Identification of Intermolecular Interactions in 1,2-Polybutadiene/Polyisoprene Blends

Sharon A. Heffner and Peter A. Mirau*

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

Received April 29, 1994; Revised Manuscript Received September 2, 1994[⊗]

ABSTRACT: The intermolecular interactions responsible for miscibility in 1,2-polybutadiene/*cis*-polyisoprene blends have been investigated using solid-state two-dimensional (2D) NMR. We find that high-resolution proton spectra can be obtained at temperatures above T_g using magic-angle spinning and that intermolecular association can be probed using nuclear Overhauser effect spectroscopy. The results reveal the existence of weak intermolecular interactions between the polyisoprene methyl group and the 1,2-polybutadiene vinyl side chain. These studies demonstrate the large effect that weak intermolecular interactions can have on the phase structure of polymer blends.

Introduction

Understanding the structure and dynamics of polymer blends is an area of intense theoretical and experimental investigation. Most binary mixtures of polymers are not miscible on the molecular level because the entropy of mixing is not favorable for high molecular weight polymers. In those blends of high molecular weight polymers where the chains mix on a molecular level, the miscibility is usually a consequence of attractive interchain interactions.[1] These interactions can be either strong (e.g., hydrogen bond)[2] or weak (e.g., van der Waals),[3] depending on the chemical structure of the monomer units. In blends of weakly interacting polymers, such as polystyrene/poly(methyl vinyl ether),[3,4] poly(vinyl chloride)/poly(methyl methacrylate),[5] or 1,2-polybutadiene/polyisoprene,[6] the identity of the interacting functional group is frequently not obvious from the chemical structure of the monomers. The molecular-level understanding of polymer blends and the prediction of polymer miscibility are critically dependent on understanding such interactions.[7,8]

We have studied intermolecular interactions in concentrated solutions of polymers capable of forming miscible blends by two-dimensional (2D) nuclear Overhauser effect spectroscopy (NOESY).[4,5,9] This approach provides detailed information about the structure of associating polymers since correlations are observed only for those pairs of protons separated by less than 5 Å, and the cross peak intensities depend on the inverse sixth power of the internuclear separations.[10,11] The success of this approach is due in part to the high resolution obtainable for solution mixtures where the lines are narrowed by chain motion.[12] Similar methods have been used to study intermolecular interactions in solid polymers by multipulse NMR on rotating solids,[13,14] but conclusions about the specific interactions are limited by the larger line widths and rapid intrachain spin diffusion. Another approach to the study of specific interactions in solid polymers is to use the solution NMR methods for solid polymer blends above T_g, where there is sufficient molecular motion to generate both intra- and interchain NOE's. The lines for most polymers above T_g are too broad for the NMR characterization of intermolecular interactions, but it has been reported that the line widths for 1,4-polybutadiene can be substantially narrowed with either multipulse decoupling or magic-angle spinning (MAS) in samples at temperatures above T_g.[15,16] Here we use the combination of MAS and NOESY spectroscopy to investigate the specific interactions in a weakly interacting polymer blend.

1,2-Polybutadiene and *cis*-polyisoprene are miscible over the entire composition range as evidenced by their spontaneous interdiffusion.[17] This blend differs from many others in that the T_g is very broad[17] and NMR[18,19] and rheological[20] measurements show that the chains have separate correlation times and temperature dependencies. Based on the chemical structures of the polymers and the observation that no large changes are observed in the IR spectra upon blend formation,[18] it has been proposed that this blend is miscible in the absence of specific interactions and that the miscibility is a consequence of the similarities in the polarizability and liquid structure of the component polymers.[17,21,22] SANS studies have demonstrated that $\chi < 0$ and that LCST behavior is observed.[23] On the basis of these data it has been suggested that the miscibility arises as a consequence of "the subtle balance of constitutent fundamental interactions" as in random copolymer blends.[23] In this study we demonstrate the existence of intermolecular interactions between the methyl group of polyisoprene and the vinyl side chain of 1,2-polybutadiene in solid blends at temperatures above T_g using 2D NMR and magic-angle spinning.

Methods and Materials

cis-Polyisoprene was obtained from Aldrich (catalog no. 18214). The 1,2-polybutadiene was a gift from Dr. Xina Quan, and the characterization of this material has been previously reported.[24] The samples were prepared as films cast from toluene under a nitrogen atmosphere and dried in a vacuum oven at 65 °C for 48 h.

