NMR STUDY OF MISCIBILITY IN POLYEPICHLOROHYDRIN/ POLY(VINYLMETHYLETHER) BLENDS

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ABSTRACT

^{129}Xe NMR spectroscopy is employed to demonstrate that polyepichlorohydrin and poly(vinylmethylether), which have virtually equal glass transition temperatures, form thermodynamically miscible blends. This conclusion is drawn from the appearance of a single resonance in the blend spectrum, at a chemical shift differing from that calculated for the fast exchange regime. ^{13}C NMR results are consistent with thermodynamic miscibility, and reflect the similarity of the component dynamics.

INTRODUCTION

The thermodynamics of polymer miscibility has received much attention over the years, and is at least qualitatively well understood. Of more relevance to the physical properties of blends, however, are the constituent dynamics; our understanding of this aspect of mixtures is much less developed. The inadequacy of available models becomes particularly evident when the components have very nearly the same glass transition temperature. Free volume ideas suggest that the glass transition temperature (T_g) and segmental relaxation times of mixtures will be intermediate to those of the pure components. Recent studies have demonstrated that this is the case only when the components have very different glass transition temperatures. Mixtures having components of nearly equal T_g exhibit interesting new physics. It has been observed that the glass transition temperature and segmental relaxation times of certain blends can be *less* than those of either neat component. This striking anomaly occurs in mixtures of poly(vinylethylene) with polychlorinated biphenyl,[1,2] poly(methylphenylsiloxane) with 1,1-*bis*-(*p*-methoxyphenyl)cyclohexane,[3] and epoxidized natural rubber with polychloroprene.[4]

An equally surprising, but opposite anomaly, has recently been seen in the segmental relaxation behavior of blends of polyepichlorohydrin (PECH) and poly(vinylmethylether) (PVME).[5] The glass transition temperatures of the neat polymers are within one degree of one another; however, a 50/50 blend has a T_g more than 2 degrees *higher* in temperature than the T_g of either neat component. Similarly, the segmental relaxation times measured at a given temperature using dielectric spectroscopy, while virtually equal for the pure components, were as much as a factor of 6 slower in the mixtures.[5] Although the results are intriguing, thermodynamic miscibility could not be definitively established in that work from the DSC experiments carried out on the PECH/PVME blends.[5]

While blends of nearly equal T_g are of current interest, an obvious difficulty in their study is that commonly employed techniques for assessing miscibility rely on a difference in component glass transition temperatures. We have demonstrated recently the utility of ^{129}Xe NMR spectroscopy for probing the phase morphology of blends.[6,7] The chemical shift of dissolved ^{129}Xe is sensitive to its environment[8-12]; consequently, a phase separated blend usually exhibits two ^{129}Xe NMR lines. The observation of a single resonance in the spectrum indicates a homogeneous morphology, which in favorable circumstances can be ascribed to thermodynamic miscibility. The NMR spectra must be obtained at temperatures above the sample's glass transition, in order to avoid the line broadening that results from trapping of xenon interstitially in a glassy matrix.[13-16] However, the ^{129}Xe chemical shift is not related to the glass transition temperature *per se*, and therefore ^{129}Xe NMR can provide phase information even for blends of equal T_g components.

In addition to the intriguing dynamics of miscible blends, PECH/PVME is of interest because both components are rubbers. There are very few elastomeric miscible blends. With the exception of trivial cases such as isotope mixtures or blends of similar copolymers, the only miscible blends comprised of solely rubbery constituents are polyisoprene with poly(vinylethylene),[17,18] poly(epichlorohydrin) with certain polyacrylates,[19] and epoxidized polyisoprene with either chlorinated polyethylene[20] or polychloroprene.[6,21]

Herein we describe the application of ^{129}Xe NMR to study miscibility in blends of polyepichlorohydrin and poly(vinylmethylether). ^{13}C NMR measurements were also carried out to examine the unusual dynamics suggested previously in dielectric spectroscopy experiments.[5]

EXPERIMENTAL

The polyepichlorohydrin [Hydrin-45, ML 1 + 4(100°C) = 45], obtained from Zeon Chemicals, Inc., was dissolved in tetrahydrofuran (THF) and filtered prior to use, to assure an absence of gel. The poly(vinylmethylether), received as a 50% aqueous solution (Scientific Polymer Products #025C, M.W. ~ 90,000), was vacuum dried at 80°C to constant weight. The blend was prepared by dissolving equal weights of the two polymers into acetone, followed by vacuum drying.

Calorimetry employed a Perkin Elmer DSC-7. The sample was cooled at 10°C/min to 30 degrees below T_g. Data was taken upon subsequent warming at the same rate.

