

Phase Transitions in Polymer Blends via ^{129}Xe NMR Spectroscopy

J. H. Walton, J. B. Miller,* and C. M. Roland

Chemistry Division, Code 6120, Naval Research Laboratory, Washington, D.C. 20375-5342

J. B. Nagode

Geo-Centers Inc., Fort Washington, Maryland 20744

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Introduction

Recently ^{129}Xe NMR has been used to study polymer blends.^{1,2} The inertness of xenon and the dependence of its chemical shift on the local environment make it an attractive probe of morphology. It is particularly advantageous for blends whose components have nearly identical glass transition temperatures, which are difficult to study with conventional techniques.² For a phase-separated, two-component blend, the ^{129}Xe NMR spectrum will exhibit two resonances, whereas the homogeneous morphology of a miscible blend results in a single NMR peak. In this work ^{129}Xe NMR is applied to mixtures of polyisoprene (PIP) and polybutadiene (PBD), which have been studied extensively in this laboratory³⁻⁶ and elsewhere.⁷⁻¹⁰ When the polybutadiene has a vinyl content of less than about 75%, mixtures with 1,4-polyisoprene exhibit a lower critical solution temperature (LCST), which has been attributed to equation of state effects³ or to the copolymer effect.¹⁰ By selecting components of the appropriate molecular weights, the phase transition can be made to occur at readily accessible temperatures, allowing study of the kinetics of phase separation or component dissolution.

Experimental Section

The blend was comprised of 34% by volume of 1,4-polyisoprene and 66% polybutadiene (8% vinyl content), mixed by dissolution in cyclohexane followed by vacuum drying. PIP and PBD, from Scientific Polymer Products, had weight-average molecular weights equal to 115 000 and 23 000, respectively (polydispersities < 1.1).

NMR samples were sealed in a xenon atmosphere (details given elsewhere²) for measurement at the ^{129}Xe frequency of 83 MHz. Free induction decays (FIDs) were generated with a 30° pulse and a high repetition rate. A mild exponential filter was applied to the FIDs prior to Fourier transformation. The reported chemical shifts are relative to gas at 0.5 atm and are precise to ± 0.2 ppm. All spectra were obtained at room temperature (<LCST), since at higher temperatures the decreased solubility of xenon in these polymers resulted in weak signal intensities.

A Perkin-Elmer DSC-2 was used for calorimetry. Specimens 5-7 mg in weight were heated at 320 °C/min to 100 °C; after a 30-min dwell time, they were quenched at >200 °C/min. The heat capacity was then measured in the conventional manner by cooling to -125 °C, followed by heating back to room temperature. The scan rate was 20 °C/min, with the data measured during the heating cycle.

Results and Discussion

In order for ^{129}Xe NMR to be applied to a given blend, the chemical shift must be different for xenon dissolved in the pure components. In Figure 1 is shown the ^{129}Xe NMR spectrum obtained for pure PIP and PBD, simultaneously in the sample chamber but physically separated. Two resonances are seen with a separation of 8 ppm. The spectrum of the mixed polymers, prepared by solution

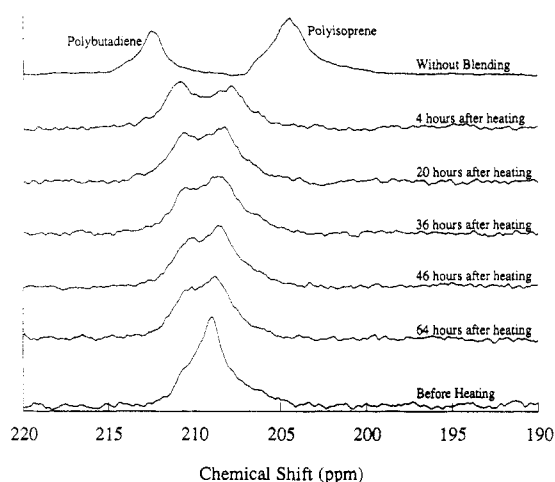


Figure 1. ^{129}Xe NMR spectra of xenon dissolved in the miscible blend (bottom), at various times after phase separation by heating, and corresponding to complete phase separation (top). The latter was actually obtained by placing physically distinct pieces of the respective pure polymers in the NMR tube. Redissolution of the components is not complete even after 64 h.

