

^{129}Xe NMR as a Probe of Polymer Blends

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SYNOPSIS

The miscibility of two-component polymer blends has been investigated using xenon-129 (^{129}Xe) nuclear magnetic resonance (NMR) to probe the phase morphology. The chemical shift of ^{129}Xe dissolved in a given polymer is unique, thus heterogeneous blends with large domain sizes exhibit two ^{129}Xe NMR lines. When a single resonance is obtained, the data are consistent with miscibility, yielding an upper bound on the domain size. The temperature dependence of the relative solubilities and chemical shifts of ^{129}Xe dissolved in the pure components may allow a determination of the phase morphology in blends exhibiting a single resonance. The method is used to demonstrate that polychloroprene and 25% epoxidized 1,4-polyisoprene form a miscible blend.

Keywords: nuclear magnetic resonance (NMR) with ^{129}Xe as probe of polymer blends • blends, ^{129}Xe as NMR probe of • rubbery polymer blends, ^{129}Xe as NMR probe of

INTRODUCTION

Polymer blends have been much investigated recently.¹⁻⁸ Given the almost negligible mixing entropy, the thermodynamics, and hence the incidence of miscibility, are governed substantially by the component interactions.¹⁻⁴ Characterization of these interactions is obviously useful in the study of polymer blends.

The chemical shift of ^{129}Xe is well known to be sensitive to its environment.⁹⁻¹⁵ To a first approximation, the chemical shift is proportional to the number of collisions per unit time the xenon experiences, or equivalently to the density of its environment.^{11,13,16-21} This is due to the large number of electrons in the xenon atom and the resulting large fluctuation of the magnetic field at the nuclear site produced by a collision.^{10,19,20} Collisions shift the ^{129}Xe resonance to higher frequency.

To a lesser extent, the chemical shift of Xe is also sensitive to the chemical structure of its collision partner.^{9,10} ^{129}Xe has been used to study internal surfaces in zeolites,^{10,11,22-24} clathrates,^{21,25} and mor-denites,²⁶ as well as void sizes in amorphous silica, alumina, and silica-alumina.²⁷

Xe is soluble in many polymers,²⁸⁻³³ with the at-

oms residing in the free volume. Since the chemical shift is proportional to the collision rate, it provides a measure of the free volume. Below the glass transition temperature, T_g , segmental motion of the polymer chains is suppressed, so that Xe atoms are trapped in different sites. The distribution in local free volume produces variations in chemical shift resulting in an inhomogeneously broadened ^{129}Xe NMR line.²²⁻²⁸ At temperatures above T_g , Xe readily diffuses between sites in response to fluctuations in the polymer segment density. Rapid diffusion collapses the inhomogeneously broadened ^{129}Xe NMR resonance into a narrow line; the observed chemical shift is an average over the inhomogeneously broadened line. In heterogeneous systems, for example, microphase-separated styrene-isoprene block copolymers, the NMR spectrum exhibits wide and narrow components when obtained at a temperature intermediate to the component T_g 's.²⁸ These correspond to ^{129}Xe in the styrene and isoprene domains, respectively.

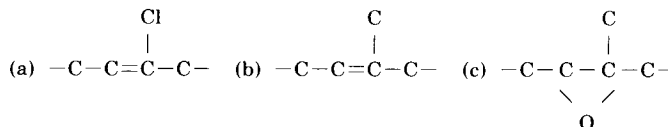
In this work we have investigated Xe dissolved in polychloroprene (PC), polyisoprene (PIP), and epoxidized polyisoprene (EPI) (where the oxirane groups of the latter are randomly situated along the chain at a concentration of either 50 (EPI50) or 25 (EPI25) mol %). These materials are shown in Table I. It has previously been demonstrated that blends of PC and EPI50 are miscible.³ A single com-

Table I. Polymers Investigated; PIP Forms Heterogeneous Blends with the Other Three Polymers^a

Polymers	T_g	Repeat Unit	Miscible with PC?
Polychloroprene (PC)	239 K	a	—
Polyisoprene (PIP)	203 K	b	No
50% Epoxidized ^b PIP (EPI50)	258 K	b and c	Yes ³
25% Epoxidized ^b PIP (EPI25)	239 K	b and c	?

^a Blends of EPI50/EPI25 were not investigated herein.

^b Random copolymer of 2,3-epoxy-2-methylbutane and 2-methyl-2-butene, where the composition refers to mol% of the former.



position-dependent glass transition temperature, intermediate to the pure components' T_g 's (239 K for PC and 252 K EPI50), is observed for the mixture.³ The miscibility results from an attractive interaction between the oxirane group on the EPI and the Cl atom of PC.^{3,4} The miscibility of EPI25 with PC is difficult to ascertain from T_g measurements due to the near equivalence of the glass transition temperatures of pure EPI25 and PC.

