

¹³C NMR Study of Component Dynamics in Aroclor/Poly(vinylethylene) Mixtures

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Introduction

It is well established that the presence of polymer modifies the reorientational dynamics of small molecules.^{1–11} Of recent interest is the peculiar nature of the modification in mixtures whose components have nearly equal glass transition temperatures. Dynamic light scattering measurements of the reorientational relaxation time of Aroclor (tradename for polychlorinated biphenyl) have shown that the addition of several percent of poly(vinylethylene) (PVE) increases the mobility of the Aroclor, even though the PVE has a higher glass transition temperature.¹² This finding was confirmed by dynamic mechanical¹³ and dielectric spectroscopy¹⁴ on the same mixture. A similar anomaly has been observed for 1,1-bis(*p*-methoxyphenyl)cyclohexane (BMC), another small-molecule glass former. A mixture of 10% poly(methylphenylsiloxane) having a higher T_g reduces the reorientational relaxation time of the BMC, as observed by dynamic mechanical⁸ and dielectric spectroscopy.¹⁵ This anomaly, wherein local relaxation times of a mixture are not intermediate between the respective values for the neat components, has also been seen in certain polymer blends.^{16–18}

An obvious explanation for mixture dynamics which do not correlate with neat component glass transition temperatures and relaxation times is a nonideal mixing volume.^{13,16} If mixing increases the unoccupied volume, relaxation times should decrease.^{5,6,19} This statement applies to both components, although only the speeding up of the lower T_g component may be regarded as "anomalous".

Another hypothesis for anomalous speeding up of the dynamics by a higher T_g additive has been suggested.¹² The proposal is based on the idea that the local relaxation time of a neat liquid, and hence its measured T_g , is strongly enhanced by intermolecular cooperativity. When the material is diluted, this intermolecular coupling is removed. Hence, the relaxation time relevant for deducing the effect of mixing on the dynamics is not the relaxation time actually measured, but rather a (much shorter) noncooperative relaxation time. When this noncooperative relaxation time is less than the corresponding value for the solvent, mixing can increase the latter's relaxation rate, notwithstanding the relative magnitudes of the components' neat T_g 's. Values for the noncooperative relaxation times can be calculated from the measured relaxation time and the intermolecular coupling strength, as described by the coupling model of relaxation.^{20–22} This argument necessarily implies that while one component speeds up, the other's dynamics must slow down. It is in this prediction that the hypothesis drawn from the coupling model differs from an explanation based on excess mixing volumes.

Bulk measurement techniques such as dynamic light scattering, dynamic mechanical, and dielectric spectroscopy provide only macroscopically averaged views of the underlying molecular motions. For mixtures, microscopic information, particularly the resolution of the individual component dynamics, is needed. In favorable

cases, combined birefringence and mechanical data^{23–25} or dielectric and mechanical results²⁶ can reveal the distinct mobilities of the components. ²H NMR spectroscopy on selectively deuterated blends has provided detailed information on component dynamics in polymer blends.^{27,28} Solid-state ¹³C NMR spectroscopy allows the components to be differentiated by their isotropic chemical shifts.^{29–31} This paper describes the use of ¹³C NMR experiments to simultaneously probe the local dynamics of both Aroclor and PVE in a mixture. The results provide a direct test of the two hypotheses concerning the origin of the anomalous speeding up of Aroclor's reorientational motion in the presence of PVE.

Experimental Section

The poly(vinylethylene) is a low molecular weight (=2000) polybutadiene (Nisso B2000 from Nippon Soda Co.), having a vinyl content equal to 88%. The Aroclor 1248 (Monsanto Chemical Co.) is a mixture of chlorinated biphenyls having an average chlorine content of 48%. The glass transition temperatures of the liquids, defined as the temperature at which their relaxation times (measured by dielectric spectroscopy¹⁴) equal 100 s, are 230 and 240 K for Aroclor and PVE, respectively. Using mechanical data instead of dielectric, these values decrease by 1 or 2 K. An equal weight mixture of the two liquids was prepared by mechanical agitation.

