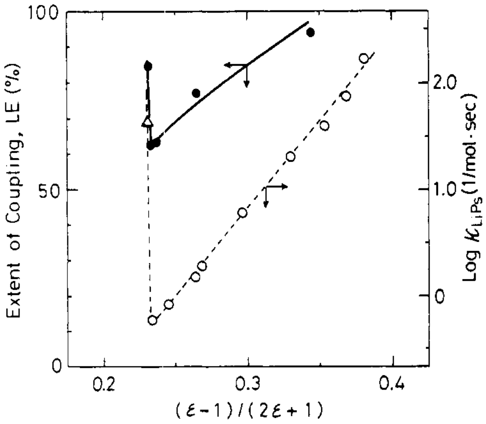

Figure 6. Comparison of the dependence of extent of coupling of living end on the dielectric constant (ϵ) which varies with the amount of added THF with that of the propagation rate constants of PSt-Li in similar mediums (○, data of Bywater and Worsfold[17]) and in benzene (△, datum of Roovers and Bywater[18]).

is present. In our experiments, it was found that Li^+ was more favorable than K^+ in a THF–benzene medium, as can be seen in Table III. This finding may be ascribed to the easy solvation of Li^+ with THF, which closely related to the ionic character of PSt-Li.

In conclusion, it may be noted that the solvent, the reaction temperature, and the counterion all affect the extent of coupling of living polystyrene, but the ionic character of the living polystyrene is the most important factor affecting the degree of the coupling.

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Cross Relaxation in Poly(vinylidene fluoride) from Transient Overhauser Measurements

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ABSTRACT: Cross-relaxation effects between the ^1H and ^{19}F spin systems in poly(vinylidene fluoride) have been examined by the procedure devised by Solomon to study the HF molecule (transient Overhauser effect). The experiment has the virtue of providing unusually good resolution of T_1 components, determination of the cross-relaxation between two abundant spin systems, and an additional sampling frequency for molecular motions from a single pulse sequence.

In systems containing more than one magnetically resonant species, quantitative analysis of relaxation data requires a knowledge of competing cross-relaxation effects. Spin exchange between like nuclei spin diffusion has often been invoked in the interpretation of polymer relaxation data; exchange between unlike nuclei, though a highly improbable process in a rigid lattice, can evidently become important in the presence of thermal motion. Poly(vinylidine fluoride) (PVF_2) provides an interesting system from the standpoint of spin dynamics, molecular motion, and physical properties of practical importance.

In this paper we specifically examine spin exchange between proton and fluoride nuclei in PVF_2 by means of the transient Overhauser experiment.[1–4] These cross-relaxation effects have been hitherto neglected in existing interpretations of NMR experiments on PVF_2.[5]

Experimental Section

The pulse experiment described by Solomon[3,4] to study cross relaxation in anhydrous hydrofluoric acid has been employed here. Briefly, at $t = 0$, a 180° pulse is applied at the resonant frequency of the hydrogen spins (designated S in the Solomon notation) and the magnetization of the fluorine spins (designated I) is monitored by the application of a 90° pulse at subsequent times. The use of crossed coils, one tuned to fluorine resonance (30 MHz) and the other to proton resonance (31.888 MHz), constituted the principal modification to the basic spectrometer.[6] A Bruker pulse programmer provided the required pulse sequences and the use of a Nicolet computer coupled to the spectrometer via a Biomation 610 digitizer allowed the accumulation of signals. Owing to the cross-coil configuration the 180° pulse for the ^1H nuclei was 18 μs. However, we believe that substantially all of the magnetization is inverted by virtue of the following experiment carried out at room temperature. Application of an 18-μs 180° pulse, followed by an 8-μs delay and a 2-μs 90° pulse, shows an initial amplitude of the free induction signal of approximately 80%

of the free induction signal following a single 2-μs 90° pulse.

