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^{31}P Two-Dimensional Solid-State Exchange NMR Characterization of Dynamics of Cross-Links in a Model Network Polymer

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ABSTRACT: Two-dimensional (2D) solid-state orientational exchange NMR has been used to investigate the motion of a cross-link unit in a model network. The ^{31}P chemical shift anisotropy provides an orientational probe of the tris(4-isocyanatophenyl) thiophosphate cross-link in the network interconnected with telechelic poly(propylene glycol). Two-dimensional spectra were taken at two temperatures near the glass transition and at a series of mix times. From the variation of the 2D-NMR pattern with temperature and mix time, the motion of the cross-link is identified as isotropic Brownian reorientational diffusion. Good simulations of the spectra were obtained using a distribution of Brownian rotational diffusion correlation times corresponding to the Williams–Watts stretched exponential correlation function. The parameters are the mean correlation time τ and the exponent α. At 30 °C $\tau = 1.0$ s and $\alpha = 0.45$; at 35 °C $\tau = 0.05$ s and $\alpha = 0.45$. The temperature dependence of the cross-link motion follows the WLF form with $C_1 = 15$ and $C_2 = 104$. The parameters derived from the NMR data are sufficient to describe the temperature dependence and breadth of both the dielectric and mechanical loss associated with the glass transition.

Introduction

One-dimensional (1D) solid-state NMR has proven to be a very powerful tool for studying the local dynamics of polymers.[2–6] It was possible to establish the relationships between segmental motions in model networks. The network designed for this investigation is comprised of telechelic monodisperse poly(propylene glycol) (PPG) of 0.4K to 3K molecular weight (MW) cross-linked with tris(4-isocyanatophenyl) thiophosphate.[6] With these specimens one can observe the dynamics of the cross-link point by ^{31}P-NMR and/or the connecting segments by ^{13}C-NMR.[6] The data over a range of temperatures showed these motions to have the same activation energy of 10.8 kcal mol^{-1}. But the correlation time for the carbon motion is shorter than the phosphorus motion by factors of 3 and 5 for networks with 1K and 3K MW PPG segments, respectively.[6] The ^{31}P line shape obtained on the model network is dominated by the chemical shift anisotropy interaction[6b,e] which reveals the orientation of the ^{31}P nuclei of the cross-links with respect to the applied field.

There are two limitations for 1D solid-state NMR. First, quantitative analysis of the 1D data in terms of specific types of molecular motion can be model dependent. For instance, the correlation times obtained from the line-shape fitting and from the relaxation times for the model network specimens do not agree; the former is about 3 times longer.[6e] This discrepancy may be attributed to the inadequacy of the relaxation model of isotropic averaging of the chemical shift anisotropy or to the overly simple motional model of the line-shape fitting, or both. Second, the NMR measurements of T_1's and $T_{1\rho}$'s were made at several tens of megahertz and tens of kilohertz, respectively. One cannot expect to relate these relaxations to the macroscopic mechanical and dielectric properties which occur with much slower bulk motions.

Recently, Spiess and co-workers[7] have developed two-dimensional (2D) solid-state exchange NMR to study slow molecular dynamics in the millisecond to second time scale. This technique overcomes the two limitations of the 1D solid-state NMR (vide supra). The 2D exchange spectral patterns are distinctive indicators of the nature of the reorientation motion. For instance, the patterns would be different for Brownian motion versus discrete jumps. Under favorable circumstances the data can be quantitatively analyzed without a model. Furthermore, the time scale of the 2D exchange solid-state NMR is comparable to that commonly employed for dielectric and mechanical measurements. Consequently, it is possible to correlate the results of NMR and bulk experiments directly, i.e., without extensive time–temperature extrapolation.

The central objective of this study is to perform ^{31}P 2D exchange NMR measurements of our model network, to quantitatively analyze the data in terms of a distribution of relaxations, to elucidate the nature of motion for the cross-links, and to relate it to the bulk mechanical and dielectric loss processes.

