Comments on the Structural Heterogeneity and Molecular Motion in Poly(vinyl chloride) (PVC) and Poly(ether−ester) Characterized by Solid State NMR

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The recent reports, in which solid state NMR relaxations were used to study the structural heterogeneity in PVC,[1−3] poly(ether−ester) (Hytrel),[1,2] and the related blend,[1−3] present two proton spin−lattice relaxation times in the rotating frame, $^{H}T_{1\rho}$, for both the pure Hytrel and PVC. It was claimed in the reports that the shorter $^{H}T_{1\rho}$ belongs to the microcrystallites and the longer one originates from the amorphous chains. For PVC, based on NMR relaxation theory and relaxation data for semicrystalline polymers, the longer $^{H}T_{1\rho}$ more probably belongs to the microcrystallites and the shorter one to the amorphous chains. For the Hytrel, no evidence was presented, either theoretical or experimental, to support their claim. This possible mistake in assignment of the region in the heterogeneous system often leads to misinterpretation of the experimental data and the wrong picture of the morphology of the studied systems. It was for these reasons that we turned to further NMR relaxation measurements and analysis in our study of the same polymer samples, Hytrel 4056 and PVC 103 EP F-76. Also our Chemagnetics CMX 200 NMR spectrometer was similar to the spectrometer the authors used. Four kinds of methods are presented here to clarify the relationship between relaxation time and morphological heterogeneity in the two samples mentioned above.

Theoretical Consideration. For a homonuclear system of protons, for example, if we use nonselective excitation, the dipolar $^{HH}T_1$[4] and $^{HH}T_{1\rho}$[5] can be expressed as

$$1/^{HH}T_1(\mathrm{dd}) = (h^2\gamma^4/20r^6)[3J(\omega) + 12J(2\omega)]$$

$$1/^{HH}T_{1\rho}(\mathrm{dd}) = (3h^2\gamma^4/40r^6)[3J(2\omega_1) + 5J(\omega) + 2J(2\omega)]$$

where γ is the gyromagnetic ratio for the proton, r is the internuclear distance, ω is the Larmor frequency, ω_1 is the spin-lock field, and $J(\omega)$ is the spectrum density function. Under extreme narrowing conditions ($\omega\tau_c \ll 1$ and $\omega_1\tau_c \ll 1$):

$$1/^{HH}T_1(\mathrm{dd}) = 1/^{HH}T_{1\rho}(\mathrm{dd}) = 3h^2\gamma^4\tau_c/2r^6$$

A typical $^{HH}T_1$ or $^{HH}T_{1\rho}$ curve has a minimum in its relaxation time vs correlation time plot, as shown in Figure 1.[6] For the studies to correlate the experimental relaxation time to the molecular motion and morphology of the systems, it is important to know whether the correlation time of the studied system is located on the slow side of the minimum or on the fast side of the minimum. That is because the slow side of the curve can be interpreted in such a way that a decrease in T_1 or $T_{1\rho}$ value indicates increased molecular motion, while the fast side of the curve can be interpreted in such way that a decrease in T_1 or $T_{1\rho}$ value indicates decreased molecular motion. For normal semicrystalline polymers, especially for those polymers where the T_g of the amorphous phase is above room temperature, the motional correlation time of the amorphous phase lies on the slow side of the minimum, poly(oxetanes),[7] PET,[8] PBT,[9] and PEN[10] for example. So, it is reasonable to think that the motion correlation time of PVC, when T_g is above room temperature,[11] lies on the slow side of the minimum. Since one expects more motion in the amorphous rather than the crystalline phase, the longer $^{H}T_{1\rho}$ should be assigned to the crystallites and the short one to the amorphous phase.

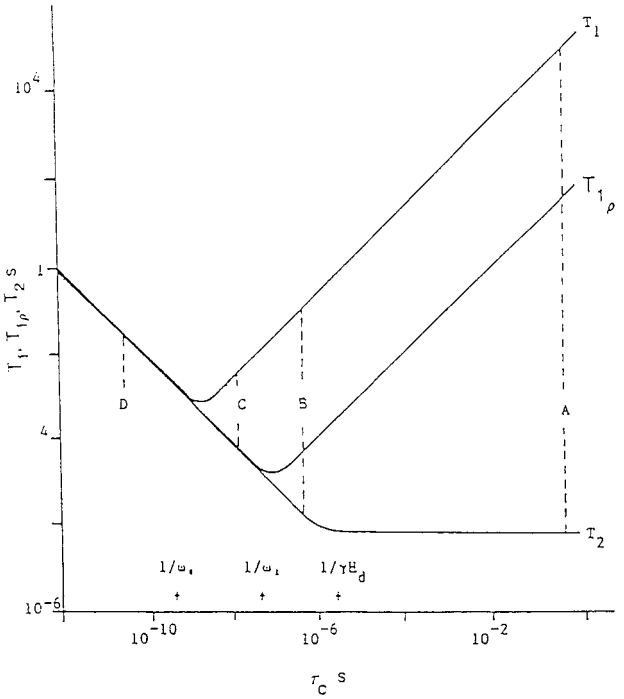

Figure 1. Dependence of T_1 and $T_{1\rho}$ on the molecular correlation times for relaxation determined by only dipole−dipole interactions.[6]