EXPERIMENTAL

Samples of the four polymers PIP, EPI50, EPI25, and PC, as well as equal-weight blends of PIP/EPI50, PIP/EPI25, PIP/PC, EPI50/PC, and EPI25/PC were studied. The sample chamber was made from polyetherimide (Ultem), in which Xe has negligible solubility according to the NMR measurements. The apparatus used to seal the chamber was similar to that used by Lee³⁴ for diamond anvil cells. The sample chamber was placed in a pressure bomb. The seal for the bomb included a viton O-ring on the outer circumference of a $\frac{1}{4}$ in. rod used to screw in the brass cap of the chamber. After evacuation, Xe gas is introduced into the bomb and chamber to yield a final pressure of 12 atmospheres at room temperature.

The NMR measurements were made in a 7.05 Tesla magnetic field at the ^{129}Xe NMR frequency of 83 MHz. Free-induction decays (FIDs) were generated with a 90 degree pulse and 100 scans taken with a repetition rate greater than $5T_1$ s. T_1 of ^{129}Xe in the individual polymers was measured at each temperature; it varied from 5 to 20 s. Precise temperature control (± 0.2 deg.) was critical to obtaining

reproducible results because the chemical shift is highly temperature dependent. The chemical shift values reported herein (referenced to the chemical shift of undissolved ^{129}Xe gas at 12 atm) correspond to the center of the resonances, as determined by fitting to the spectra, as appropriate, one or two Lorentzians. The results were reproducible to ± 0.1 ppm. The solubility of Xe in PC, EPI50, and EPI25 was measured relative to that in PIP by integration of the NMR spectral intensities in blends of PIP with these polymers.

RESULTS AND DISCUSSION

Figure 1 shows the ^{129}Xe spectra obtained from the four pure polymers present simultaneously but physically separate in the sample chamber. Four peaks are apparent in Figure 1, although the lines due to ^{129}Xe in PC and EPI50 partially overlap. This figure demonstrates that the chemical shifts of ^{129}Xe are indeed different in these polymers.

The results for the blends PC/PIP, EPI50/PIP, and EPI25/PIP are shown in Figure 2. These blends are known to be immiscible, and indeed two ^{129}Xe NMR lines are observed due to the presence of Xe residing in either phase. The lines in these blends occur at the same chemical shift as those in the corresponding pure polymer. The observation of two resonances is direct, unambiguous evidence for a phase-separated morphology. From a knowledge of the diffusion coefficients, the domain sizes could be determined using two-dimensional NMR techniques.³⁵

Figures 3 and 4 show the ^{129}Xe NMR spectra for the respective blends EPI50/PC and EPI25/PC

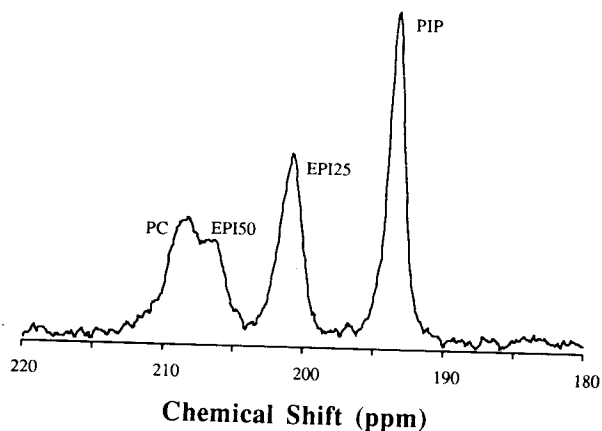


Figure 1. Room temperature ¹²⁹Xe NMR spectrum obtained with four pieces of the pure polymers simultaneously in the sample chamber. The Xe NMR line from each is readily apparent.