NMR spectra were run on a Bruker MSL 300 using a static magnetic field of 7.0 T (Larmor frequency = 75.5 MHz). The experiments were carried out with a double-tuned magic angle spinning (MAS) probe equipped for 7-mm-o.d. sample rotors. Cross-polarization spectra³² were acquired using the Hartmann–Hahn cross-polarization technique.^{33,34} Higher temperature spectra were obtained with a single-carbon 90° pulse of 5 μs. All spectra were obtained with magic angle spinning and high-power proton decoupling throughout acquisition of the free induction decay. A B_1 (= B_2) field of 3.1×10^5 rad/s (=50 kHz) was utilized for cross polarization and decoupling. The cross-polarization contact time was 1 ms, with a 2-s relaxation delay. The MAS rotor frequency was 1.6×10^4 rad/s ± 0.2% (=2.5 kHz).

Results and Discussion

The ¹³C NMR spectra measured for the Aroclor, the PVE, and the 50% mixture show temperature-dependent line widths (Figure 1). There are two effects responsible for this line broadening. Molecular motions which modulate the chemical shift anisotropy (CSA) can interfere with the MAS modulation of the CSA,³⁵ while molecular motions which modulate the proton–carbon dipolar interaction can interfere with the proton–decoupling modulation of the dipolar interaction.³⁶ These interferences require molecular motions in the kilohertz range (i.e., at the MAS spinning rate) and the tens of kilohertz range (proton decoupling RF field), respectively. Maximal line broadening occurs at temperatures for which a substantial fraction of the relevant nuclei has molecular motion occurring in the frequency range from about 1.6×10^4 to 3.1×10^5 rad/s (2.5–50 kHz), corresponding to correlation times between 63 and 3 μs.

In Figure 2 are shown Arrhenius plots of the relaxation times measured by dielectric spectroscopy for the neat Aroclor and PVE.¹⁴ The ¹³C NMR time scale (3–63 μs) is denoted in the figure by horizontal lines, whose intersection with the curve defines the expected temperature range for NMR line broadening. From Figure 1 we estimate the temperatures of maximum line width for the aromatic carbons of Aroclor and the vinyl carbons of the PVE to be 266 and 280 K, respectively. These values, indicated in Figure 2 by the vertical lines, fall

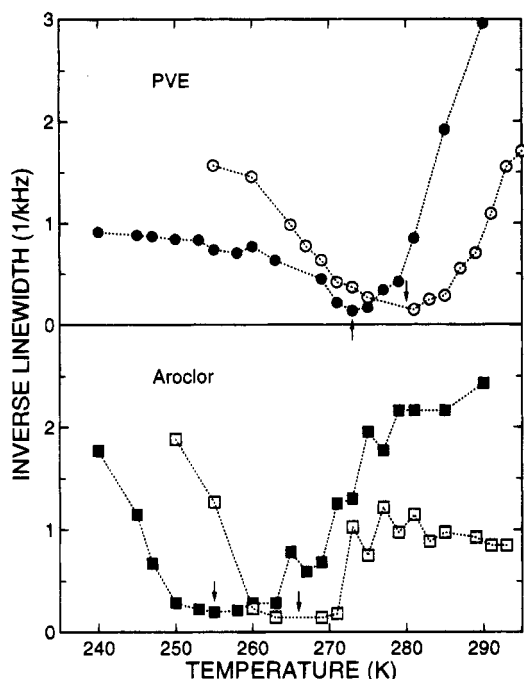


Figure 1. Inverse of the line widths measured by solid-state ^{13}C MAS NMR with radio-frequency decoupling for neat Aroclor and neat PVE (hollow symbols) and for the two components in a 50% mixture (solid symbols). The arrows indicate the temperatures at which the respective resonances have their maximum breadth.