Experimental Section

Tris(4-isocyanotophenyl) thiophosphate from Mobay was recrystallized. Nearly monodisperse 425 MW α,ω-dihydroxypoly(propylene glycol) was supplied by Aldrich. The synthesis of network polymer from them has been described in detail before.[6b] The NMR pulse sequence for ^{31}P solid-state 2D exchange NMR spectroscopy is analogous to the NOESY pulse sequence in liquids.[7c] The ^{31}P resonance frequency depends on the orientation of the P=S axis with respect to the direction of the external magnetic field. This dependence arises from the chemical shift anisotropy. The four periods of the experiment are preparation, evolution, mixing, and detection. The initial ^{31}P transverse magnetization is created by cross polarization via protons with a contact time of 1.5 ms. The frequencies during the evolution and detection period, ω_1 and ω_2, may differ if a molecular reorientation occurs during the mixing time (t_m). Thus the frequency change during t_m can be directly observed from the 2D NMR pattern in which the correlated frequencies ω_1 and ω_2 reveal molecular reorientation. When there is no motion, essentially

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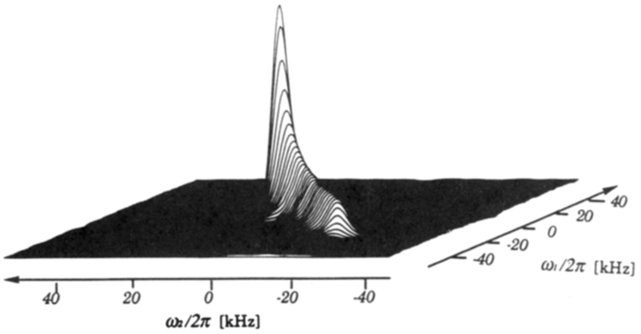

Figure 1. ^{31}P 2D exchange 121-MHz NMR spectrum of the network at −20 °C for t_m = 100 ms.

a ^{31}P powder pattern occurs along the diagonal of the 2D diagram. Any off-diagonal intensity indicates a change of orientation due to either molecular motion or spin diffusion.

The ^{31}P 2D static powder spectra were acquired on a Bruker MSL-300 spectrometer at a frequency of 121 MHz. Both ^{31}P and ^{1}H $\pi/2$ pulses were 5 μs, and the receiver dead time is estimated to be 5 μs. The sweep width was 125 kHz with 128 data points in t_1 (evolution period) and 256 points in t_2 (detection period). The recycle time was 3 s. A Gaussian apodization function was applied in both dimensions. The RuSH[8] method was used to obtain pure absorption phase spectra. The real pattern (cosine part) and imaginary pattern (sine part) were collected in two separate acquisitions and combined during processing.

All spectral simulations were performed on the Clark University VAX cluster using programs closely following the approach developed by Wefing and co-workers.[7]

Results

The network polymer shows no ^{31}P reorientation for t_m = 100 ms at −20 °C. All the intensity in this experiment, shown in Figure 1, lies along the diagonal. This is consistent with the fact that the −20 °C temperature is well below the glass transition temperature (T_g) of about 30 °C which was obtained from the dynamic storage modulus at 10 Hz.[6e] The absence of off-diagonal intensity in Figure 1 has another significant implication: there is no observable ^{31}P spin diffusion occurring in the 100-ms time scale at −20 °C, and this exchange mechanism need not be considered further. This diagonal pattern is easily simulated by a rigid axial chemical shift tensor with $\sigma_{\parallel} - \sigma_{\perp}$ = 251 ppm.

Figure 2 shows a series of two-dimensional patterns obtained at 30 °C as a function of mixing time. As the t_m is increased from 1 ms to 1 s, the off-diagonal intensity increases steadily over the 2D plane. When t_m reached 100 ms, significant off-diagonal intensity arises, giving evidence of molecular reorientation on this time scale. As the mixing time is further increased to 1 s, the 2D pattern fully spans the available 2D plane. A similar set of spectra at 35 °C were acquired and are presented in Figure 3. The off-diagonal intensity spreads over the 2D plane as a function of increasing mixing time from 200 μs to 500 ms. It is apparent by comparison of the spectra in Figures 2 and 3 that the rate of molecular dynamics is much faster at 35 °C than at 30 °C. In the former case there is a dramatic increase of off-diagonal intensity even at short mixing time (e.g., t_m = 10 ms). There is a strong temperature dependence of segmental motion which is characteristic of glass transition dynamics.