(only the former is known to be miscible).³ To allow comparison with the chemical shifts in the corresponding pure polymers, the spectra of ¹²⁹Xe in phase separated blends of these with PIP are also shown in the figures. In Figure 3 the ¹²⁹Xe lines of the pure polymers are approximately 2.5 ppm different with 2 ppm linewidths. The ¹²⁹Xe resonance in the blend falls between those of the pure polymers and also has a linewidth of about 2 ppm. These linewidths and separations are just sufficient to be resolved. Note the lineshape for the PC/EPI50 blend is different from the lineshape seen in Figure 1, for which separate pieces of the pure polymers were in

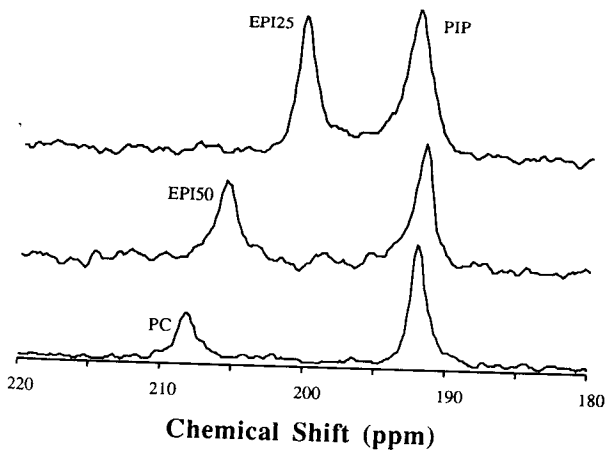


Figure 2. ¹²⁹Xe NMR spectra of three immiscible blends (PC/PIP, EPI50/PIP, and EPI25/PIP). The chemical shifts and lineshapes are equivalent to those measured in the corresponding pure polymers. Data were taken at approximately 48°C.

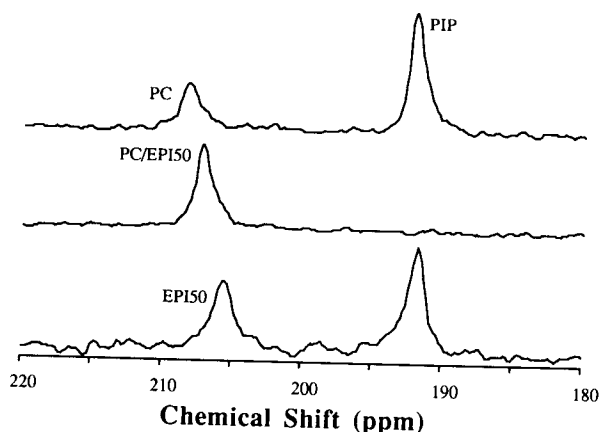


Figure 3. Spectra of blends PC/PIP, EPI50/PIP, and PC/EPI50. The NMR line of ¹²⁹Xe in PC/EPI50 blend (the known miscible blend) is between that of PC and EPI/50. Data were taken at approximately 48°C.

the sample chamber together. The peaks in the spectrum in Figure 4 for the blend (of unknown phase morphology) are more clearly resolved. While the pure component lines are still 2 ppm wide, they are separated by about 8 ppm. Their blend exhibits one NMR line at a frequency between those of the pure components.

The observation in Figures 3 and 4 of a single ¹²⁹Xe NMR line is consistent with, but not conclusive evidence for, miscibility in the mixtures. There are two physical circumstances which will produce one ¹²⁹Xe NMR peak. The blend may in fact be miscible, or the blend may be phase separated into small domains. In the latter situation, sufficiently rapid

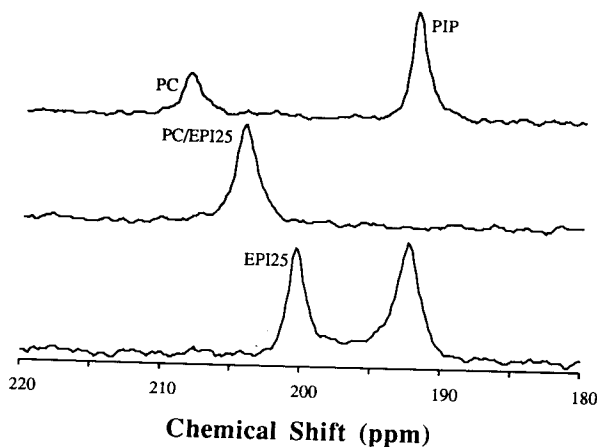


Figure 4. Spectra of blends PC/PIP, EPI25/PIP, and PC/EPI25. The NMR line of ¹²⁹Xe in PC/EPI25 blend is between that of PC and EPI/25. Data were taken at approximately 48°C.

diffusion will allow a Xe atom to move between the chemically distinct phases many times on the NMR time scale. This rapid exchange, known as chemical exchange,^{36,37} would collapse the two resonances into a single chemical shift. The transition from the slow to the fast exchange limit has been observed for ¹²⁹Xe in biological systems.¹² To assess miscibility the occurrence of this chemical exchange process must be distinguished from a single line arising from a miscible blend morphology. In the latter, the ¹²⁹Xe chemical shift simply is averaged over the distribution of available free-volume sites. In the fast exchange limit, averaging occurs over the distinct distributions of the two separate phases.