Proton NMR spectra were acquired at 400 MHz on a Varian Unity NMR spectrometer using a magic-angle spinning probe from Doty Scientific Inc. The spectra were acquired using either 1.4 or 5.5 μs $\pi/2$ pulses and a spinning speed of 3.5 kHz. Phase-sensitive 2D NOESY spectra were acquired using the ($\pi/2-t_1-\pi/2-\tau_m-\pi/2-t_2$) pulse sequence, where τ_m is the mixing time.[25] The 2D data were acquired with 512 complex points in the t_2 dimension and 256 complex points in the t_1 dimension with mixing times between 0.005 and 0.05 s using 3 kHz sweep widths in each dimension. The data were processed with 5 Hz line broadening in each dimension.

Results

NMR spectroscopy has been extensively used to study the mixing of polymer blends[26] and to characterize

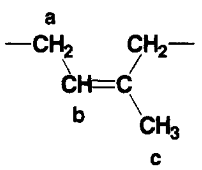
---

[⊗] Abstract published in *Advance ACS Abstracts,* November 1, 1994.

specific intermolecular interactions.[4,27] Information about specific interactions can be obtained by measuring chemical shift changes following blend formation[28] or by measuring dipolar couplings between pairs of protons or other nuclei on the polymer chains.[29,30] The minimum requirement for the analysis of specific intermolecular interactions is that the resolution must be sufficiently high that separate signals can be resolved for the groups on the different polymer chains. Such resolution is typically not observed in the proton spectra of solid polymers, but studies have shown that the line widths are greatly decreased at temperatures above T_g by rapid chain motion.[15,31] However, the line widths are still larger than those observed in solution due to incomplete averaging of the static dipolar interactions.[15] In this study we use magic-angle spinning (MAS) above T_g to narrow the line widths for 1,2-polybutadiene/*cis*-polyisoprene blends to make possible the identification and characterization of intermolecular interactions.

We have previously used concentrated solutions of polymers capable of forming miscible blends as a model system to probe intermolecular interactions.[30] These experiments were unsuccessful in polyisoprene/1,2-polybutadiene blends, and we were unable to observe intermolecular NOE's or rotating frame NOE's[32] for mixtures with concentrations as high as 50 wt % (not shown). We interpret this to mean that the interactions in this blend are considerably weaker than in blends such as polystyrene/poly(methyl vinyl ether)[9] or poly(vinyl chloride)/poly(methyl methacrylate),[5] where intermolecular NOE's are observed in polymer solutions at concentrations greater than 30 wt %.

Since concentrated solutions do not appear to be an effective way to study this blend, we have used proton NMR above T_g to probe the intermolecular interactions. Figure 1 shows the 400 MHz proton NMR spectra of the 1:1 1,2-polybutadiene/*cis*-polyisoprene blend at 60 °C. This blend has previously been shown to have a broad T_g at a temperature intermediate between the T_g's of the homopolymers (−50 and −7 °C) and is miscible over the entire composition range.[17] Figure 1a shows that two groups of signals are resolved in the static spectrum. The band between 1 and 2.5 ppm contains the methyl, methylene, and methine protons, and the lower field band (4.5−6 ppm) is assigned to the protons attached to double-bonded carbons. Since both peaks contain signals from both polymers, the resolution is not sufficient to study the intermolecular interactions. The resolution is only slightly improved at a higher field strength (500 MHz) and a higher temperature (100 °C) (data not shown).



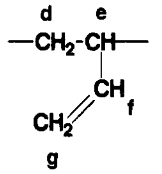


Figure 1b shows the spectrum for the same sample acquired with magic-angle spinning at 3.5 kHz. The line widths are reduced by MAS and the peaks can be assigned to specific protons, as shown in the figure. The assignments are made by comparison with the solution spectra of homopolymers and our 2D studies, and the lines are only slightly broader than those observed for 30 wt % solutions in toluene (not shown). Separate signals are observed for all the protons except the methylene protons of polyisoprene (protons a) and the methine protons of 1,2-polybutadiene (protons e).