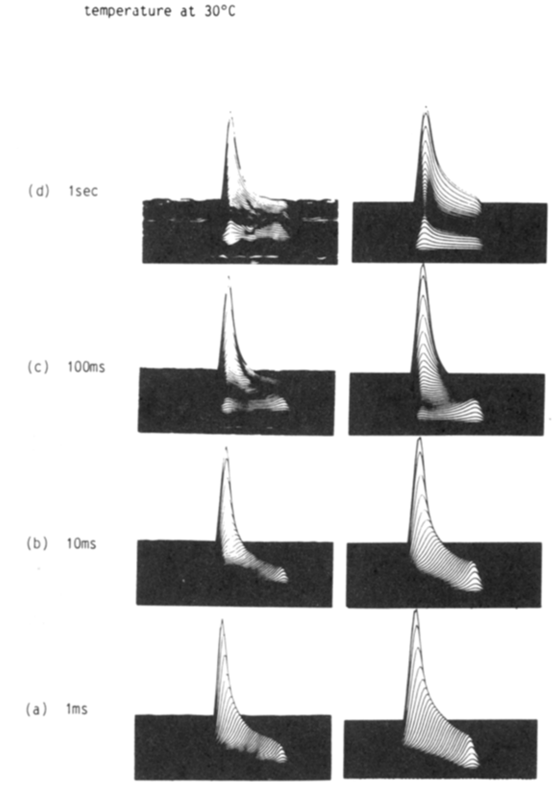

Figure 2. ^{31}P 2D exchange spectra at 30 °C as a function of mixing time: (a) t_m = 1 ms; (b) t_m = 10 ms; (c) t_m = 100 ms; (d) t_m = 1 s. The simulation pattern to the right is to be compared with the corresponding experimental pattern to the left.

Interpretation

The observed 2D pattern can be compared to various models for reorientational motion. For discrete jump motions, 2D powder spectra exhibit elliptical ridges.[7d,e] No elliptical ridges are present in our case, but a broad featureless off-diagonal intensity pattern gradually spreads over the 2D frequency plane as the mixing time is increased. This pattern is characteristic of Brownian rotational diffusion, so the reorientation dynamics of the cross-links can be described as isotropic motion by small angular steps.

The experimental spectra, for instance, Figure 2c for t_m = 100 ms and 30 °C or Figure 3d for t_m = 5 ms and 35 °C, cannot be described by a single correlation time. We found that all the experimental spectra can be described by Brownian rotational diffusion with a distribution of correlation times. Direct examination of the spectra for a series of mixing times shows clearly that slow (diagonal) and fast (off-diagonal) motions exist over a wide range of t_m. For a homogeneous distribution of correlation times this transition could be narrower. The Williams–Watts stretched exponential correlation function has been successful in interpreting NMR line shapes and relaxation times[3f] as well as the results of many other dynamical experiments on a polymeric system. This correlation function is expressed as

$$\phi(t) = \exp[-(t/\tau)^{\alpha}] \qquad 0 < \alpha < 1 \qquad (1)$$

where τ is the center correlation time and the exponent α provides a measure of the effective breadth of the distribution of correlation times. For the simulation computations the stretched exponential is transformed to a sum of exponential correlation functions weighted according to the method of Bendler previously detailed.[3f] The correlation time of each exponential correlation function is then identified as a Brownian rotational diffusion correlation time.

The T_g measured by dynamic mechanical thermal analysis is about 30 °C as defined by a drop in the modulus. The 2D exchange patterns at this temperature for mixing times of 1 ms to 1 s can be simulated satisfactorily with