An estimate can be made of the largest domain size for which the observation of a single NMR line is possible. The average distance a molecule diffuses in time τ is:³⁸

$$X_{\text{RMS}} = (2D\tau)^{1/2} \quad (1)$$

where D is the diffusion coefficient. In the fast exchange limit,

$$\tau(\delta\omega) \ll 1 \quad (2)$$

where $\delta\omega$ is difference in the chemical shifts of Xe in the pure components. Combining eqs. (1) and (2) yields an upper bound on the domain size:

$$X_{\text{domain}} \ll (2D/\delta\omega)^{1/2} \quad (3)$$

The diffusion coefficient for Xe in polyisoprene at 25°C is reported to be ca. 4×10^{-7} cm²/s.²⁸ Literature values for the diffusion coefficient of Xe in the other polymers studied are unavailable, but if 10^{-6} cm²/s is assumed for the average diffusion constant of xenon in the PC/EPI25 blend, an upper bound for the domain size of 0.6 μm is obtained.

When the domains are small and diffusion is fast, the spectral position of the collapsed resonance can

Table II. Chemical Shifts and Relative Solubilities (Referenced to PIP) of ¹²⁹Xe in the Polymers^a

Polymer	Temperature (°C)	Solubility Relative to PIP (PIP = 1)	Polymer Chemical Shift (ppm)	PIP Chemical Shift (ppm)
PC (-0.228 ppm/°C)	47.6	0.50 ± 0.011	208.2	192.2
	31.6	0.49 ± 0.005	211.5	195.6
	14.7	0.37 ± 0.006	215.6	199.3
EPI50 (-0.218 ppm/°C)	-5.2	0.34 ± 0.009	220.2	203.5
	48.2	0.80 ± 0.020	205.7	192.0
	31.8	0.72 ± 0.008	209.1	195.3
EPI25 (-0.219 ppm/°C)	14.7	0.53 ± 0.016	213.0	199.0
	47.8	0.78 ± 0.031	200.4	192.6
	31.6	0.87 ± 0.025	204.0	195.8
PC/EPI25 (-0.219 ppm/°C)	15.0	0.86 ± 0.026	207.7	199.3
	-5.0	0.84 ± 0.008	212.0	203.4
	47.6	—	207.2	—
PC/EPI50 (-0.219 ppm/°C)	31.6	—	210.4	—
	14.7	—	214.0	—
	47.5	—	204.3	—
PC/EPI25 (-0.212 ppm/°C)	31.5	—	207.6	—
	14.5	—	211.3	—
	-5.0	—	215.4	—
PC/EPI50 calculated (-0.227 ppm/°C)	47.6	—	206.6	—
	31.6	—	210.1	—
	14.7	—	214.1	—
PC/EPI25 calculated (-0.205 ppm/°C)	47.5	—	203.5	—
	31.5	—	206.7	—
	14.5	—	210.0	—
	-5.0	—	214.3	—

^a The chemical shifts are given relative to the gas peak at 12 atmospheres. For the blends, the calculated chemical shifts were obtained using eq. 4. The measured chemical shifts are precise to ± 0.1 ppm and the errors in the calculations are < 0.1 ppm. The slopes of the chemical shift versus temperature curves, obtained from linear least-squares fitting, are given in parentheses. The slope for PIP is 0.211 ppm/°C.

be calculated. The chemical shift value in the fast-exchange limit is:

$$\sigma_{\text{avg}} = \frac{((1 - w_b)\rho_a\sigma_a + w_b\rho_b\sigma_b)}{((1 - w_b)\rho_a + w_b\rho_b)} \quad (4)$$

where the chemical shifts of the ^{129}Xe in the two components of the blend are represented by σ_a and σ_b , respectively, ρ_a and ρ_b are the relative solubilities of ^{129}Xe per unit mass of components a and b , and w_b is the mass fraction of component b in the blend. Thus, the frequency of the Xe resonance from the blend should depend only on the frequency of the pure component lines and the relative solubilities of Xe in the two components. On the other hand, if the mixture were truly miscible, the homogeneous morphology could impart a complex dependence of the spectral frequency on the interactions between the components. Thus, comparison of calculated and observed chemical shifts provides a means to further assess the phase morphology. If the observed value is different from the chemical shift calculated using eq. (4), then the blend is miscible.

The relative solubilities of Xe in the polymers are listed in Table II, along with the calculated and measured chemical shifts. The solubility of ^{129}Xe in PC, EPI50, and EPI25 relative to PIP was measured by direct integration of the ^{129}Xe peaks from the 50% by weight blends of PIP with the other polymers. The measured chemical shifts are reproducible to ± 0.1 ppm, and the errors in the calculated chemical shift, obtained by propagation of errors through eq. (4), were determined to be < 0.1 ppm.