The powder PVF_2 sample used in this study was obtained commercially (Kynar 821, Pennwalt Corp.). Of crystal form II, the crystallinity was about 50% and molecular weights were $M_n = 2.1 \times 10^5$ and $M_w = 4 \times 10^5$, respectively.[5]

Theory

The fundamentals of cross relaxation between two unlike spins were established by Solomon and co-workers.[3,4] Cross relaxation between systems of unlike spins in the solid state has subsequently received attention from Bloembergen,[7] Provotorov,[8] Goldman,[9] and others. In the main, these analyses have emphasized rigid lattice conditions. However, Provotorov's formalism includes spin–lattice relaxation in an apparently consistent way. The theoretical treatment of relaxation in the solid state is different from that in liquids in three principal, related aspects: anisotropy of molecular motion may leave part of the dipolar Hamiltonian time independent, the heat capacity of this time-independent term cannot in general be neglected, and the motional correlation times may become longer than T_2. Here, we use the Provotorov results to argue that the simpler and more generally familiar equations of Solomon et al.,

$$\begin{aligned} dI_z/dt &= -\rho(I_z - I_0) - \sigma(S_z - S_0) \\ dS_z/dt &= -\rho'(S_z - S_0) - \sigma(I_z - I_0) \end{aligned} \qquad (1)$$

adequately represent the behavior of the spins in poly(vinylidene fluoride) for the particular experiment and conditions used. According to Provotorov, the inverse spin temperature, α_I, of the I spin species obeys the equation

$$\frac{d\alpha_I}{dt} = -\frac{1}{T_{12}}(\omega_I\alpha_I - \omega_S\alpha_S - \Delta\beta) - \frac{1}{T_1{}^1}(\omega_I\alpha_I - \omega_I\beta) - \frac{1}{T_1}(\omega_I\alpha_I - \alpha_L\omega_I) \qquad (2)$$

where $\Delta = \omega_I - \omega_S$.

The dipolar inverse spin temperature, β, and α obey analogous equations in the absence of rf excitation. These results can be brought into correspondence with the form of Solomon's equations through the following observations.

Preparation of the thermally equilibrated spin system by a 180° pulse applied to the I spins makes the dipolar temperature approximately two or three times that of the lattice.[10] The contribution of the inverse dipolar temperature to the evolution of the first term of eq 2 is therefore negligible owing to the facts that $(\omega_I\alpha_I - \omega_S\alpha_S) \sim (\omega_I + \omega_S)\alpha_L$ after the 180° pulse and $\Delta \ll \omega_I$ or ω_S. Examination of Provotorov's spin-lattice interaction operator G reveals that he has, for his purposes, ignored the contribution of the time dependent part of the I–S flip–flop Hamiltonian, which is expected to make the dominant contribution to the relaxation observed in our system when the motional correlation time approximates Δ^{-1}. However, since this term is entirely analogous to parts of the dipolar Hamiltonian already included, one can expect that its inclusion will simply make additional equal magnitude contributions to both the cross-relaxation rate and the spin–lattice relaxation. Therefore, except for long correlation times, $\tau_c \geq T_2$, the second term is negligible and indeed, since β does not differ grossly from α_L, the second term may be combined with the third term. When the inverse spin temperatures are expressed in terms of magnetizations these considerations lead to Solomon's equations. Of course, other experiments and systems can be exploited to explore and emphasize the features of Provotorov's results specific to solids. However, we believe that the results presented here are adequately characterized by Solomon's equations and indeed the unexplained interesting features of the spectra seem more likely assignable to the composite nature of the polymer system rather than spin-dynamics, even when $\omega_c \geq \tau_c$.

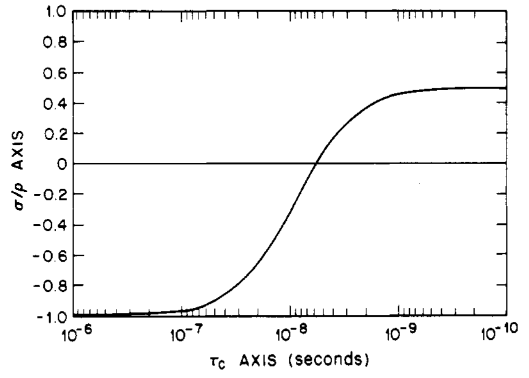

Figure 1. Theoretical dependence of the ratio σ/ρ upon the correlation time τ_c.

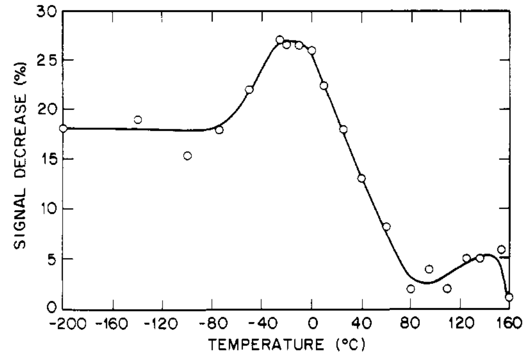

Figure 2. Observed decrease in signal amplitude as a function of temperature.