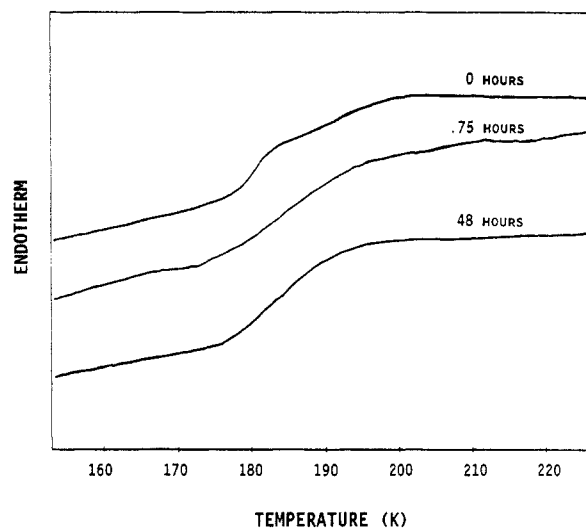


Figure 2. DSC results for the blend annealed at room temperature for the indicated time periods subsequent to a 30-min period at 100 °C. The latter is above the LCST and thus gives rise to a phase-separated morphology. The redissolution of the components is reflected in the DSC data; however, after just 45 min of annealing the thermogram suggests homogeneity, notwithstanding the NMR data in Figure 1.

blending or annealed at room temperature for several weeks, reveals a single peak indicative of a homogeneous phase morphology. (Fast diffusional exchange of the xenon between small phase-separated domains was ruled out using the technique described in ref 2.) This result agrees with the known miscibility of the blend under these conditions.³ When the sample is heated to 100 °C for 30 min, followed by quenching to room temperature, splitting of the resonance is observed. This clearly demonstrates that phase separation has occurred, consistent with the previously reported LCST = 70 °C for this mixture.³ As the sample is maintained at room temperature (<LCST), the splitting of the resonance and its breadth is reduced over time, reflecting redissolution of the components.

In Figure 2 are shown the DSC results obtained on the same blend subjected to an equivalent thermal history. While the phase separation effected by heating to 100 °C causes a smearing out of the thermal transition, this evidence of a phase-separated structure is not as distin-

guishing as the xenon NMR spectrum. Moreover, after only 45 min of annealing at room temperature, distinct indication of a multiphase structure is gone; the DSC thermogram has nearly assumed the appearance seen for the original homogeneous sample. Notwithstanding the persistence of a phase-separated structure as directly evidenced by the NMR data in Figure 1, the DSC measurement no longer senses the presence of distinct phases. At least for this particular blend, the xenon NMR experiment provides a higher resolution probe of phase morphology than the more conventional DSC technique.

The detailed relationship between the phase morphology and the NMR spectrum is described by theories for chemically exchanging systems.^{11,12} In the slow exchange limit (whereby a xenon atom remains in a particular domain for a time long on the NMR time scale), the observed chemical shifts will be exactly equal to the chemical shifts of xenon in the respective pure environments. This is the situation prevailing in previous studies of blends lying well within the two-phase region of the phase diagram.^{1,2} However, xenon diffuses rapidly between smaller domains, reducing the separation of the respective NMR resonances as given by

$$\delta\omega = \delta\omega_{\infty} \left[1 - \frac{2}{\tau^2(\delta\omega_{\infty})^2} \right]^{1/2} \quad (1)$$

where τ is half the average time the xenon atom resides in a given domain and $\delta\omega_{\infty}$ is the frequency difference between the sites when there is no exchange. This relation explicitly assumes $\delta\omega_{\infty}$ is much larger than the line width of the individual resonances and the xenon populations in the two domains are equal, with the xenon spending equal time in each domain. As seen in Figure 1, for these polymers $\delta\omega_{\infty}$ is about 6 times the natural line widths, so that the first assumption is valid. Although the polybutadiene is present in approximately 2-fold excess, the xenon populations in the two polymers are nearly equal, as determined by the relative integrated intensities of the two peaks at the top of Figure 1; thus, the second assumption is also valid. The third assumption is valid because the rapid diffusion of xenon between the two domains and the slow change in composition of the domains maintain an equilibrium with respect to the two xenon populations.