For ^{129}Xe NMR, samples were exposed to 2.7 atmospheres of xenon gas for 21 days at room temperature. NMR measurements were subsequently carried out using a Bruker MSL 300 at the ^{129}Xe Larmor frequency of 83.0 MHz. Free induction decays were generated with a 45 degree pulse until sufficient signal intensity was obtained to clearly identify the peaks. No apodization of the decay was used prior to Fourier transformation. All spectra were obtained at room temperature. The reported chemical shifts are relative to the resonance of the undissolved ^{129}Xe gas contained in the NMR tube. Relative solubilities were determined by integration of the NMR signal measured with both neat polymers present, but physically separated, within the NMR tube.

^{13}C NMR spectra were also obtained using the Bruker NMR, with a double-tuned multinuclear magic angle spinning (MAS) probe equipped for 7 mm sample rotors. The Hartmann–Hahn cross polarization (CP) technique[22] was employed at temperatures where a sufficient static heteronuclear dipolar interaction was available for efficient cross polarization, as evidenced by observable CP signal intensity. At higher temperatures, where molecular motions substantially average the heteronuclear dipolar interaction, a single ^{13}C $\pi/2$ pulse (5 μs) was used with high power proton decoupling[23] during acquisition of the free induction decay. All spectra were obtained using magic angle spinning[24,25] at 3.0 kHz ± 5 Hz, along with 50 kHz radio frequency irradiation for proton decoupling.

RESULTS

^{129}XE NMR SPECTROSCOPY

^{129}Xe NMR spectrum of the pure polymers was obtained simultaneously by having both polymers present in the sample chamber but physically separated. As shown in Figure 1, the PVME and PECH have resonances at 209.8 ppm and 230.5 ppm respectively, a separation of 11,320 rad/s. A mixture of the polymers will exhibit only one resonance if the components are miscible. However, since the spectra are obtained above T_g, the xenon can readily diffuse between different sites. If a phase separated morphology exists in the blend, sufficiently rapid diffusion can collapse the ^{129}Xe NMR spectrum into a single line. Hence, small domains may appear in the NMR experiment as a homogeneous morphology; this is referred to as the fast exchange limit. In the opposite situation, corresponding to slow diffusion of the xenon between large domains, the splitting of the peaks equals that of xenon in the neat (physically

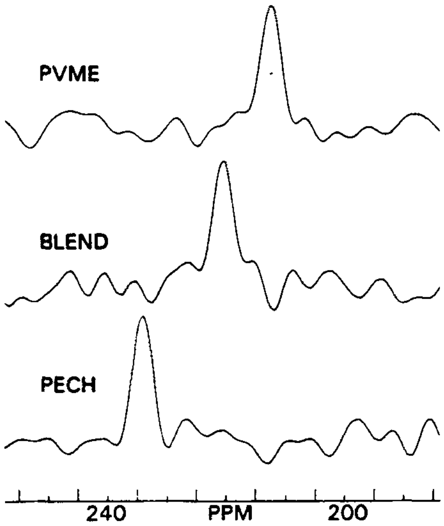

FIG. 1. — Room temperature ^{129}Xe NMR spectra for neat PVME, neat PECH, and a blend containing equal weights of the two polymers.

separated) materials. In this slow exchange limit, the splitting is maximal and insensitive to domain size.

Diffusion of xenon between domains will reduce the separation of the respective NMR resonances from that observed for the neat polymers according to[26,27]

$$\delta\omega = \delta\omega_\infty \sqrt{1 - \frac{2}{\tau^2(\delta\omega_\infty)^2}}, \tag{1}$$

where τ is the average time a xenon atom resides in a given domain and $\delta\omega_\infty$ is the frequency difference of the resonances for the neat components (= 11,320 rad/s). For sufficiently fast diffusion of xenon between the domains, $\delta\omega$ goes to zero, whereby only a single resonance is observed. This is known as the "fast exchange limit". Equation (1) assumes that the linewidth of the individual resonances is much less than $\delta\omega_\infty$. From the spectra in Figure 1, the pure polymers have a peak breadth of about 300 Hz, which is at least about a factor of 6 less than their separation; thus, Equation (1) can be applied.

