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SEGMENTAL AND CROSSLINK POINT MOTION IN NETWORKS

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Abstract: ^{13}C - and ^{31}P -NMR spin lattice relaxation in the rotating frame have been measured on a series of networks prepared from monodisperse and deliberately bimodal poly(propylene glycols) (PPG) crosslinked with tris(4-isocyanatophenyl) thiophosphate. The $T_{1\rho}^{\text{C}}$ minima correspond to loss maxima in the DMTA (Dynamic Mechanical Testing) measured at 10Hz. The $T_{1\rho}^{\text{P}}$ minima fall at higher temperatures than those of $T_{1\rho}^{\text{C}}$ for the same network indicating that these crosslinks lag the segments in frequency of motion at a given temperature. The carbon relaxation is biphasic below T_g of the segments indicating two relaxation domains which we assign to bulklike PPG segments and PPG segments proximal to the crosslink. Lineshape analysis by a diffusional model indicates crosslink reorientation is not isotropic until well above T_g . Relaxation and lineshapes for the bimodal networks indicate that junctions are not uniformly plasticized by the segments.

INTRODUCTION

With the advancement in a number of techniques the interest in networks and refined details of elasticity theory has increased markedly in the past eight years. Small angle neutron scattering has been used to definitively show that single chains in PDMS [poly(dimethylsiloxane)] networks do not deform affinely (Ref.1). Fluorescence labels have been used to quantitate segmental reorientation in at-equilibrium, swollen and stretched polyisoprene networks. (Ref.2). A number of laboratories have explored use of NMR in a variety of sophisticated ways including ^2H -NMR studies of orientational order induced by uniaxial deformation (Refs. 3 and 4) and

discernment of entanglements by dependence of orientational degree on network preparation method (Ref. 5). Proton spin-spin relaxation has also been exploited to describe gel structure in swollen and molten polymers.(Ref.6,7) High resolution ^{29}Si -NMR in PDMS gels has also been used to explore the variety of species present in PDMS elastomers (Ref.8).

The work presented here is part of a larger project exploring the motions of segments and crosslinks in a series of networks prepared from α,ω -dihydroxypoly(propylene glycols) and tris(4-isocyanatophenyl) thiophosphate. The virtues of this system are that there are very few cyclics and dangling ends because the reaction is virtually complete, PPG is not crystalline and is available commercially with a good range of molecular weights and with very low polydispersity, the crosslinker can be kept at very high purity and the stoichiometry can be made very precisely. The presence of the ^{31}P nucleus as the crosslink point can be exploited with its NMR sensitivity for comparison with the segmental (^{13}C) motion. ^{31}P -NMR offers the possibility of observing changes in constraints with extension through measurement reorientational frequencies and angles. These results can be obtained independent of elasticity theories and thus will broaden our description of molecular elasticity. Some of our work on these systems, including the details of preparation of the networks, has been previously published. (Refs.9-12)

RESULTS AND DISCUSSION

Low Dispersity Networks. Figures 1 and 2 show the $T_{1\rho}^{\text{C}}$ at 50 kHz spin lock as a function of inverse temperature for preparation of the carbon magnetization by direct (DP, simple $\pi/2$ ^{13}C pulse) and cross (CP) polarization, respectively. On the lower part of Figure 1 are the corresponding dynamic mechanical (DMTA) loss moduli measured at 10 Hz versus temperature for two samples. The DP data show typical spin relaxation minima which occur at the glass transition (T_g) of the propylene glycol segments. It is surprising that the transition measured by DMTA at a low frequency and the NMR relaxation measured at a thousand fold higher frequency correspond so closely. This must indicate that the molecular reorientation measured under spin lock is far more local than the mechanical contribution to the DMTA. Even more surprising is the very big difference between the DP and CP results. CP of course selects the carbons with more rigid proton-carbon dipolar interactions. The CP

relaxation in samples of molecular weight between crosslinks (M_c) < 3000 do not show minima in the expected T_g range and furthermore the carbon magnetization shows biphasic decay. Only the $M_c = 3000$ sample shows typical relaxation due to segmental motion near the glass transition. Although there is no positive basis for assignment as yet, it seems most likely that DP is detecting segments in bulk-like, center chain environments, and CP is detecting chain segments near the crosslink point.