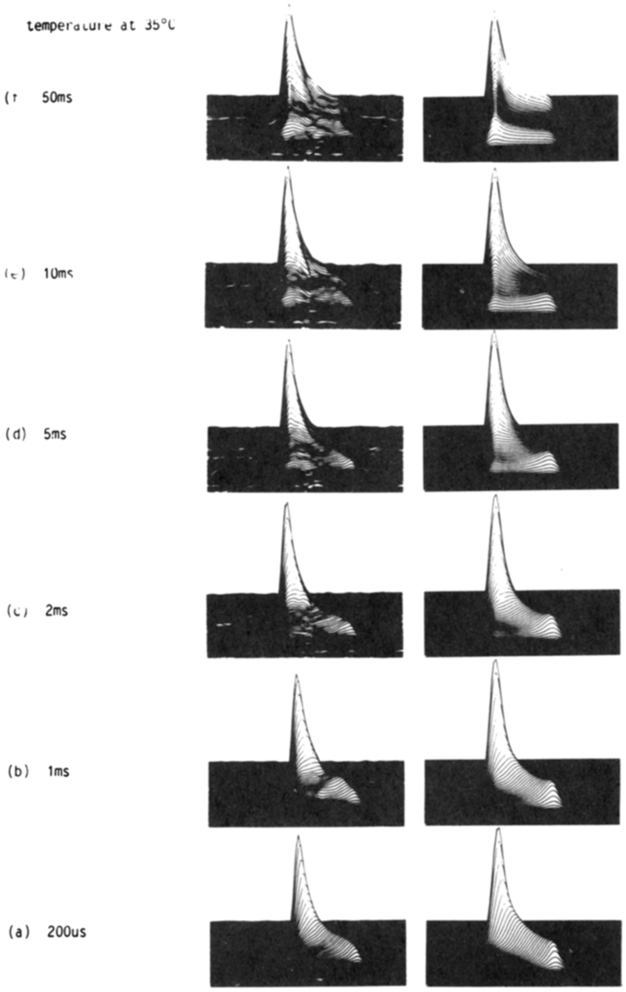

Figure 3. ^{31}P 2D exchange spectra at 35 °C as a function of mixing time: (a) t_m = 200 μs; (b) t_m = 1 ms; (c) t_m = 2 ms; (d) t_m = 5 ms; (e) t_m = 10 ms; (f) t_m = 50 ms. The simulation pattern at the right is to be compared with the corresponding experimental pattern to the left.

a peak correlation time, τ = 1.0 s, and an exponent of 0.45 (Figure 2). In other words, the correlation times are distributed about a characteristic value of about 1.0 s, with the width of the distribution spanning about 6 decades (Figure 4). We emphasize that the distribution used for the simulation must match *all* mixing times at a particular temperature. For example, a simulation with two narrow distributions of correlation times leads to a satisfactory simulation of the t_m = 100 ms spectrum but fails to match the spectra with t_m = 10 ms and 1 s.

A set of good simulations of the experimental results at 35 °C were obtained by using τ = 50 ms and α = 0.45 and given in the right-hand set in Figure 3. When the temperature changes from 30 to 35 °C, the center correlation time undergoes a 20-fold decrease from 1.0 to 0.05 s. Significant deviations of the simulations from the observed spectra were seen for $\alpha \pm 0.05$ and peak $\tau \pm 0.5$ s (30 °C) or peak $\tau \pm 0.005$ s (35 °C).

For temperatures just above T_g, the temperature dependence of the characteristic correlation time is expected to follow the empirical Williams–Landel–Ferry (WLF) equation which was developed originally for viscoelastic behavior.[9]

$$\log\left(\tau(T)/\tau(T_0)\right) = C_1(T - T_0)/[C_2 + (T - T_0)] \quad (2)$$

This equation should be suitable for the strong temperature dependence region between 30 and 35 °C. In the absence of any WLF parameters from another experimental source for comparison, it is desirable to determine whether the NMR time-scale distribution data can also satisfactorily account for both the mechanical and dielectric loss behavior.[6] The mathematical form of the equation used to predict the mechanical loss from the NMR data is[3a]

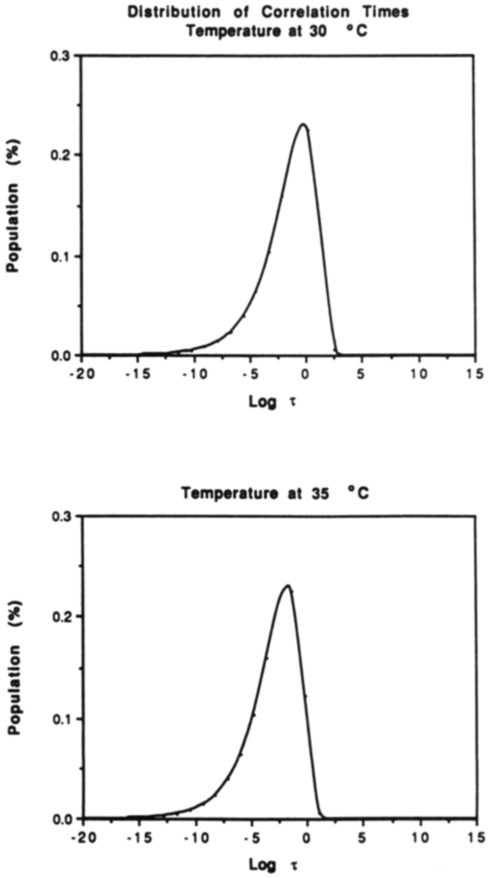

Figure 4. Distribution of correlation times used to simulate the ^{31}P motion in a model network at 30 and 35 °C.