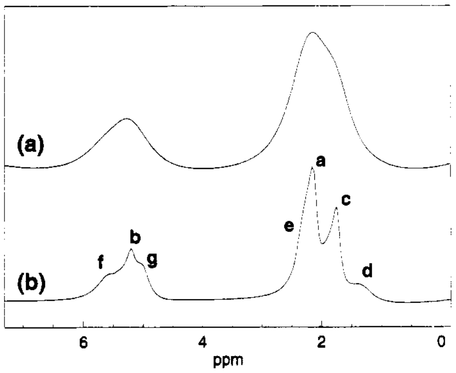


Figure 1. 400 MHz proton NMR spectrum of *cis*-polyisoprene/1,2-polybutadiene blends cast from toluene at 60 °C. Spectrum a was obtained on a static sample while spectrum b was obtained with 3.5 kHz spinning at the magic angle.

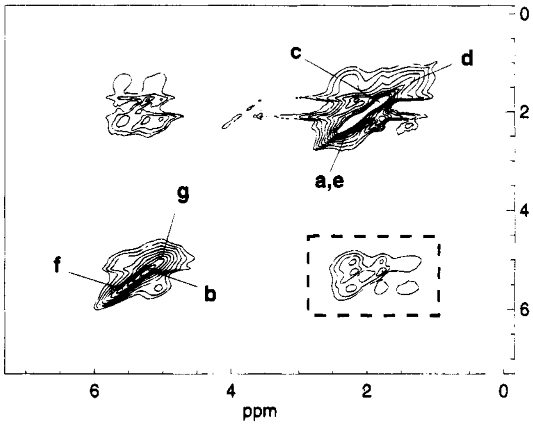


Figure 2. 2D NOESY spectrum of the *cis*-polyisoprene/1,2-polybutadiene blend obtained at 60 °C with a mixing time of 0.02 s. The spectrum was obtained with 3.5 kHz spinning at the magic angle. The area enclosed in the box is shown in stacked plot form in Figure 3.

The resolution in the MAS spectra is sufficiently high that the intermolecular interactions can be studied by 2D NOESY spectroscopy, and Figure 2 shows a contour plot of the 2D spectrum of the 1:1 blend acquired with a 0.02 s mixing time at 60 °C and magic-angle spinning at 3.5 kHz. The most intense signals appear along the diagonal and correspond to the lines observed in the one-dimensional spectra. The smaller off-diagonal peaks arise from through-space dipolar interactions between pairs of protons separated by less than 5 Å and may include both inter- and interchain interactions. Many cross peaks are observed both between the groups of signals and within the groups. The relative intensities of the cross peaks are more easily visualized in the stacked plot representation of the data shown in Figure 3 for the cross peaks between 4 and 6 ppm in the t_1 dimension and between 1 and 3 ppm in the t_2 dimension.

Both intra- and intermolecular cross peaks are observed in the stacked plot shown in Figure 3. Cross peaks between the protons marked b and c in polyisoprene and peaks marked d, f, and g in 1,2-polybutadiene can be unambiguously assigned since these signals are well resolved, while interactions with protons a and e cannot be unambiguously identified because of the peak overlap.

Among the strongest of the well-resolved intramolecular cross peaks are those between the methyl and CH protons (c and b) of polyisoprene. These peaks

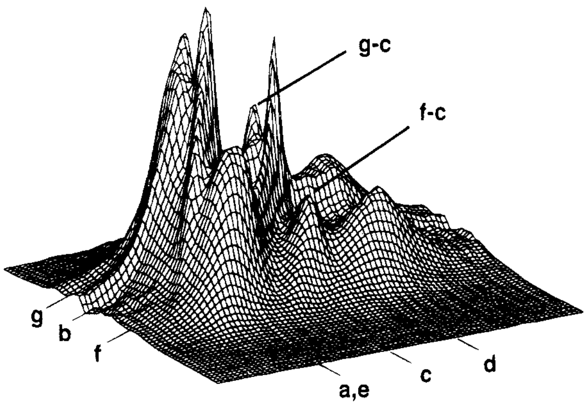


Figure 3. Stack plot representation of the cross peaks from the 2D NOESY spectrum shown in Figure 2. The data are plotted for the cross peaks between 4 and 6 ppm in the t_1 dimension and between 1 and 3 ppm in the t_2 dimension. The cross peak assignments are noted.

appear most intense in part because the methyl protons have the smallest line widths. Intramolecular cross peaks are also observed between the CH and CH_2 protons (f and g) in the side chain of 1,2-polybutadiene and the main chain methylene (d). Cross peaks between the side chain protons f and g can be seen in the contour plot shown in Figure 2.