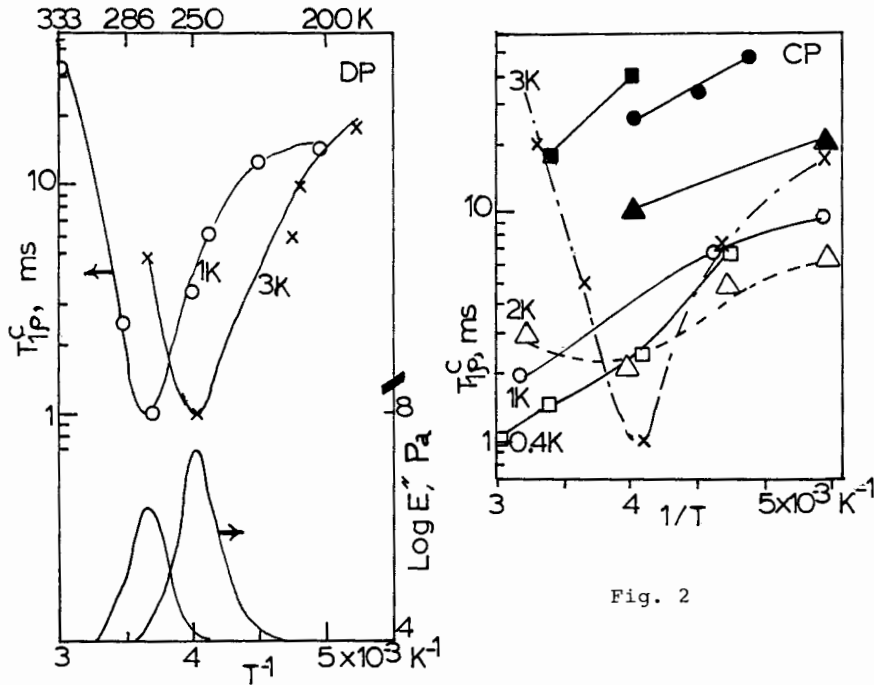


Fig. 2

Figure 1. Upper: ^{13}C - $T_{1\rho}$ as a function of temperature for the M_c 1000 and 3000 samples for carbon magnetization obtained by simple $\pi/2$ pulse. Lower: loss modulus from DMTA measurements at 10 Hz. E'' is in Pascals.

Figure 2. ^{13}C - $T_{1\rho}$ as a function of temperature for $M_c = 400(\square)$, 1000(0), 2000(Δ) and 3000(x). Filled symbols are for longer $T_{1\rho}$ in case of biphasic decay.

The absence of clear minima for the $M_c = 400$, 1000, and 2000 samples, and the extremely short $T_{1\rho}^C$ values over a wide range of temperature mean that the relaxation is dominated by some very effective mechanisms.

One plausible explanation would be the smearing out of methyl relaxation due to tighter packing in the crosslinking region, but of course the motion of the aromatic rings and other dipolar mechanisms of relaxing the carbons must be considered for the crosslink region. With $M_c = 3000$ the carbons detected by CP become the same as those for DP. The transition from $M_c=2000$ to $M_c=3000$ seems abrupt and it seems that one would expect there still to be a significant amount of CP detectable rigid crosslink regions. The absence of a wide rapidly relaxing region in the $M_c=3000$ sample indicates some 'threshold of plasticization' by the longer chains. Indeed the rule of thumb for achievement of Gaussian statistics for a chain is 100 bonds and that occurs for $M_c=1933$ so the $M_c=3000$ sample is the only one truly in the Gaussian region.