$$E(\omega)^{\mathrm{loss}} = [\langle \sigma(0)^2 \rangle / k_B T] \int \sin(\omega t)\, \phi'(t)\, \mathrm{d}t \quad (3)$$

where $\phi'(t)$ is the derivative of the correlation function as expressed in eq 1 and σ is a measure of the magnitude of the coupling to the loss arising from the molecular event. A similar equation can be used for dielectric loss. Figure 5 shows the fit of the mechanical loss at 10 Hz and the dielectric loss at 1 kHz with the time-scale (τ) and breadth (α) parameters of the stretched exponential obtained from the NMR experiment. The WLF parameters used in the fitting are C_1 = 15 and C_2 = 105 with the reference temperature of 27 °C set for a frequency of 1 Hz.

The value of C_1 is close to its "universal" value of 17.4, while that of C_2 is about twice its "universal" value of 51.6. If the normal interpretation of the WLF parameters in terms of free volume is adopted, then[9]

$$C_1 = B/f_g; \quad C_2 = f_g/\alpha_f \quad (4)$$

where B is normally assumed to be close to unity. Then f_g, the fractional free-volume at T_g, would be close to 0.025, while the expansion coefficient for the free volume would be about twice as great is it could be if C_2 assumed its "universal" value. It is found generally that C_1 is quite close to the "universal" value for a large number of polymers, whereas C_2 tends to vary considerably. For example, C_2 is 104 for polyisobutylene.[9] Thus the temperature dependence of the micro-Brownian diffusion

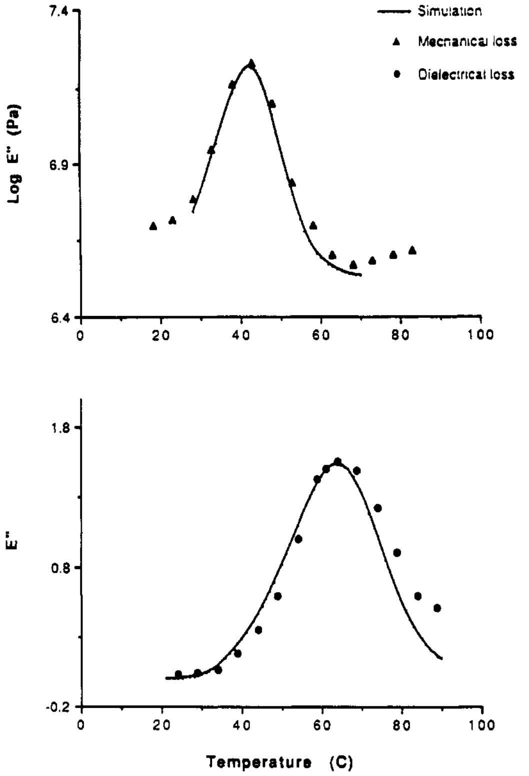

Figure 5. Variation of experimental mechanical loss at 10 Hz (▲) and dielectric loss at 1 kHz (●) of a model network polymer versus temperature. Solid lines are simulations calculated from the NMR-determined parameters.

motions accompanying T_g in the network can be well represented in terms of the free-volume theory.

Figure 5 shows that the NMR data simulated the same temperature for maximum mechanical and dielectric loss as well as the width in temperature for these loss functions. There are only small-temperature discrepancies of about 2–4 °C between the NMR, mechanical, and dielectric data, which is close to the combined temperature uncertainties for any two of these measurements. The NMR experiment measures only the cross-link motion, while the motion of the poly(propylene glycol) units may also contribute differentially to the mechanical and dielectric loss. Nevertheless, the agreement of the NMR data with the loss data suggests that cross-link motion is closely associated with the dielectric and mechanical loss in the vicinity of the glass transition.