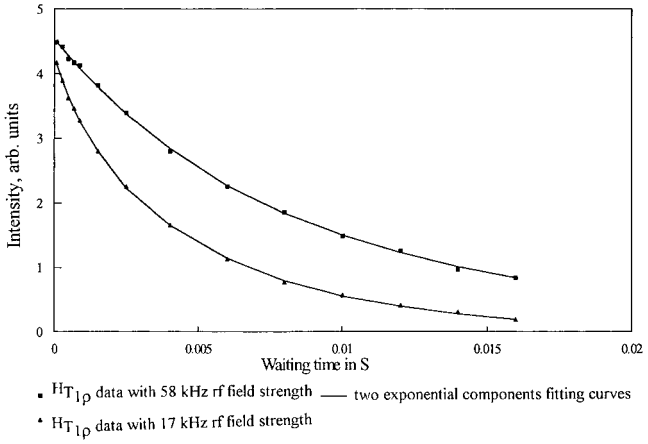

Figure 2. Plot of the methylene carbon of PVC vs delay time for the measurement of $^{H}T_{1\rho}$, at 20 °C and two radio frequency fields, 58.0 and 16.7 kHz, respectively, as well as two exponential fitting curves.

Method 1, Dependence of $^{H}T_{1\rho}$ on the Radio Frequency Field. One experimental approach to prove our conclusion is to observe the effect of varying the radio frequency (rf) field. Figure 2 shows a plot of the ^{13}C NMR resonance intensity of the methylene carbon of PVC vs delay time for the measurement of $^{H}T_{1\rho}$, for two radio frequency fields, 58.0 and 16.7 kHz, respectively, at 20 °C, as well as a fit of the data to two exponentials. Two $^{H}T_{1\rho}$ values, 6.0 ± 0.4 and 13.3 ± 1.2 ms, respectively, are derived from the relaxation curve

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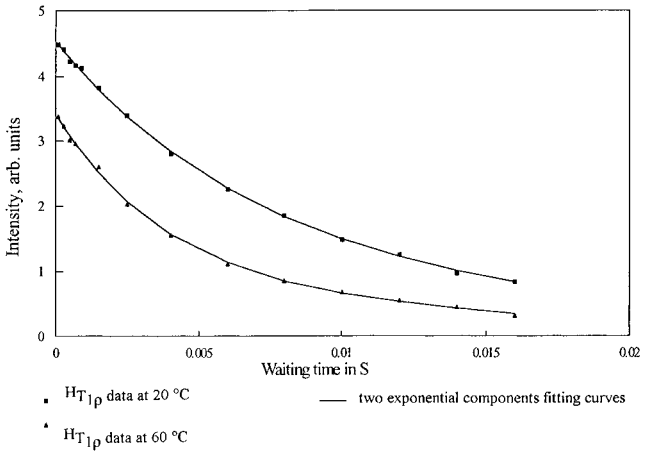

Figure 3. Plot of the intensity of the methylene carbon of PVC vs delay time for the measurement of $^{H}T_{1\rho}$ at 20 and 60 °C as well as two exponential fitting curves. The radio frequency field for spin lock is 58.0 kHz.

obtained at 58 kHz rf field, while the lower two $^{H}T_{1\rho}$ values, 1.1 ± 0.15 and 5.6 ± 0.15 ms, respectively, were obtained for the curve obtained at 16.7 kHz. The fact that the $^{H}T_{1\rho}$ does change, decreasing when the rf field strength decreases, indicates that the correlation time lies on the slow side of the minimum. Insensitivity to a change in the radio frequency field would typify the short-correlation-time regime. The off-resonance effect at low spin lock field should be considered. This is not the problem for the data presented here. For PVC, the carry frequency of spin lock was set between the two close resonances. Therefore, the spin lock is almost on resonance. For Hytrel, due to the higher mobility, the off-resonance effect is not so important.