It is often the case in solids that there exist fairly well-resolved groups of molecular correlation times where each group may be associated with a particular molecular motion and the data analyzed in terms of a mean correlation time for the motion. This is a great saving grace for complex systems such as polymers and is assumed to be appliable here.

For a single pair of unlike nuclei, with motion characterized by a single correlation time, the ratio of cross-relaxation rate to spin–lattice relaxation rate, the Overhauser ratio, is,

$$\frac{\sigma}{\rho} = \frac{6J_2(\omega_I + \omega_S) - J_0(\omega_I - \omega_S)}{6J_2(\omega_I + \omega_S) + 3J_1(\omega_I) + J_0(\omega_I - \omega_S)} \qquad (3)$$

where $J_i(\omega) = \tau_c/(1 + \omega^2\tau_c^2)$.

For protons and fluorine nuclei

$$\frac{\sigma}{\rho} = \frac{5 + 4.97\tau_c^2 - 60.14\tau_c^4}{10 + 88.6\tau_c^2 + 61.46\tau_c^4} \qquad (4)$$

Figure 1 exhibits the ratio σ/ρ as a function of τ_c. Clearly there will be homonuclear and impurity spin–lattice relaxation mechanisms, in parallel with the one described by eq 3, that do not cause cross relaxation. In this case $|\sigma/\rho| < 1$ even when $J_0(\omega_I - \omega_S)$ dominates cross relaxation and $|\sigma/\rho|$ may go through a maximum at $\tau_c\Delta \sim 1$ if the competing relaxation path is comparable to that caused by the I–S flip–flop Hamiltonian and provided its temperature dependence is mild compared to the process for which $\Delta\tau_c \sim 1$. It should be noted that such homonuclear and impurity interactions are included in both Provotorov and Solomon equations; only in eq 3 and 4, which are introduced solely to illustrate the dependence of the Overhauser effect on τ_c, are homonuclear and impurity effects ignored.

Solomon has derived the following solution to eq 1 subject to the pulse sequence chosen.[3]

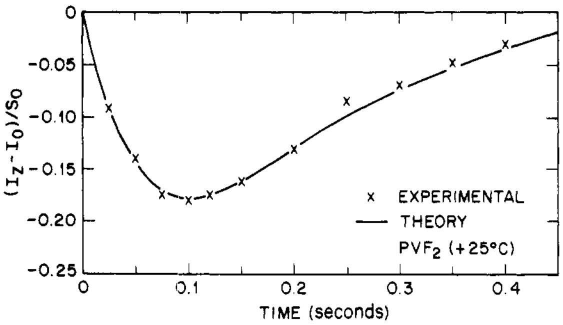

Figure 3. Experimental variation of $(I_z - I_0)/S_0$ as a function of the time, t, between the 180° proton pulse and the 90° fluorine pulse. The solid curve is described by eq 4 in the text.

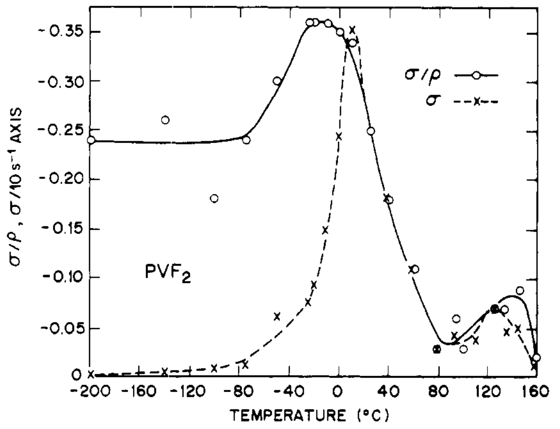

Figure 4. Temperature dependence of σ (X) and the ratio σ/ρ (O).

$$I_z - I_0 = S_0[e^{-t/D_1} - e^{-t/T_1}]$$

$$S_z - S_0 = S_0[e^{-t/D_1} + e^{-t/T_1}] \qquad (5)$$

where the relaxation times T_1 and D_1 are defined as

$$T_1 = (\rho + \sigma)^{-1};\ D_1 = (\rho - \sigma)^{-1} \qquad (6)$$

Equations 5 obviously imply yet another mechanism besides a composite system and spin diffusion for nonexponential spin–lattice relaxation.