Of primary interest in these studies are the intermolecular cross peaks that are indicative of specific intermolecular interactions. The strongest intermolecular cross peak is observed between the methyl protons of polyisoprene and the CH_2 in the 1,2-polybutadiene vinyl group (c−g). A weaker cross peak is observed between the methyl protons and the double-bonded CH of the 1,2-polybutadiene side chain (c−f). Conversely, we note that the main chain 1,2-polybutadiene methylene protons (d) do not show intermolecular correlations. These data show that the relative orientations of the polymers in the blend are not random, but the monomers are orientationally ordered such that the methyl group of polyisoprene is closest to the vinyl side chain of 1,2-polybutadiene. These conclusions are confirmed in studies as a function of mixing time (not shown). We believe that the observation of such cross peaks is a consequence of specific intermolecular interactions. We propose that such weak interactions can critically affect the miscibility of polyisoprene and 1,2-polybutadiene.

Discussion

These and previous studies shown that miscibility in polymer blends is frequently determined by weak intermolecular interactions and that the identification of these interactions is important for a molecular-level understanding of polymer blends and for predicting polymer miscibility. Evidence for the specific intermolecular interactions that contribute to miscibility are most commonly obtained from optical clarity or T_g measurements using DSC, dielectric, or dynamic mechanical spectroscopy,[1] where the strategy is to study a series of monomers and to draw conclusions about the molecular-level interactions from the effect of monomer structure on the miscibility. By contrast, IR[33] and NMR[30] spectroscopy can be used to identify the molecular-level interactions because the signals can be assigned to specific sites on the polymer chain.

We have shown than 2D NOESY studies can provide a valuable insight into the specific interactions that drive miscible blend formation and that the results obtained from our studies on concentrated solutions can be correlated with other methods that probe these interactions in the solid state. In polystyrene/poly(methyl vinyl ether) blends, for example, both the solution[4] and solid-state[3,34] studies have identified a specific interaction between the polystyrene phenyl ring and the ether side chain of poly(methyl vinyl ether). In these studies we extend the solution NOESY methods to include polymer blends above T_g, where the lines are narrowed by the combination of chain motion and magic-angle spinning. The results show that the chains are sufficiently mobile under these conditions that both intra- and intermolecular NOE's can be observed. We anticipate that a wide variety of polymer blends will be amenable to analysis by these methods.

The NOE's can be used to probe the structure of associating polymers because the cross peak intensities depend on the inverse sixth power of the internuclear separation.[10,11] In concentrated solutions we were able to show that such cross peaks are only observed under conditions leading to the formation of miscible blends.[5] We argued that these results show that the polymer pairs have a defined intermolecular structure since cross peaks between specific functional groups were observed rather than equal-intensity cross peaks between all pairs of protons on the two polymers. Here we extend these arguments to studies of polymer blends above T_g. We believe that random packing of polymer chains would place many of the pairs of protons on different chains in close proximity and lead to many intermolecular cross peaks. The observation of functional group interactions is taken as evidence for the orientational ordering of functional groups due to more specific intermolecular interactions. We also recognize that such NMR methods are sensitive to the local structure but may not reveal all of the interactions that contribute to the miscibility.

In these studies we do not observe equal-intensity intermolecular cross peaks, but rather the strongest intermolecular cross peaks are observed between the methyl protons of polyisoprene and the vinyl protons of 1,2-polybutadiene. We were unable to observe these interactions in concentrated solutions (data not shown), suggesting that they are considerably weaker than those in polystyrene/poly(methyl vinyl ether),[4,27] polycaprolactone/poly(methyl vinyl ether),[4] or poly(vinyl chloride)/poly(methyl methacrylate) blends.[5] In this case the favorable interaction appears to arise from the intermolecular association of the electron-deficient methyl group of *cis*-polyisoprene with the electron-rich vinyl side chain of 1,2-polybutadiene. Such a weak but specific interaction could explain the observation that miscibility in isoprene/butadiene polymers strongly depends on the polymer microstructure.[17,23] It has been previously reported that methyl groups can strongly affect the miscibility in a variety of polymer blends, including polystyrene[35,36] and polycarbonate blends.[37]

Acknowledgment. We would like to thank Dr. Xina Quan for providing the 1,2-polybutadiene samples.

