 cm^{-1}.

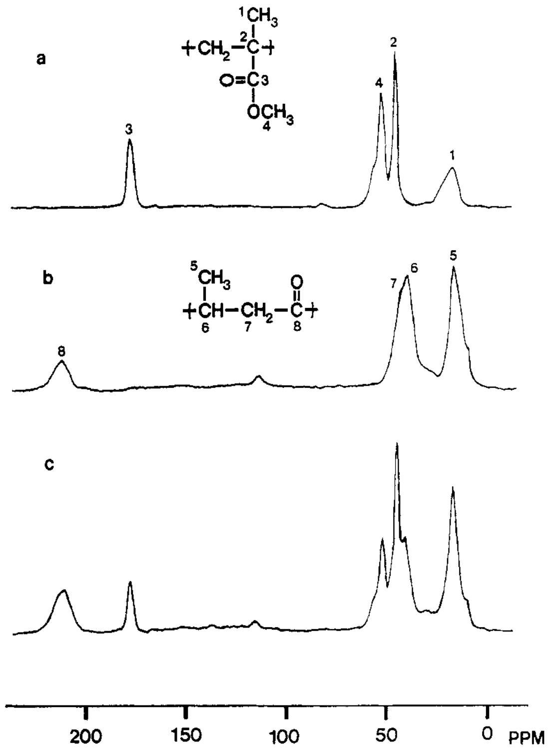


Figure 7. Solid-state NMR carbon spectra of pure PMMA, pure P-CO, and 30:70 PMMA/P-CO blend.

NMR relaxation times offer the potential to probe blend miscibility on a different scale. For this reason, solid-state NMR was used to further evaluate the PMMA/P-CO blends. Solid-state NMR carbon spectra of pure PMMA, pure P-CO, and the 30:70 PMMA/P-CO blend are shown in Figure 7. Generally speaking, the NMR peaks were well separated, and relaxation measurement on each individual peak can be performed.

In the solid-state experiment, spin energy can propagate between neighboring nuclei by an energy conserved "flip flop" process termed spin diffusion. Spin diffusion is induced by the dipolar interactions of nuclear spins, which produce spin flips between nuclei. This spin flipping leads to an adiabatic transfer of magnetization between neighboring spins. For highly coupled nuclei such as protons, this spin diffusion can be the dominant process for the relaxation.[14] By determining the T_1^{H} and $T_{1\rho}^{\mathrm{H}}$ values for a blend in comparison to the corresponding values for pure component polymers, it may be possible under certain circumstances to estimate an upper limit to the scale of heterogeneity present in the blend. If the scale of the phase separation in the blend is sufficiently small to permit rapid diffusion of proton spin energy such that a single-component relaxation process is observed, eq 4 may be used to estimate the maximum diffusion path length or upper limit to the domain size,[20,21,23,27,28]

$$\langle L^2 \rangle = \left(\frac{t}{T_2}\right)\langle l_0^{\,2} \rangle \tag{4}$$

where $\langle L^2 \rangle$ is the mean-square length over which magnetization is transported. $\langle l_0 \rangle$ is the mean jump length, which is taken as the distance between neighboring protons, typically 0.1 nm. T_2 is the proton spin–spin relaxation time, and t is the time over which spin diffusion takes place, set equal to $T_1^{\rm H}$ or $T_{1\rho}^{\rm H}$ in the laboratory or rotating frame. For the PMMA/P–CO blends, substituting in $T_2 = 10$ μs, the maximum diffusion path lengths for spin–lattice relaxations in the rotating frame (8 ms) and in the laboratory frame (0.5 s) are approximately 30 and 200 Å, respectively. Assuming the spin–lattice relaxation times are different for the two pure components, if the blends show a single $T_{1\rho}^{\rm H}$, the blends can be said to be miscible on the scale of 30 Å, which indicates that the separated phases, if present, are smaller than ca. 30 Å. Similarly, a single $T_1^{\rm H}$ yields the miscibility on the scale of 200 Å.

Miscibility at 200 Å is required by the single $T_{\rm g}$ of the blends. Therefore, single-$T_1^{\rm H}$ behavior is expected for the blends. The experimental results confirmed this expectation. The $T_1^{\rm H}$'s were 0.38, 0.46, 0.51, 0.68, and 0.92 s for the pure PMMA, the 70:30, 50:50, and 30:70 PMMA/P–CO blends and pure P–CO, respectively.

Measurements of $T_{1\rho}^{\rm H}$ were made through the change in carbon intensity under cross-polarization after a variable ^{1}H spin-lock time, τ.[9] The carbon signal intensity decay curves were fitted to a standard first-order kinetic expression.[17] If the protin spin system is tightly coupled, the relaxation times should be independent of the carbon peak used to monitor signal decay. This was observed to be the case for this blend system; relaxation times were independent of the peak chosen for the calculation. Figure 8 shows the decay curves of the ^{13}C signal intensity on a logarithmic scale versus proton spin-lock time for pure PMMA, the 70:30, 50:50, and 30:70 PMMA/P–CO blends, and pure P–CO. A single-exponential decay behavior is observed for all of them. For the pure PMMA, the single-component relaxation process gave a time constant, $T_{1\rho}^{\rm H}$, of 9.1 ms. Similarly, the $T_{1\rho}^{\rm H}$ of pure P–CO was calculated to be 5.0 ms. It is readily apparent that the relaxation processes for the blends are intermediate in value as compared to the pure components. These results suggested that the blends are miscible on the scale of 30 Å. In other words, the separated phases, if present, are smaller than 30 Å. However, because of the uncertainty of the exact value of the spin diffusion rate, these upper limit numbers are subject to error limits of ±50% of the reported value.[20]

Conclusion

The PMMA/P–CO blends were found to be miscible by both $T_{\rm g}$ and solid-state NMR relaxation studies. The β-relaxation of P–CO was observed by DETA. NMR spin-lattice relaxation in the rotating frame measurement showed that the average distance between PMMA and P–CO in the intimately mixed phase is less than 30 Å. The relative IR intensity ratio of the two carbonyl bands changed with different blend compositions, which indicated that the specific interaction involving one or both carbonyl groups may be the driving force for mixing.