$T_{1\rho}^P$ as a function of temperature for $M_c=400, 1000$, and 3000 are shown in Figure 3. Each sample shows a typical spin relaxation minimum, but for a given sample the minimum in the ^{31}P relaxation occurs at a higher temperature than that for the corresponding ^{13}C relaxation as will be explored below. Currently available equations (Ref.13) for the chemical shift anisotropy (CSA) reorientation mechanism of relaxation of the ^{31}P nuclei can be used to predict the value of the minimum from the values of the chemical shift tensor determined at low temperature and low molecular weight samples ($\sigma_{\perp} = 143$ ppm, $\sigma_{\parallel} = -120$ ppm). The relaxation of the phosphorus nuclei clearly does not reach the predicted $T_{1\rho}^P$ minimum, however as the molecular weight between crosslinks increases the discrepancy decreases. The equations developed on the isotropic model for $(T_{1\rho}^P)^{-1}$ include a $(\sigma_{\perp} - \sigma_{\parallel})^2$ factor but it seems likely that the crosslink points in this case are not likely to be isotropically tumbling either because there are three chains attached to the junction point or the tris(4-isocyanatophenyl) thiophosphate acts as a very bulky, slow-to-move unit. Any such slow movement on the scale of $(\sigma_{\perp} - \sigma_{\parallel})\gamma B_0 = 20$ kHz would diminish the contribution of the anisotropy factor to the relaxation and thus the predicted values of relaxation time for the isotropic model would be shorter than those observed. This is the case for these networks so it appears that the junction points are not undergoing isotropic motion at the temperature of their minima. Examination of the lineshapes (Ref.11) corresponding to the temperatures at which the relaxation minima occur also corroborate that the reorientation of the P=S moiety is not isotropic until about 50°C above T_g .

^{31}P -NMR lineshapes as a function of temperature are shown in Figure 4 for the $M_c=1000$ sample. These lineshapes are obtained from the spin echo and are free of the phase distortion of our previously published spectra (Ref.11). The lineshapes in the range 291-400°K can be well fitted by a diffusion model based on the work of Sillescu (Ref.14). The model is for diffusion in an octant of the chemical shift ellipsoid with steps between