The criterion for determination of miscibility is that the ^{129}Xe NMR data from a blend not agree with the fast exchange model. As seen in Table II and Figure 5, the data for the blend PC/EPI25 does not agree with the calculation [eq. (4)] which assumes the fast exchange limit. Thus, by contradiction the blend PC/EPI25 is demonstrated to be miscible. This conclusion could not be drawn from measurements of glass transition temperatures due to the similarity of the component T_g 's.³

For the miscible blend of PC with EPI50 there is coincidental agreement near 15°C between the predicted and measured chemical shift (Fig. 5). Fortuitous agreement between the experimental data and the fast exchange limit calculations is, of course, possible at some temperature. Only agreement at all temperatures demonstrates the exchange model. If the blend is actually miscible, however, agreement at all temperatures is unlikely. Chemical shifts are observed to have linear temperature dependencies over moderate temperature ranges.³⁹⁻⁴¹ In PC/

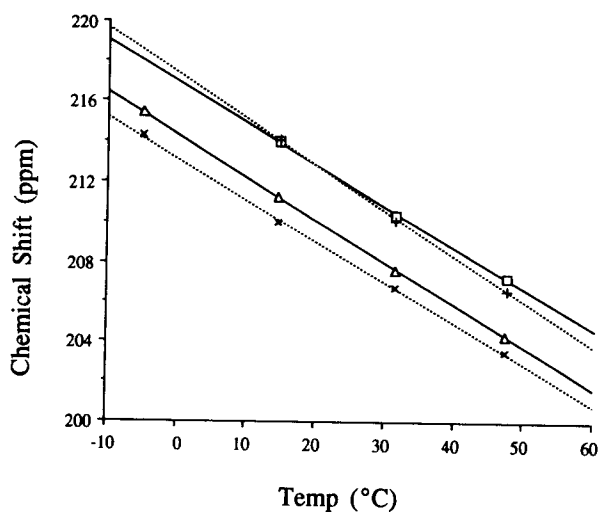


Figure 5. Chemical shifts measured at various temperatures for blends PC/EPI25 (Δ) and PC/EPI50 (\square), respectively. Solid lines are linear least-squares fits to the data. Also shown are calculations using eq. (4) for PC/EPI25 (\times) and PC/EPI50 ($+$) with their corresponding linear least-squares fits as dashed lines. Error bars for the calculation are approximately the size of the symbols.

EPI50 the experimental and calculated plots of chemical shift versus temperature have very different slopes, however, which is evidence for their phase homogeneity. Thus a stronger criterion for proof of miscibility is that the temperature dependence of the predicted and measured shifts be different.

Additional corroboration of miscibility can be attempted by cooling the sample in order to lower the diffusion coefficient and thus move away from the putative fast exchange limit. In this event the NMR line will split into two lines and exhibit spectra as seen for the immiscible blends (Fig. 2). The NMR spectra of PC/EPI50 and PC/EPI25, however, showed no evidence of such splitting; the respective resonances simply broadened as the temperature was reduced. This broadening accounts for the lack of a data point at -5°C for the blends containing EPI50 in Figure 5.

CONCLUSIONS

The phase morphology of two-component polymer blends has been investigated using ^{129}Xe NMR. The technique has been shown to be a useful probe of polymer blends, with the observation of two lines in the ^{129}Xe spectrum providing an unambiguous signature of a phase separated morphology. The spatial resolution of this morphological probe depends both on the diffusion constant of the Xe and the difference in chemical shifts of xenon in the components.

One line in the NMR spectrum of a blend is consistent with miscibility. However, such an observation does not prove thermodynamic miscibility, since small domains and rapid diffusion could give this result. By measuring the temperature dependence of both the relative solubility and the chemical shift of ^{129}Xe in the polymers, a corroboration of miscibility can be attempted.

This approach has been employed here to demonstrate that a blend of polychloroprene and 25% epoxidized polyisoprene form a miscible mixture. More common techniques for assessing miscibility, which rely on a difference in T_g 's of the components, are inapplicable to this blend. Miscibility in the mixture arises from attractive forces between the oxirane group on the EPI and the Cl atoms of the PC. These interactions underlie miscibility in PC/EPI50 blends,^{3,4} wherein the density of interaction sites is twice that for the EPI25 containing mixture. At a low enough concentration of oxirane groups, the excess enthalpy arising from the specific interactions will be overwhelmed by the endothermic van der Waal's energy, thus effecting immiscibility.

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