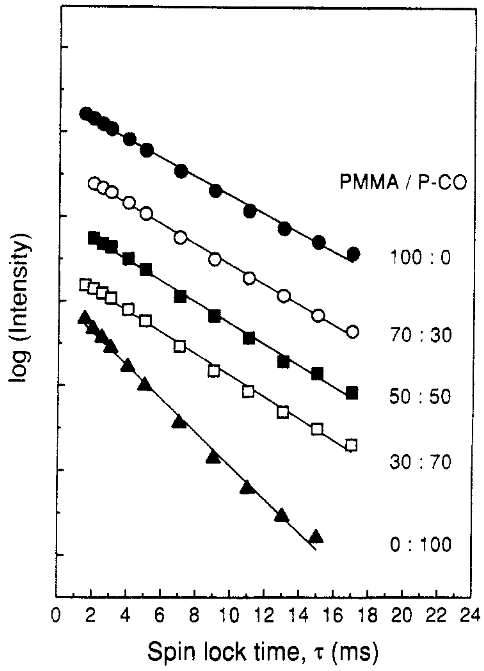


Figure 8. Decay curves of ^{13}C signal intensity on a logarithmic scale versus proton spin-lock time, τ, for pure PMMA, 70:30, 50:50, and 30:70 PMMA/P–CO blends, and pure P–CO. For clarity each line is begun at a separate origin on the y-axis.

Acknowledgment. This work was supported by the Cooperative University of Massachusetts–Industry Research Programs at Amherst and benefited by the Central Facilities of the Materials Research Laboratories.

References and Notes

(1) Jiang, Z.; Dahlen, G. M.; Houseknecht, K.; Sen, A. *Macromolecules* **1992**, *25*, 2999.

(2) Batistini, A.; Consiglio, G.; Suter, U. W. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 303.

(3) Chien, J. C. W.; Zhao, A. X.; Xu, F. *Polym. Bull.* **1992**, *28*, 315.

(4) Batistini, A.; Consiglio, G. *Organometallics* **1992**, *11*, 1766.

(5) Batistini, A.; Consiglio, G.; Suter, U. W. *Polym. Mater. Sci. Eng.* **1992**, *67*, 104.

(6) Xu, F. Y.; Zhao, A. X.; Chien, J. C. W. *Makromol. Chem.* **1993**, *194*, 2579.

(7) Wong, P. K.; van Doorn, J. A.; Drent, E.; Sudmeijer, O.; Stil, H. A. *Ind. Eng. Chem. Res.* **1993**, *32* (5), 986.

(8) Xu, F. Y.; Chien, J. C. W. *Macromolecules* **1993**, *26*, 3485.

(9) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1977**, *10*, 384.

(10) McBrierty, V. J.; Douglass, D. C.; Kwei, T. K. *Macromolecules* **1978**, *11*, 1265.

(11) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 495.

(12) McCrum, N. G.; Read, B. E.; William, G. *Anelastic and Dielectric Effects in Polymeric Solids*; Dover: New York, 1991.

(13) Coleman, M. M.; Graf, J. F.; Painter, P. C. *Specific Interactions and the Miscibility of Polymer Blends*; Technomic: Lancaster, PA, 1991.

(14) Koenig, J. L. *Spectroscopy of Polymers*; American Chemical Society: Washington, DC, 1992.

(15) Gribov, L. A. *Intensity Theory for Infrared Spectra of Polyatomic Molecules*; Consultants Bureau: New York, 1964.

(16) Albert, B.; Jerome, R.; Teyssie, P.; Smyth, G.; Boyle, N. G.; McBrierty, V.; J. *Macromolecules* **1985**, *18*, 388.

(17) Assink, R. A. *Macromolecules* **1978**, *11*, 1233.

(18) Dickinson, L. C.; Yang, H.; Chu, C. W.; Stein, R. S.; Chien, J. C. W. *Macromolecules* **1987**, *20*, 1757.

(19) Stejskal, E. O.; Schaefer, J.; Sefcik, M. D.; McKay, R. A. *Macromolecules* **1981**, *14*, 275.

(20) Parmer, J. F.; Dickinson, L. C.; Chien, J. C. W.; Porter, R. S. *Macromolecules* **1989**, *22*, 1078.

(21) Gao, Z.; Molnar, A.; Morin, F. G.; Eisenberg, A. *Macromolecules* **1992**, *25*, 6460.
(22) McBrierty, V. J. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon Press: Oxford, 1989; Vol. 1, p 397.
(23) McBrierty, V. J.; Douglass, D. C. *Macromol. Rev.* **1981**, *16*, 295.
(24) Voelkel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1468.
(25) Simmons, A.; Natansohn, A. *Macromolecules* **1991**, *24*, 3651.
(26) Chu, C. W.; Dickinson, L. C.; Chien, J. C. W. *J. Appl. Polym. Sci.* **1990**, *41*, 2311.
(27) McBrierty, V. J. *Magn. Reson. Rev.* **1983**, *8*, 166.
(28) Smith, P.; Hara, M.; Eisenberg, A. In *Current Topics in Polymer Science*; Ottenbrite, R. M., Utracki, L. A., Inoue, S., Eds.; Hanser: New York, 1987; Vol. 2, p 255.