The ^{129}Xe NMR spectrum for the PECH/PVME blend (Figure 1) consists of only a single peak at 217.7 ppm (relative to the xenon gas resonance), with a linewidth no greater than that observed in the pure components' spectra (*ca.* 300 Hz). Although this is indicative of a homogeneous phase morphology, it does not necessarily correspond to thermodynamic miscibility. We can calculate the maximum domain size capable of yielding a single resonance in the blend spectrum, that is, the largest domains for which fast exchange can still prevail. In a time period t, the Xe will diffuse an average distance given by

$$R = (6Dt)^{1/2}, \tag{2}$$

where D is the diffusion coefficient. Equating this t with 2τ, Equations (1) and (2) can be combined, whereby the largest domain size for fast exchange can be calculated; *i.e.*

$$R = 4.12\sqrt{\frac{D}{\delta\omega_\infty}}. \tag{3}$$

Although we do not know the diffusion coefficient of xenon in the present polymers, a value has been reported for natural rubber at 25°C, $D = 1.4 \times 10^{-7}$ cm^2/s.[28] Since PECH and PVME have a significantly higher T_g than natural rubber, we make the assumption that this value of D is an upper limit on the diffusion coefficient of xenon herein. Using this, along with the peak separation of the pure polymers ($\delta\omega_\infty$ = 11,320 rad/s), we calculate from Equation (3) that $R \sim 0.1$ μm. This demonstrates that extremely small domains would be necessary for the fast exchange limit to be achieved in this blend. It is more likely that the polymers are thermodynamically miscible.

This miscibility can be confirmed by comparing the chemical shift measured for xenon in the blend spectrum to that calculated for the fast exchange limit. The latter is given by[6]

$$\delta\omega_{\mathrm{fe}} = \frac{\phi_i x_i \delta\omega_i + \phi_j x_j \delta\omega_j}{\phi_i x_i + \phi_j x_j}, \tag{4}$$

where x_i is the relative solubility per unit mass of ^{129}Xe in the i^{th} component, and ϕ_i is the mass fraction of that component in the blend. Of course, if the mixture is actually thermodynamically miscible, the fast exchange prediction does not apply; hence, a comparison of the calculated and observed chemical shifts allows a corroboration of the phase morphology. Using the relative solubilities measured for ^{129}Xe in the two neat components (see Table I), we calculate from Equation (4) that $\delta\omega_{\mathrm{fe}}$ = 214.0 ppm. This predicted chemical shift differs significantly from the measured $\delta\omega_{\mathrm{exp}}$ = 217.7 ppm. Thus, the NMR results for PECH/PVME do not conform to that of a phase separated system in the fast exchange limit. The single resonance in the xenon spectrum is due to a homogeneous morphology associated with thermodynamic miscibility.

^{13}C NMR SPECTROSCOPY

^{13}C NMR spectroscopy was also carried out on the neat polymers and their mixture. At most temperatures, MAS averages out ^{13}C chemical shift anisotropy, while the radio frequency irradiation averages the ^{1}H–^{13}C dipolar interactions. This averaging gives rise to narrow resonances in the NMR spectra. At some temperature range, however, molecular motions transpiring on the time scale of the MAS (3 kHz) interferes with the MAS modulation of chemical shift anisotropy, causing inhomogeneous line broadening. At roughly this same temperature range, molecular motions occurring at the proton RF field strength (50 kHz) may also interfere with the modulation of the heteronuclear (^{1}H–^{13}C) dipolar interaction. Thus, there exists a temperature range over which significant spectral broadening will be observed. Temperature dependent ^{13}C NMR spectroscopy provides a measure of the range of temperature at which motion occurs within a certain range of frequencies (roughly 3 to 50 kHz herein). Interferences with MAS or RF decoupling do not occur at lower temperatures because the molecular motions are too slow, nor at higher temperatures for which the motions are too fast. This technique has been previously applied to various polymers.[29-34] Since the components of a blend can be distinguished from one another by their isotropic chemical shifts, the ^{13}C NMR technique enables the dynamics of the components within a mixture to

TABLE I

EXPERIMENTAL DATA

	T_g[a]	Xe solubility[b]	$\delta\omega$[c]	^{13}C transition[d]
PECH	249 K	0.202	230.5 ppm	280 K
PVME	250 K	0.798	209.8 ppm	285 K
BLEND	—	—	217.7 ppm	285 K

[a] DSC at 10 deg/min.

[b] Relative solubility of ^{129}Xe in polymer.

[c] ^{129}Xe chemical shift relative to the gas peak.

[d] Midpoint of temperature over which resonances broaden.

be resolved. In fact, this method provided the first direct evidence for differences in local chain dynamics between the components of a miscible polymer blend.[35]

Figure 2 shows representative ^{13}C NMR spectra of neat PVME acquired over the temperature range 250–300 K. All three of the chemically distinct carbon nuclei are well resolved at the lower (250 K) and upper (300 K) temperature extremes. As temperature is raised above 250 K, the methylene (40 ppm) and methine (76 ppm) backbone carbon resonances become increasingly broad, with maximum linewidth occurring between 280–290 K. Above 290 K, the peaks narrow as the timescale associated with molecular motion decreases. As discussed, the broadening is attributable to molecular motions occurring on the timescale of the magic angle spinning (3 kHz) and/or the proton decoupling field (50 kHz). The central resonance of PVME (57 ppm), corresponding to the pendant methoxy group, does not broaden significantly over this temperature range. This is because the C3 rotational motion of the methoxy group is fast relative to the timescale of magic angle spinning and proton decoupling.[36]