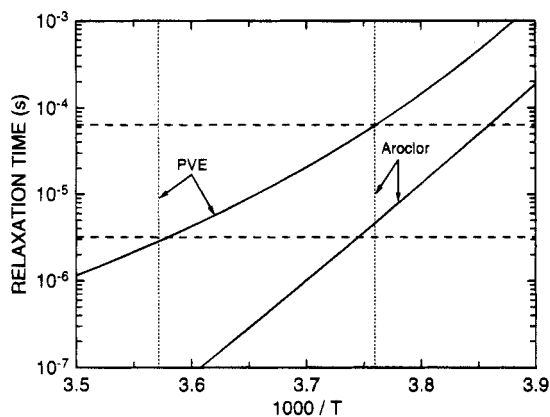


Figure 2. Dielectric relaxation times for neat Aroclor and neat PVE (solid lines represent the fit of the Vogel-Fulcher equation, taken from ref 14). The horizontal dashed lines define the range over which molecular motions interfere with the NMR line narrowing; their intersection with the relaxation curves represents the temperature span over which significant broadening of the NMR resonances is expected. The actual temperatures at which the resonances exhibit maximum line widths are indicated by the vertical dotted lines (corresponding to the arrows in Figure 1).

in the vicinity of the intersection points of the horizontal lines representing the NMR time scale. Thus, there is a consistency between the dielectric relaxation times and the NMR results. The data in Figure 2 suggest that the NMR peak broadening is dominated by motional interference with the heteronuclear dipolar interaction, as opposed to CSA. This is unlikely, however, since the unsaturated carbons of PVE and Aroclor have relatively large chemical shift anisotropies. There is no reason to expect exact quantitative agreement between the NMR relaxation times and those measured by dielectric spectroscopy.

We also point out that any potential line broadening by incoherent interference with the coherent averaging of CSA and ^1H - ^{13}C dipolar interactions depends upon

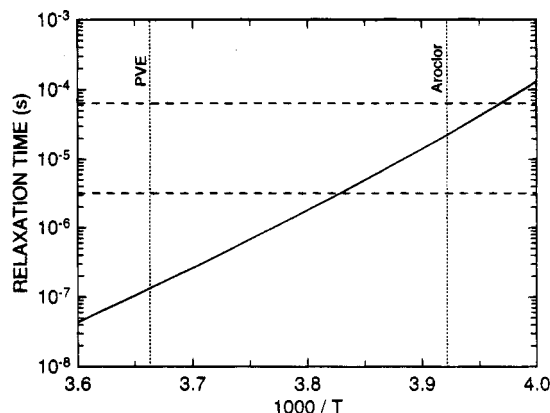


Figure 3. Dielectric relaxation time measured for a 50% mixture of PVE and Aroclor, with the temperatures at which the respective NMR resonances are broadest indicated by the vertical dotted lines (corresponding to the arrows in Figure 1). Note that for Aroclor this line intersects the relaxation curve within the temperature range defined by the NMR time scale (denoted by the dashed horizontal lines) for MAS and dipolar decoupling via radio-frequency irradiation.

the spectral density (power spectrum) of molecular motions transpiring on the time scale of these interactions. Since the unsaturated carbons of PVE and Aroclor have relatively large chemical shift anisotropies (and therefore very broad resonances in the absence of coherent averaging), it is unlikely that resonance line broadening could result solely from incoherent interference with proton decoupling. This would occur only in the event (unlikely) that spectral density associated with motions on the 3 kHz time scale was too small to cause any broadening, while spectral density at 50 kHz was sufficiently large to cause all the observed line broadening.

The relationship between the temperature range for solid-state ^{13}C MAS NMR line broadening and the temperature dependence of the relaxation times as measured by bulk spectroscopic techniques has been demonstrated previously for a number of polymers.³⁷ Note that the steeper slope of the Aroclor curve in Figure 2 causes the span defined by the 3 to 63 μs time scale to encompass a narrower range of temperatures. This is consistent with the results in Figure 1, in which the NMR resonance for neat Aroclor broadens more abruptly than does the neat PVE resonance.