Discussion

The nature of the motion of the junction points in this poly(propylene glycol)/urethane network can be described as isotropic rotational diffusion, and the glass transition is attributed to the onset of this type of molecular reorientation according to 2D exchange patterns. The same type of motion has been identified in un-cross-linked linear polymers.[7b–d] A distribution of Brownian rotational diffusion times is required for a full interpretation which is qualitatively apparent in the 2D patterns. Consider the spectrum with a mixing time of 100 ms at 30 °C in Figure 2c or a mixing time of 5 ms at 35 °C in Figure 3d; the outer edges of the off-diagonal signal indicate the occurrence of large reorientation for some of the ^{31}P cross-links, while the intensity near the diagonal indicates that others undergo only very small angle reorientations. Therefore, the motion of the cross-linking point is heterogeneous, describable only by a distribution of correlation times. The distribution of correlation times from the 2D simulation extends over more than 6 decades of time as shown in Figure 4. This breadth is somewhat on the broad end of what is typically seen for polymeric glasses which are characterized by α parameters in the range of 0.35–0.8.[3g]

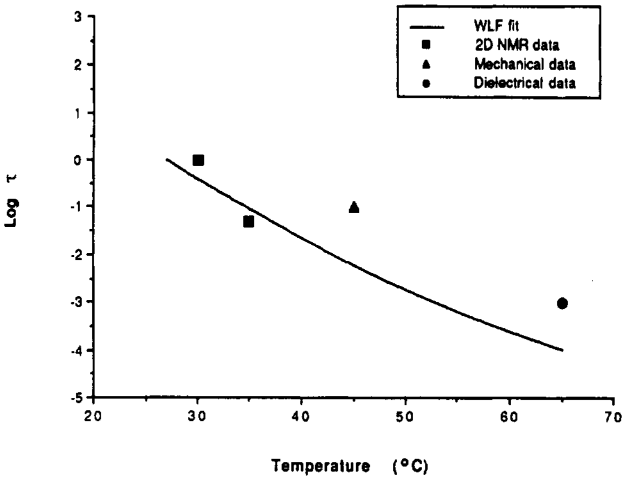

Figure 6. Relaxation map of the characteristic times for the NMR data. The mechanical and dielectric maxima are shown along with the WLF fit of these points.

These results join a growing number of studies which complete slow motions seen by NMR with mechanical data for a variety of systems including polystyrene[10] and polypropylene.[11]

The WLF equation can be recast in the Vogel–Tammann–Fulcher form following Angell[12] as

$$\frac{T}{T_0} = \exp\left[\frac{-DT_\alpha}{T - T_\alpha}\right] \qquad (5)$$

where D and T_α can be calculated from C_1 and C_2 of the WLF equation to yield 18.5 and 0.45, respectively. The values of 18.5 for D place the network toward the "fragile" glass end of the range of polymers.

Fragile liquids tend to have low values of α in the stretched exponential correlation function, which is consistent with the value of 0.45 just reported. In inorganic glasses, the presence of tetrahedral covalent network bonding tends to produce just the opposite results from that obtained here or a "strong liquid". Of course, in an inorganic glass there are many more covalent network bonds per atom than in even the rather highly cross-linked polymers studied here.

The distribution of correlation times determined from NMR and that evidenced by the width of the mechanical and dielectric loss peaks are quite consistent. One might have thought the mechanical and dielectric response would contain contributions from the other parts of the network beyond the cross-link which is monitored in the NMR experiment. Evidently the range of cooperative motion associated with the glass transition must include both the thiophosphate cross-links and the linear poly(propylene glycol) segments.

The comparison of the characteristic time constants of the NMR data, the mechanical loss maximum, and the dielectric loss maximum is shown in Figure 6. The correspondence between the data sets is acceptable. The scatter probably reflects the temperature calibration of the various instruments (vide supra). The fact that the correlation times are changing rapidly with temperature in the vicinity of T_g magnifies this problem. It is, nevertheless, apparent that a stretched exponential correlation function with a WLF temperature-dependent characteristic time provides a suitable framework for interrelating the three experiments. The successful use of a temperature-independent α is interesting, since this must be varied to match some sets of NMR data with mechanical response.[7f]

It should be pointed out that, in the simulation of the loss peaks, the intensity of the loss peak is adjusted to match the experimental result. Only the temperature and width of the loss are calculated from the NMR-derived correlation function.