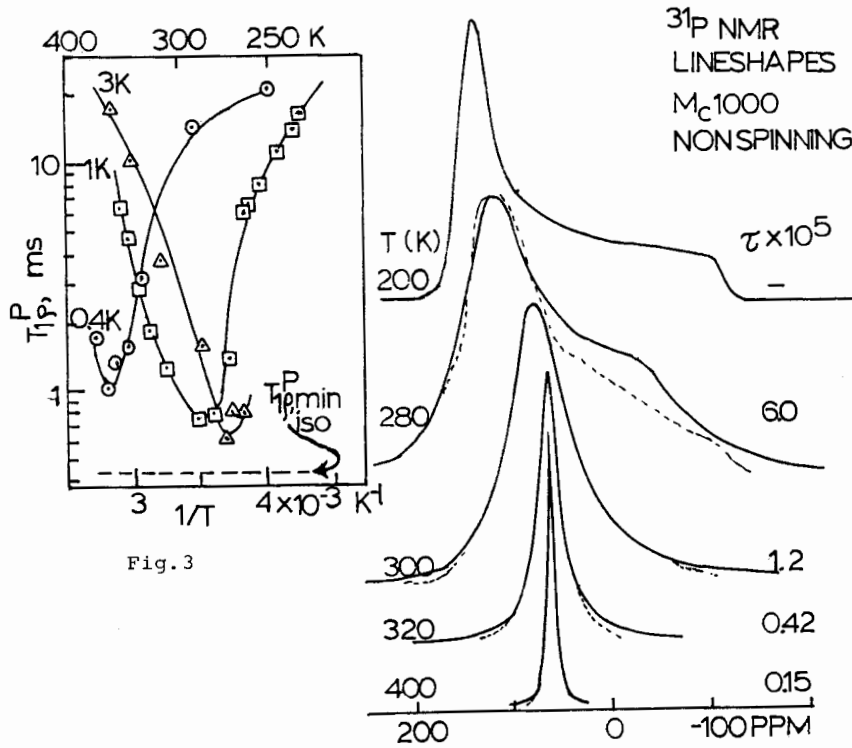


Fig. 3

Fig. 4

Figure 3. ^{31}P - $T_{1\rho}$ versus inverse temperature for $M_c=400$ (○), 1000 (□) and 3000 (Δ).

Figure 4. ^{31}P -NMR lineshapes for $M_c=1000$ as a function of temperature: observed(---), diffusion model calculated (—) yielding τ values shown.

sites separated by an angle increment $\partial\theta$ at a rate τ^{-1} . The resulting

correlation times τ are plotted in Figure 5 for several choices of $\delta\theta$. At temperatures below about 350 K for the M_c1000 sample the increment step size makes little difference. Above that temperature there is a strong dependence upon $\delta\theta$ of the τ necessary to fit the spectrum. If the size of the jump is constrained to be constant at 1.8° there appears to be a change in slope of the dependence of τ on $1/T$. If the linear dependence of the τ 's from the ^{31}P relaxation data (dotted line in Figure 5) implies that the correlation times from lineshapes should also be linear then there must be a transition at which the step angle increases. The discrepancy between

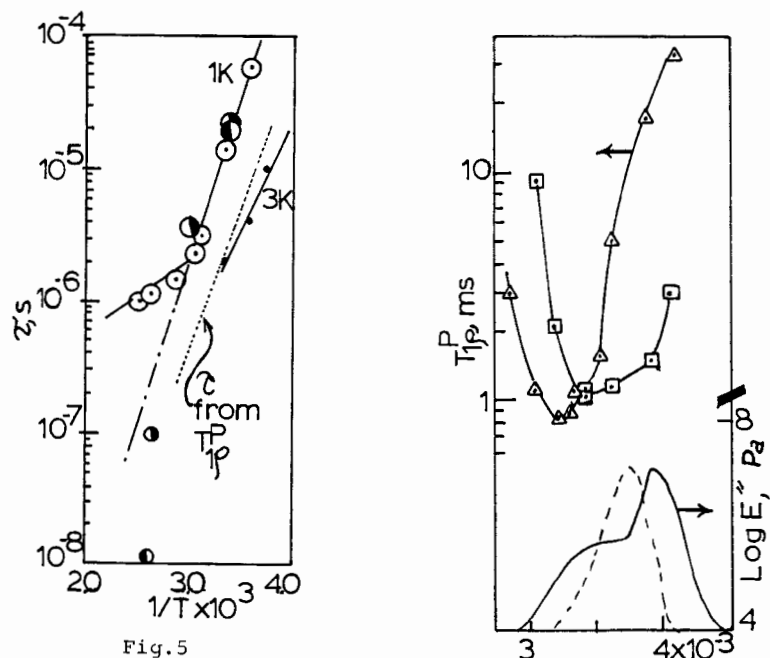


Fig.5

Fig 5. Correlation times for M_c1000 derived from lineshapes using diffusion model for 1.8° (\circ), 3.6° (\bullet), and 5.4° (\bullet) steps. Dashed line indicates τ derived from $T_{1\rho}^C$. τ for M_c3000 (1.8°) steps are also shown (\bullet)

Fig.6.Upper: ^{31}P - $T_{1\rho}$ for bimodal networks prepared from molar ratios of 2/1 (Δ) and 0.7/1 (\square) 400/3000 PPG. Lower: Corresponding loss moduli in Pascals from DMTA

the τ values from lineshape and relaxation times is about a factor of 5 and

is not very surprising given the limitations of the computer lineshape diffusion model and the assumption of isotropic reorientation in the relaxation time equations. The slopes, however, are in approximate agreement with activation energies of 11.5 and 10.2 kcal/mol, respectively.