The exchange mechanism for xenon in polymers is Fickian diffusion. In three dimensions the root-mean-square distance a xenon atom travels in a time period t is given by

$$X_{RMS} = (6Dt)^{1/2} \quad (2)$$

where D represents the xenon diffusion coefficient in the polymer. Identifying t as 2τ and combining eqs 1 and 2, an average domain size is calculated to equal

$$X_{RMS} = \left[\frac{288D^2}{(\delta\omega_{\infty})^2 - (\delta\omega)^2} \right]^{1/4} \quad (3)$$

In the fast exchange limit there is no splitting, while in the slow exchange limit the splitting approaches its maximum and is insensitive to domain size. Since the diffusion coefficient of xenon is temperature dependent, when either limiting condition prevails, experiments can be conducted at another temperature so that the intermediate exchange regime is attained.

It is tempting to suggest that eq 3 allows the measurement of domain size as a function of time. However, this implies the unphysical situation that the domains of the two phases are simply getting smaller. In fact the two

polymers are recombining by interdiffusion, creating a concentration gradient between the phase-separated domains.¹³ Thus, there is a smooth variation in the polymer composition as a function of distance, with the densities evolving continuously in time. This time-dependent variation makes proper mathematical treatment of the ^{129}Xe NMR line shape as a function of time extremely difficult. Since the xenon chemical shift is sensitive to its local environment, knowledge of the average local environment during the course of the xenon diffusion would be required. Furthermore, the average local environment (morphology) in a blend is not the average of the environments of the two pure components due to concentration fluctuations^{14,15} and, for example, nonzero excess mixing volumes.^{1,3} Nonetheless, if the polymer blend remains above the LCST long enough for substantial phase separation to occur, initially a two-phase model is appropriate.

We assume complete phase separation into the pure polymer components as the initial condition. From the chemical shifts of the two peaks in the xenon spectrum a value of X_{RMS} can be obtained. Using the appropriate values in eq 3 ($D = 1.4 \times 10^{-7} \text{ cm}^2/\text{s}$ in polyisoprene; $\delta\omega = 2100 \text{ rad/s}$; $\delta\omega_{\infty} = 4200 \text{ rad/s}$), an initial average polyisoprene domain size produced by the annealing at $T > \text{LCST}$ is calculated to be on the order of $0.3 \mu\text{m}$. This is sufficiently large that distinct glass transitions can be resolved using DSC,¹⁶⁻¹⁸ as was observed herein. The polymers then interdiffuse. When the polymer composition within a defining volume, whose diameter is given by the distance over which xenon can diffuse on the time scale of the experiment, is the same for all defining volumes within the sample, the NMR spectrum will exhibit one line.

The time required for a single resonance to appear in the NMR spectrum is in a convoluted way related to the diffusion constants of the polymers. As has been addressed in studies of the rate at which adhesion develops via interdiffusion across an interface, this is a complicated problem.¹⁹⁻²³ If we assume that the time required for collapse of the NMR lines, 60 h, is roughly the time required for diffusion over approximately $0.3 \mu\text{m}$, from eq 2 a value for an average polymer diffusion coefficient of $\approx 5 \times 10^{-15} \text{ cm}^2/\text{s}$ is obtained. This certainly represents an lower bound, since the 60 h is a measure of the time for homogenization of the morphology, not simply polymer translation. Note also that if the assumptions that the blend phase separates into the pure polymer components and that phase separation was complete after heating above the LCST are incorrect, the estimate of X_{RMS} will be too low. This would also lead to underestimation of the diffusion constant of the polymers.