The absolute relationship between a molecular motion and the magnitude of a bulk mechanical response remains as a problem to be solved. Still, it is quite clear that the motion of the cross-link seen in the NMR experiment closely corresponds to the mechanical and dielectric response of the bulk material.

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References and Notes

(1) (a) Department of Chemistry, University of Massachusetts, Amherst, MA. (b) Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA.

(2) Sillescu, H. *J. Chem. Phys.* **1971**, *54*, 2110.

(3) (a) O'Gara, J. F.; Jones, A. A.; Hung, C. C.; Inglefield, P. T. *Macromolecules* **1985**, *18*, 1117. (b) Roy, A. K.; Jones, A. A.; Inglefield, P. T. *Macromolecules* **1986**, *19*, 1356. (c) Roy, A. K.; Inglefield, P. T. *Prog. NMR Spectros.* **1990**, *22*, 569. (d) Jones, A. A. In *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; Komoroski, R. A., Ed.; VCH: Deerfield Beach, FL, 1986; p 247. (e) Chin, Y. H.; Zhang, C.; Wang, P.; Inglefield, P. T.; Jones, A. A.; Kambour, R. P.; Bendler, J. T.; White, D. M. *Macromolecules* **1992**, *25*, 3031. (f) Jones, A. A.; O'Gara, J. F.; Inglefield, P. T.; Bendler, J. T.; Yee, A. F.; Ngai, K. L. *Macromolecules* **1983**, *16*, 658. (g) Chin, Y. H.; Wang, P. W.; Zhang, C.; Inglefield, P. T.; Jones, A. A.; Kambour, R. P.; White, D. M. *Macromolecules*, in press.

(4) Laupretre, F.; Monnerie, L.; Virlet, J. *Macromolecules* **1984**, *17*, 1397.

(5) Hirschinger, J.; Miura, H.; Gardner, K. H.; English, A. D. *Macromolecules* **1990**, *23*, 2153.

(6) (a) Dickinson, L. C.; Morganelli, P. L.; MacKnight, W. J.; Chien, J. C. W. *Makromol. Chem., Rapid. Commun.* **1987**, *8*, 425. (b) Dickinson, L. C.; Morganelli, P. L.; Chu, C. W.; Petrovic, Z.; MacKnight, W. J.; Chien, J. C. W. *Macromolecules* **1988**, *21*, 338. (c) Dickinson, L. C.; MacKnight, W. J.; Chien, J. C. W. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 191. (d) Dickinson, L. C.; Chien, J. C. W.; MacKnight, W. J. *Macromolecules* **1988**, *21*, 2959. (e) Dickinson, L. C.; Chien, J. C. W.; MacKnight, W. J. *Macromolecules* **1990**, *23*, 1279. (f) Dickinson, L. C.; Shi, J. F.; Chien, J. C. W. *Macromolecules* **1992**, *25*, 1224.

(7) (a) Schmidt, C.; Blumich, B.; Spiess, H. W. *J. Magn. Reson.* **1988**, *79*, 269. (b) Wefing, S.; Spiess, H. W. *J. Chem. Phys.* **1988**, *89*, 1219. (c) Wefing, S.; Kaufmann, S.; Spiess, H. W. *J. Chem. Phys.* **1988**, *89*, 1234. (d) Kaufmann, S.; Wefing, S.; Schaefer, D.; Spiess, H. W. *J. Chem. Phys.* **1990**, *93*, 197. (e) Schmidt-Rohr, K.; Speiss, H. W. *Macromolecules* **1991**, *24*, 5288. (f) Schmidt-Rohr, K.; Spiess, H. W. *Phys. Rev. Lett.* **1991**, *66*, 3020.

(8) States, D. J.; Haberkorn, R. A.; Ruben, D. J. *Magn. Reson.* **1982**, *48*, 186.

(9) Aklonis, J. J.; MacKnight, W. J. *Introduction to Polymer Viscoelasticity*, 2nd ed.; John Wiley & Sons: New York, 1983.

(10) Pschorn, V.; Rösslev, E.; Sillescu, H.; Kaufmann, S.; Schaefer, D.; Spiess, H. W. *Macromolecules* **1991**, *24*, 398.

(11) Schaefer, D.; Spiess, H. W.; Suter, U. W.; Fleming, W. W. *Macromolecules* **1990**, *23*, 3431.

(12) Angell, C. A. *J. Non-Cryst Solid* **1991**, *131–133*, 13.