Method 2, Dependence of $^{H}T_{1\rho}$ on Temperature. A second experimental way to find out which side of the $^{H}T_{1\rho}$ minimum the system is located in is to measure the $^{H}T_{1\rho}$ at two different temperatures. Figure 3 shows a plot of the intensity of the methylene carbon of PVC vs delay time for the measurement of $^{H}T_{1\rho}$ at 20 and 60 °C with radio frequency fields of 58 kHz. Two $^{H}T_{1\rho}$ values, 3.4 ± 0.8 and 11.8 ± 1.2 ms, respectively, are obtained for the curve obtained at 60 °C. The fact that $^{H}T_{1\rho}$ decreases as the temperature increases indicates that the correlation time lies on the slow side of the minimum.

Method 3, Measurement of $^{H}T_{1\rho}$ for Different Lines Associated with Different Regions. For the thermal plastic elastomer, Hytrel 4056, the solid state high-resolution ^{13}C chemical shift of OCH_2 in the hard segment and soft segment are different; moreover the motional correlation time of the hard segment is expected to be longer than that of the soft segment. Assignment of the different OCH_2 peaks to the soft and hard segments would then permit a measurement of the respective $^{H}T_{1\rho}$'s assignment with each region. Figure 4 shows the CP/MAS spectra acquired at different decoupler field strengths, which can be used unambiguously to assign the soft and hard OCH_2 resonance. At a decoupler field strength lower than 5.6 kHz, only the soft segment OCH_2 resonance at 71 ppm survives, while the strong dipolar interaction in the hard segment strongly broadens the resonance at 65 ppm. This assignment is also consistent with our results based on the CP/MAS delayed decoupling experiment. Table 1 lists the results of $^{H}T_{1\rho}$ and $^{H}T_1$ measurements for different regions of the Hytrel. None of the $^{H}T_1$ curves is single-exponential, although data for best attempts to fit to a single-exponential are listed in the table.

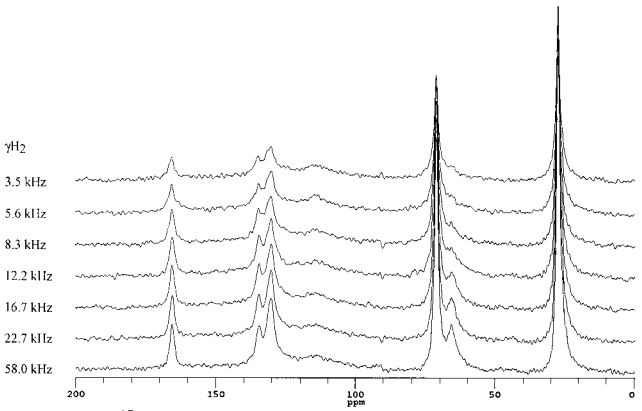

Figure 4. ^{13}C CP/MAS stack spectra of Hytrel with different decoupling strengths γ_{H_2}.

Table 1. Results of $^{H}T_{1\rho}$ and $^{H}T_1$ Measurement for Different Regions of the Poly(ether−ester)[a]

carbons	chemical shift (ppm)	$\langle^{H}T_{1\rho}\rangle^{b}$	$^{H}T_{1\rho}$ (ms)		$\langle^{H}T_1\rangle^{b}$ (ms)
overlapped CH_2	26	3.0	1.7	8.9	260
hard segment OCH_2[c]	65	2.4	1.5	2.7	310
soft segment OCH_2[c]	71	3.0	1.8	8.6	260

[a] Measurements are within 15% experimental error. [b] Data obtained on the basis of one-exponential fitting. [c] Data based on the intensities after deconvolution of the two overlapping OCH_2 resonances.

Although these average $^{H}T_{1\rho}$'s and $^{H}T_1$'s are rather close to one another, the soft segments have the large average $^{H}T_{1\rho}$ and small $^{H}T_{1.}$

Conclusion. (1) For PVC, the longer $^{H}T_{1\rho}$ component belongs to the microcrystallites and the shorter one originates from the amorphous phase. (2) For the thermal plastic elastomer Hytrel, we present several experimental results to demonstrate the procedure assigning the components. (3) NMR relaxation studies of polymer morphology for complex systems like semicrystalline polymer blends with thermal plastic elastomers are seldom reported in the literature due to the system complexity. Further research remains the subject of active investigation.

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Supporting Information Available: ^{13}C stack spectra of $^{H}T_{1\rho}$ measurement of PVC and Hytrel at two radio frequency fields, 58 and 16.7 kHz, and two temperatures, 20 and 60 °C, respectively; ^{13}C stack spectra of $^{H}T_1$ measurement of Hytrel at two temperature, 20 and 60 °C, respectively; two exponential component curve fitting plots of $^{H}T_{1\rho}$ and $^{H}T_1$ measurements for the three resonances at 26, 65, and 71 ppm; ^{13}C CP/MAS delay decoupling spectra of Hytrel (7 pages total). Ordering information is given on any current masthead.

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