Selected ^{13}C spectra of neat PECH are shown in Figure 3 over the same temperature range, 250–300 K. Although there are three chemically distinct carbons in PECH, only two are resolvable due to the near equivalence of the respective chemical shifts of the backbone methylene and methine resonances. These spectra exhibit similar line broadening characteristics as observed for neat PVME. Maximum linewidth occurs between 275–285 K, which is several degrees lower than for PVME. This observation is qualitatively consistent with the slightly lower calorimetric glass transition temperature of PECH (see Table I).

Similar ^{13}C NMR measurements were carried out on an equal weight blend of PVME:PECH in order to observe possible effects of blending on molecular mobility of the components. Figure 4 shows representative spectra. As observed for the neat components, narrow carbon resonances occur below 250 K and above 300 K, indicating an absence of motion in the critical frequency range of 3–50 kHz at these temperatures. Maximum carbon peak broadening is observed over the range 275–290 K for both the downfield and upfield resonances. It is not possible to resolve the individual resonances of PVME and PECH because of the similarity of their chemical shifts. Only the PVME methoxy carbon can be unambiguously distinguished in the blend, and it does not broaden due to the rapid C3 rotation in this temperature interval. However, a large difference in the molecular mobilities of the blended PVME and PECH

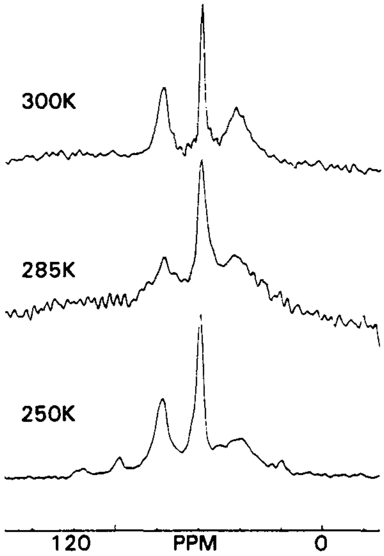

FIG. 2. — Representative ^{13}C NMR spectra of neat PVME obtained at the indicated temperatures using 3 kHz magic angle spinning and 50 kHz proton decoupling.

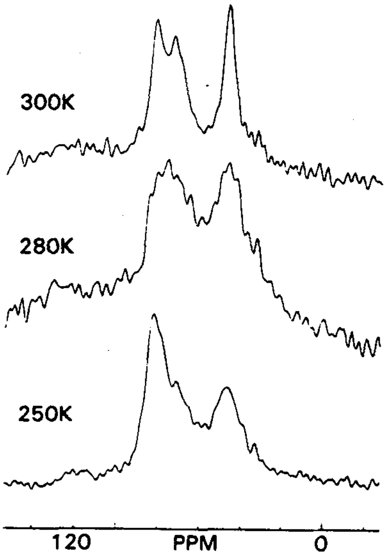

FIG. 3. — Representative ^{13}C NMR spectra of neat PECH obtained at the indicated temperatures using 3 kHz magic angle spinning and 50 kHz proton decoupling.

components would be observable, resulting in a superposition of broad and narrow peaks. This is clearly not the case. There is no evidence for any significant variation in the timescale of motion of the components, either within the mixture or relative to the neat samples. Unlike the "dynamic heterogeneity" seen in other polymer blends,[35,37-39] mixing does not significantly alter the dynamics of the individual components. This is due at least in part to the similarity of their segmental motions when neat,[5] one aspect of which is the near equivalence of the T_g's.

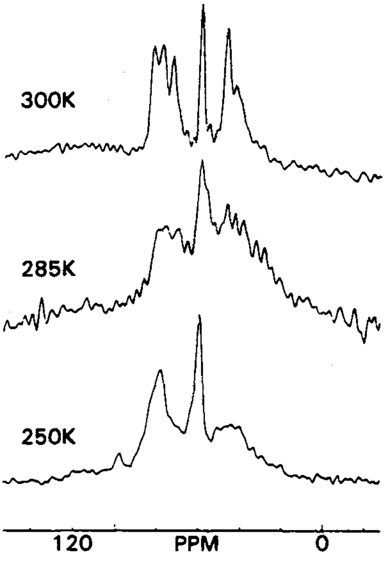

FIG. 4. — Representative ^{13}C NMR spectra of an equal weight of PVME and PECH obtained at the indicated temperatures using 3 kHz magic angle spinning and 50 kHz proton decoupling.

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