Conclusions

For the polyisoprene/polybutadiene blend studied herein, the resolution advantage of ^{129}Xe NMR over a more conventional method such as DSC for probing blend morphologies has been demonstrated. The time scale over which the ^{129}Xe NMR can distinguish separate domains is remarkably longer than DSC. The relative insensitivity of DSC is due, in part, to the difficulty in detecting changes in slope in the DCS curves (as opposed to peak separation in the NMR) and, in the present case, the relatively small differences in T_g of the two polymers (approximately 30 K). In general, the relative merits of xenon NMR spectroscopy will vary according to the magnitude of $\delta\omega_{\infty}$ and the diffusion coefficient of xenon in the particular system of interest. However, the latter quantity is not

expected to vary greatly among polymers, and recent measurements in our laboratory reveal a wide range of values for the chemical shift for xenon dissolved in various polymers.²⁴ This indicates that $\delta\omega_\infty$ will be large for many blend systems, suggesting that ^{129}Xe NMR can be usefully applied.

Herein we have used xenon NMR to follow, at least in a qualitative fashion, the kinetics of phase redissolution following a temperature jump. A previous study² demonstrated how upper bounds on domain sizes can be extracted from xenon NMR data when the system is in the slow exchange limit; i.e., the lifetime of a xenon atom in a particular domain is long on the NMR time scale. Although domain sizes can also be determined from 2-D NMR experiments²⁵ when the domain sizes are static, the method is difficult to employ when domain sizes are changing over time.

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References and Notes

- (1) Brownstein, S. K.; Roovers, J. E. L.; Worsfold, D. J. *Magn. Reson. Chem.* **1988**, *26*, 392.
- (2) Walton, J. H.; Miller, J. B.; Roland, C. M. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 527.

- (3) Trask, C. A.; Roland, C. M. *Polym. Commun.* **1988**, *29*, 332.
- (4) Roland, C. M.; Trask, C. A. In *Advances in Polymer Blends and Alloys Technology*; Kohudic, M. A., Finlayson, K., Eds.; Technomic: Lancaster, PA, 1989; p 100.
- (5) Roland, C. M. *Rubber Chem. Technol.* **1989**, *62*, 456.
- (6) Tomlin, D. W.; Roland, C. M. *Macromolecules* **1992**, *25*, 2994.
- (7) Bartenev, G. M.; Kongarov, G. S. *Rubber Chem. Technol.* **1963**, *36*, 668.
- (8) Cohen, R. E. *Adv. Chem. Ser.* **1982**, *193*, 489.
- (9) Kawahara, S.; Akiyama, S.; Ueda, A. *Polym. J.* **1989**, *21*, 221.
- (10) Sakurai, S.; Jinnai, H.; Hasegawa, H.; Hashimoto, T.; Han, C. C. *Macromolecules* **1991**, *24*, 4839.
- (11) Gutowsky, H. S.; Holm, C. J. *Chem. Phys.* **1956**, *25*, 1228.
- (12) Pople, J. A.; Schneider, W. G.; Bernstein, H. J. *High Resolution Nuclear Magnetic Resonance*; McGraw-Hill: New York, 1959.
- (13) Hashimoto, T.; Tsukahara, Y.; Kawai, H. *Macromolecules* **1981**, *14*, 708.
- (14) Roland, C. M.; Ngai, K. L. *Macromolecules* **1991**, *24*, 2261.
- (15) Roland, C. M.; Ngai, K. L. *J. Rheol.* **1992**, *36*, 1691.
- (16) Kaplan, D. S. *J. Appl. Polym. Sci.* **1976**, *20*, 2615.
- (17) Braun, H. G.; Rehage, G. *Angew. Macromol. Chem.* **1985**, *131*, 107.
- (18) Roland, C. M. *Rubber Chem. Technol.* **1989**, *62*, 456.
- (19) Skewis, J. D. *Rubber Chem. Technol.* **1966**, *39*, 217.
- (20) Kramer, E. J.; Green, P. F. *Polymer* **1984**, *25*, 473.
- (21) Green, P. F.; Doyle, B. L. *Phys. Rev. Lett.* **1986**, *57*, 2407.
- (22) Roland, C. M. *Macromolecules* **1987**, *20*, 2557.
- (23) Roland, C. M.; Nagode, J. B. *Polymer* **1991**, *32*, 505.
- (24) Miller, J. B.; Walton, J. H.; Roland, C. M. *Macromolecules*, submitted for publication.
- (25) Ernst, R. R.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*; Clarendon: Oxford, U.K., 1987.