References and Notes

(1) Walsh, D.; Rostami, S. *Adv. Polym. Sci.* **1985**, *70*, 119.
(2) Coleman, M.; Lichkus, A.; Painter, P. *Macromolecules* **1989**, *22*, 586.
(3) Larbi, F.; Leloup, S.; Halary, J.; Monnerie, L. *Polym. Commun.* **1986**, *27*, 23.
(4) Mirau, P.; Tanaka, H.; Bovey, F. *Macromolecules* **1988**, *21*, 2929.
(5) Kogler, G.; Mirau, P. *Macromolecules* **1992**, *25*, 598.
(6) Trask, C. A.; Roland, C. M. *Macromolecules* **1989**, *22*, 256.

(7) Coleman, M.; Yang, X.; Painter, P.; Graf, J. *Macromolecules* **1992**, *25*, 4414.
(8) Yang, X.; Painter, P.; Coleman, M.; Pearce, E.; Kwei, T. *Macromolecules* **1992**, *25*, 2156.
(9) Mirau, P.; Bovey, F. A. *Macromolecules* **1990**, *23*, 4548.
(10) Jeneer, J.; Meier, B.; Bachmann, P.; Ernst, R. *J. Chem. Phys.* **1979**, *71*, 4546.
(11) Ernst, R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon Press: Oxford, 1987; p 610.
(12) Heatley, F. *Prog. NMR Spectrosc.* **1979**, *13*, 47.
(13) Caravatti, P.; Neuenschwander, P.; Ernst, R. *Macromolecules* **1989**, *19*, 1889.
(14) Caravatti, P.; Neuenschwander, P.; Ernst, R. *Macromolecules* **1985**, *18*, 119.
(15) English, A. D. *Macromolecules* **1985**, *18*, 178.
(16) English, A. D.; Debowski, C. *Macromolecules* **1984**, *17*, 486.
(17) Roland, C. M. *Macromolecules* **1987**, *20*, 2557.
(18) Roland, C. M. *J. Polym. Sci., Part B: Polym. Phys.* **1988**, *26*, 839.
(19) Chung, G. C.; Kornfield, J. A.; Smith, S. D. *Macromolecules* **1994**, *27*, 964.
(20) Roovers, J.; Toporowski, P. M. *Macromolecules* **1992**, *25*, 3454.
(21) Trask, C. A.; Roland, C. M. *Polym. Bull.* **1988**, *20*, 471.
(22) Tomlin, D. W.; Roland, C. M. *Macromolecules* **1992**, *25*, 2994.
(23) Sakurai, S.; Jinnai, H.; Hasegawa, H.; Hashimoto, T.; Han, C. C. *Macromolecules* **1991**, *24*, 4839.
(24) Quan, X.; Johnson, G.; Anderson, E.; Lee, H. *Macromolecules* **1991**, *24*, 6500.
(25) States, D.; Haberkorn, R.; Ruben, D. *J. Magn. Reson.* **1982**, *48*, 286.
(26) Assink, R. *Macromolecules* **1978**, *11*, 1233.
(27) Crowther, M.; Levy, G. *Macromolecules* **1988**, *21*, 2924.
(28) Simmons, A.; Natansohn, A. *Macromolecules* **1992**, *25*, 3881.
(29) Wang, P.; Jones, A. A.; Inglefield, P. T.; White, D. M.; Bendler, J. T. *New Polym. Mater.* **1990**, *2*, 221.
(30) Mirau, P.; Heffner, S.; Koegler, G.; Bovey, F. *Poly. Int.* **1991**, *26*, 29.
(31) Miller, J.; McGrath, K.; Roland, C.; Trask, C.; Garroway, A. *Macromolecules* **1990**, *23*, 4543.
(32) Bax, A.; Davis, D. *J. Magn. Reson.* **1985**, *63*, 207.
(33) Lu, J.; Benedetti, E.; Hsu, S. *Macromolecules* **1983**, *16*, 1525.
(34) White, J. L.; Mirau, P. A. *Macromolecules* **1993**, *26*, 3049.
(35) Dickinson, L.; Yang, H.; Chu, C.; Stein, R.; Chein, J. *Macromolecules* **1987**, *20*, 1757.
(36) Cowie, J. M. G.; Fernadez, M. E.; et al. *Polymer* **1992**, *33*, 2744.
(37) Kim, C.; Paul, D. *Macromolecules* **1992**, *25*, 3097.