Results and Discussion

Over the complete temperature range studied, −196 to +160 °C, a decrease in the ^{19}F resonance signal was observed as shown in Figure 2. These data points have been obtained from plots of $(I_z - I_0)/S_0$ vs. t, the time between the 180° proton pulse and the 90° fluorine pulse. Figure 3 shows a typical plot where the solid curve represents the theoretical fit of eq 5 and 6 to the experimental data. In fitting the curve it was convenient to use the following simple procedure. It is first recognized that the maximum observed magnitude of $(I_z - I_0)/S_0$, designated $-V_{\max}$, is related to $x = \sigma/\rho$ according to

$$-V_{\max} = \left(\frac{1-x}{1+x}\right)^{(1+x)/2x} \frac{2x}{1-x} \qquad (7)$$

Thus $V_{\max}$ immediately provides σ/ρ. A second expression relates σ to x and $t_{\max}$, the time for which the signal decrease is maximum.

$$\sigma = \frac{1}{2t_{\max}} \ln \frac{1+x}{1-x} \qquad (8)$$

Hence σ and ρ and correspondingly T_1 and D_1 may be derived. Figure 4 shows the temperature dependence of σ/ρ and σ while Figure 5 presents T_1 and D_1 as a function of temperature.

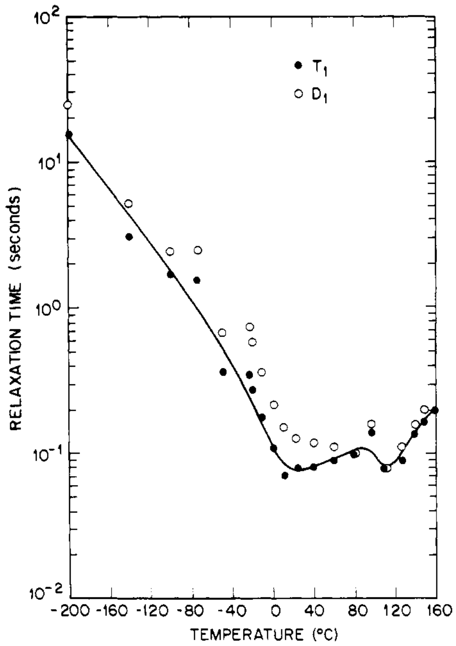

Figure 5. Temperature dependence of the resolved spin–lattice relaxation times T_1 and D_1.

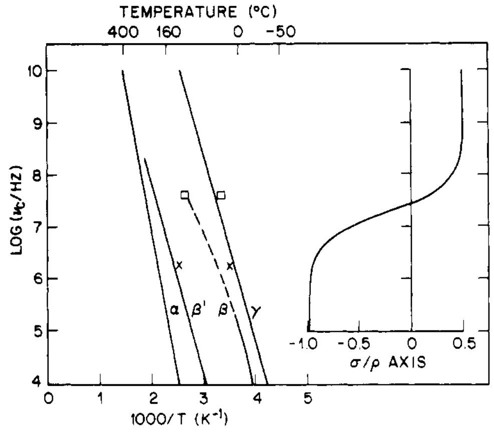

Figure 6. Relationship between the transition map for PVF$_2$ (ref 5) and the theoretical dependence of σ/ρ upon correlation frequency ν_c.

The principal feature of interest in the spin–lattice relaxation data is the observation of two T_1 minima located at +25 and +110 °C, respectively. Earlier measurements[5] were unable to resolve the higher temperature minimum which probably manifests the β relaxation. Underlying the inability to resolve the two T_1's in the earlier work is the fact that in this experiment we are observing the difference in two exponentials rather than the sum (see eqs 5). Additionally, the component T_1's differ by less than a factor of 2 in almost all cases. The additional point corresponding to the resolved high-temperature minimum is included in the transition map for PVF$_2$ in Figure 6.

Any process leading to an Overhauser effect is a mixture of relaxation to the lattice and exchange of energy between the spin systems. Except for the contribution of overlap of the tails of the two nuclear resonances, the mutual spin flip term, $J_0(\omega_I - \omega_S)$, will require an interaction with the lattice to conserve energy and is therefore allowed only in the presence of lattice motions characterized by frequencies corresponding to $(\omega_I - \omega_S)$ and might be termed phonon assisted spin diffusion. The remaining contribution to σ, $J_2(\omega_I + \omega_S)$, is a pure relaxation effect in that one spin of each type flips with a corresponding transfer of energy to the lattice. In addition, for these two processes to contribute to σ the thermal motions must involve modulation of the direct interaction between unlike spins.