A direct comparison of the carbon (Fig.1) and phosphorus relaxation (Fig.3) for the $M_c=1000$ and $M_c=3000$ networks shows clearly that the two minima are displaced in temperature. Even though the ^{31}P is relaxing primarily by CSA reorientation and the ^{13}C is probably relaxing by the H-C dipolar (IS) mechanism, it can be shown with few assumptions that both mechanisms depend upon the same spectral densities (Ref.15). This means that at a given frequency of observation, the $T_{1\rho}$ will have the same functional dependence upon τ but with different prefactors. Clearly the $T_{1\rho}$ minima for the two nuclei in a given sample occur at different temperatures. Since the minimum occurs at $\omega\tau=1$ and both nuclei are observed in the same spin lock field of $\omega=\gamma hB_1/2\pi = 50$ kHz it follows that at a given temperature the correlation time for carbon 13 is faster than the correlation time for the phosphorus 31. The ^{31}P minimum of the $M_c=1000$ at 287°K is only 7° above that for $M_c=3000$ while the ^{13}C minima occur at 273° and 240°, respectively. Apparently the junction point motion lags the segmental motion in these networks. Simple plots of $\ln \tau$ versus $1/T$ which are linear show that the lag factor is about 3 for the $M_c=1000$ and 6 for the $M_c=3000$ sample. τ was determined from $1/T_{1\rho}=A^2 \tau/(1 + \omega^2 \tau^2)$ with A empirically determined at the minimum. This larger lag factor for the $M_c=3000$ network implies that the crosslink is behaving as a sort of anchor with its own motion which is not greatly affected by the segmental bath.

Bimodal networks. The study of bimodal networks offers the possibility of observing differing mobilities of longer and shorter chains and of junctions with different length chains attached. To this end bimodal networks with molar ratios of 0.5 (=L) and 1.4 (=H) of $M_c=3000$ to $M_c=400$ were prepared. Plots of $T_{1\rho}^{\text{P}}$ and loss modulus versus $1/T$ are shown in Figure 7. The NMR minima are decidedly broader than in the case of the monodisperse networks of Figure 3 with Sample H showing a particularly unusual shape. In data not shown the $T_{1\rho}^{\text{C}}$ relaxation show minima not very different in shape than the data of Figure 1 with minima temperature fairly near those of the DMTA loss maxima of Figure 7. The observation

that the carbon relaxation minima are not affected in shape by the bimodal distribution strongly supports a model where the chains even in these bimodal networks mutually plasticize on another to produce a uniform segmental motion. The greatly increased breadth of the phosphorus relaxation minima strongly suggests that the reorientation of different crosslink bondings are not 'plasticized' by the longer chains. That is, each phosphorus can be connected topologically to either 3 short, 2 short/1 long, 1 short/2 long, or 3 long PPG chains. Each of these species seems to have its own reorientational motion almost independent of the segmental bath.

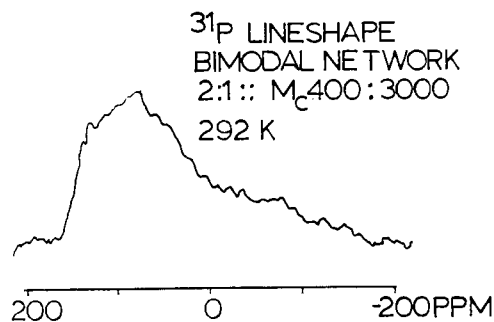


Fig.7. ³¹P-NMR lineshape for 2/1::400/3000 bimodal network at 292 K

This model is further supported by the nonspinning lineshape, for example of sample L shown in Figure 7 which appears to be some linear combination of the axially symmetric spectrum at the top of Figure 4 and some of the more motionally averaged shapes seen at higher temperatures. Further analysis of the bimodal data is underway.

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