The dielectric relaxation times for the 50% mixture are displayed in an Arrhenius plot in Figure 3. Notwithstanding that light scattering, dielectric, and mechanical spectra all exhibit only one dispersion,¹²⁻¹⁴ representing an average of the relaxation process, NMR line broadening of the components does not occur at the same temperature (Figures 1 and 3). The temperatures of maximum NMR broadening in the mixture are 255 and 272 K for the Aroclor and PVE, respectively. This phenomenon of dynamic heterogeneity in a morphologically homogeneous mixture is due to differences in the components' intrinsic mobilities, as well as to the effect of local composition on their dynamics.^{27,38-43} However, usually the relaxation times, and hence line-broadening temperatures, for the components are shifted closer by blending; that is, the lower T_g component has a higher transition temperature in the blend, while the component of higher T_g exhibits a lower transition temperature. In the present Aroclor/PVE mixture, this is not the case. As seen in Figure 1 and through comparison of the vertical lines in Figures 2 and 3, both components have their transitions shifted to lower temperature by blending. For the lower T_g Aroclor, at least, this is

anomalous—the reorientational motion of a fluid accelerates upon introduction of a higher T_g component.

The advantage of the present experiment is the ability to simultaneously monitor the motion of both the Aroclor and the PVE. We observe in Figure 3 that the dielectric data are in good agreement with the ^{13}C NMR results for Aroclor. The NMR data for the PVE component fall at higher temperatures (i.e., has slower motion) than inferred from the bulk dielectric measurement on the mixture. Evidently, the more polar Aroclor dominates the dielectric response of the mixture.

The important point is that both Aroclor and PVE experience faster dynamics in the mixture compared to their neat behavior. This observation enables us to assess the two hypotheses concerning the mechanism for the anomaly. Originally, Rizos and Ngai proposed that the higher T_g of PVE is predominantly a reflection of stronger intermolecular coupling (intermolecular cooperativity) in comparison to Aroclor. Using the coupling model,^{20–22} they deduced that the noncooperative relaxation time of a low molecular weight PVE, having a T_g 19 K higher than Aroclor's T_g , was actually shorter than reorientation relaxation time for Aroclor. Since the difference in time scales for local motion of the polymer and solvent governs the modification of the solvent dynamics, it was concluded that the PVE's shorter noncooperative relaxation time gave rise to the anomalous speeding up of the Aroclor reorientational motion.¹²

Subsequently, dynamic mechanical experiments on Aroclor containing a small quantity of high molecular weight PVE, having a T_g 34 K higher than that of Aroclor 1248, demonstrated the same anomalous speeding up of Aroclor's motion; however, the coupling model in this case does not predict that the polymer's noncooperative relaxation time is smaller than Aroclor's.¹³ Moreover, it was found¹³ that the volume change upon mixing was atypically positive. The consequent increase in available volume could cause the speeding up of the Aroclor relaxation.

The NMR data enable a determination of the dominant mechanism underlying the modification of the dynamics in the Aroclor/PVE mixtures. If the relative magnitudes of the noncooperative relaxation times (i.e., relaxation times calculated assuming an absence of intermolecular coupling^{12,20–22}) governed the behavior, acceleration of the Aroclor motion would be accompanied by a slowing down of the PVE dynamics. This does not occur. Both components have a lower transition temperature, implying faster motion at fixed temperature, in the mixture compared to when neat. This observation is consistent only with the positive excess volume being the cause of mixture relaxation times that are not intermediate to those of the pure components.

Summary

Although mixtures of Aroclor and PVE exhibit a single glass transition temperature and only one segmental relaxation dispersion in light scattering, dynamic mechanical, and dielectric spectra, the ^{13}C NMR results demonstrate that the motions of the components occur at very different time scales. Moreover, while affirming the existence of the anomaly of faster motion of Aroclor upon addition of PVE (which has a higher T_g), the present results reveal that the PVE also relaxes faster in the mixture. From this we conclude that the primary mechanism underlying the anomalous speeding up of the Aroclor dynamics is the increase in volume (decreased density) accompanying mixing with PVE. At

least for this particular mixture, any contribution to the relaxation behavior from cooperativity dynamics, as described by the coupling model,¹² is of secondary importance.

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