At low temperatures the experimentally determined σ/ρ ratio is only about two-thirds of the maximum value observed, which is, in turn, one third of the magnitude expected from a process described by a single correlation time and interaction only between unlike nuclei. As mentioned earlier, a distribution of correlation times may lead to a reduced magnitude for $|\sigma/\rho|$ as will interactions between like nuclei. The maximum in $|\sigma/\rho|$ probably results from the presence of a parallel relaxation mechanism which may originate from the "tails" of a higher temperature process or from dissolved oxygen or paramagnetic impurity. In a system dilute in impurity relaxation sinks, ρ is effectively increased by spin diffusion to these sinks,[11] whereas σ is insensitive to the spin diffusion process.

As the temperature rises above 0 °C, σ/ρ begins to decrease in accordance with expectations. However, the rapid approach toward positive σ/ρ is stemmed and, instead, a maximum in σ/ρ of about -0.08 occurs in the region of +140 °C. At this point we consider this departure from theoretical prediction, based upon a single molecular motion in terms of the several molecular motions known to take place in PVF_2. Figure 6 relates the σ/ρ behavior to the correlation frequency–temperature dependence for the various motions in PVF_2.[5] σ/ρ begins to increase when molecular motions are characterized by a correlation frequency of about 10^6 Hz. For the γ relaxation this occurs at ~0 °C, in agreement with the experimentally observed increase (Figure 4). In the absence of competing relaxation processes, the γ relaxation would create positive σ/ρ values at temperatures of ca. 33 °C. However, the unresolved β process is characterized by strongly negative values for σ/ρ in this temperature region and the combined effect of the two unresolved relaxations is to maintain σ/ρ negative. A positive σ/ρ would again be expected for temperatures in excess of 100 °C if it were not for the intervention of the β' relaxation at this temperature. The contribution from this relaxation is sufficiently strong to result in the observed negative peak in σ/ρ at ca. +140 °C. Alternatively stated, both σ and ρ are the sum of four components corresponding to the four relaxations, which are individually grossly characterized by single correlation times:

$$\sigma/\rho = \sum_{i=1.4} \sigma_i \Big/ \sum_{i=1.4} \rho_i$$

As a particular ρ_i becomes dominant the corresponding σ_i is also likely to become dominant in the numerator. Thus, in a particular temperature range where one pair of ρ_i and σ_i favors a positive σ/ρ ratio the ρ_i and σ_i corresponding to the next relaxation process leads to a strongly negative ratio and the overall effect is to maintain σ/ρ negative over the temperature range studied. Ultimately σ/ρ should be positive at temperatures greater than ca. +250 °C. While each process may be associated with a distribution of correlation times, experience shows the feasibility of transition maps[12] which indicates that processes may be separately identified by a *mean* correlation time.

Referring to Figure 4 it is observed that σ exhibits maxima at +10 °C and ca. +125 °C. At these temperatures the spectral density term $J_0(\omega_I - \omega_S)$ in the numerator of eq 2 becomes dominant. This is analogous to the observation of $T_{1\rho}$ minima at the difference frequency $(\omega_I - \omega_S)$ at these temperatures ($\log \nu_c = 6.3$). The two points obtained by this observation are included in the transition map of Figure 5 and are conveniently located in the otherwise inaccessible range between the T_1 and $T_{1\rho}$ sensitive regions.

Conclusions

In the absence of more sophisticated and sensitive techniques[13-15] for examining cross relaxation this experiment provides an unusually convenient means of data collection and analysis of all the parameters pertinent to spin relaxation via molecular motion in systems with two abundant spin species: two resolved T_1 components, the relaxative strength of the coupling between the two spin systems, as well as correlation frequency information not normally available in the usual T_1, $T_{1\rho}$, and T_2 measurements. At any one temperature all the information is contained in a single experimental determination, namely, the maximum decrease in signal observed, $V_{\max}$, and the interval, $t_{\max}$, between the two pulses for this to occur.[16]

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(16) NOTE ADDED IN PROOF: Reconstruction of the spectrometer probe to use a doubly resonant single coil configuration provides a π pulse at both 30 and 31.888 MHz of 6 μs. Preliminary data indicate that the magnitude of observed Overhauser effect increases somewhat with this improvement but that the conclusions obtained using the earlier system are not substantially altered.