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25322-68-3; PTMG (SRU), 25190-06-1; (PPG)(MDI)(BD) (block copolymer), 106208-51-9.

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Cross-Link Point Mobility in Swollen Polymer Networks by Phosphorus-31 Spin–Lattice Relaxation in the Rotating Frame

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ABSTRACT: Spin–lattice relaxation of ^{31}P nuclei in the rotating frame at 50 KHz, $T_{1\rho}{}^{\mathrm{P}}$, has been measured as a function of the linear swelling ratio ($\lambda = (V/V_0)^{1/3}$) and of M_c (molecular weight between cross-links) for a series of nearly monodisperse trifunctional α,ω-dihydroxypoly(propylene oxide) (M_c = 425, 1000, 2000, 3000) networks with tris(4-isocyanatophenyl) thiophosphate as the cross-linking agent. $T_{1\rho}{}^{\mathrm{P}}$ is strongly dependent upon both λ and M_c and offers a direct measure of the cross-link point motion. For M_c of 2000 or less, the $T_{1\rho}{}^{\mathrm{P}}$ versus λ plot has a minimum. Both line shapes and $T_{1\rho}{}^{\mathrm{P}}$ reach limits near full swell, indicating molecular motion is constrained by the swollen chains. For M_c = 3000, $T_{1\rho}{}^{\mathrm{P}}$ increases monotonically with increase of λ; the swollen chains do not appreciably restrict the motion of the cross-link. The results are entirely consistent with our previous studies on the motion of the chain by $T_{1\rho}{}^{\mathrm{H}}$ and $T_{1\rho}{}^{\mathrm{C}}$ in these networks where the effect of the cross-links is pronounced only for $M_c \leq 2000$.

Introduction

The level of understanding of the structure and dynamics of networks has been greatly elevated by recent improved spectroscopic and scattering techniques. Small angle neutron scattering (SANS) of labeled chains has shown the nonaffine elongation of single chains in networks.[1] Orientational dynamics has been studied by magnetic resonance relaxation and fluorescence correlation techniques. The central purpose of this work is to obtain quantitative information about the motion of the cross-link point itself in a series of cleanly synthesized model networks.

Nuclear magnetic resonance (NMR) has long been used to study rubbery materials. Nishi[2] studied T_2 of protons in carbon black filled natural rubber and was able to distinguish regions of restricted motion near the filler particles which were not affected by swelling in CCl_4. Rowland[3] and Charlesby[4] investigated the proton relaxation, $T_1{}^{\mathrm{H}}$, in several rubbery polymers as a function of temperature and cross-link density and found that the

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relaxation was not greatly affected until the cross-link density was high. With wide-line NMR spectroscopy available at that time, T_2 was found to be better than T_1 in discriminating entanglement and cross-link effects.[3] Segment mobility in swollen poly(dimethylsiloxane) gels has also been studied with proton T_2.[5] Orientational order in strained poly(butadiene) networks has been investigated by introduction of deuterium probes and monitoring the quadrupolar splitting as a function of extension.[6] Some four-branch star networks comprised of poly(butadiene) deuteriated near the junction point were shown by ^{2}H NMR to undergo nonaffine and inhomogeneous deformation of individual chains.[7] A recent series of elegant ^{2}H NMR probe studies has shown a strong dependence of orientational order after stretching upon preparation conditions.[8] A line-shape study of the ^{1}H NMR resonance for swollen poly(ethylene oxide) gels reported activation energies for segmental motion in two solvents.[9] Fluorescence polarization in deformed poly(isoprene) has been used to follow segmental orientational mobility,[10] and the results implicate both conformational and steric effects of segments especially at high extension as outlined by the theory of Erman and Monnerie.[11]

The present measurements were made on model networks having a range of uniform molecular weight between cross-links (M_c). In the first phase the segmental motion was monitored by spin–lattice relaxation in the rotating frame, $T_{1\rho}(^{13}C)$, which can discriminate those segments near to and far from the cross-link region.[12,13] Most important the segmental motion for $M_c > 2000$ is indistinguishable for network and linear extended polymers, but they are different for $M_c < 2000$ attributable to the restraining effect of the cross-links.

In the second phase of this work the ^{31}P relaxation and line-shape data on these same networks have been obtained as a function of swelling ratio. Relatively clear quantitative information about junction reorientation rates in these systems can be extracted from these results. A note on the ^{31}P NMR line shapes in unswollen networks as a function of temperature and M_c has appeared elsewhere.[14]

Experimental Section

Network samples were prepared from purified tris(4-isocyanatophenyl) thiophosphate and dry α,ω-dihydroxypoly(propylene oxide) (PPO).[12] Molecular weights of PPO were 425, 1000, 2000, and 3000. These samples were stored in a vacuum dessicator at 5 °C as the cross-link is known to hydrolyze slowly. Segmental motion studies were made in the networks shortly after their synthesis. The present ^{31}P NMR measurements were made on these same batches of samples. Since some months had lapsed, $T_{1\rho}{}^{C}$ was measured as an index of stability for comparison with the previously obtained value soon after synthesis. Several M_c 425 samples were rejected with 4 times higher $T_{1\rho}{}^{C}$. A M_c 1000 sample had a 1.5 times higher $T_{1\rho}{}^{C}$ but was studied anyway to see the effects of deterioration. This latter sample showed the anomalous behavior discussed, and no sound M_c 1000 samples were available.

Samples were ground to powders at 77 K and contained in 7-mm Al_2O_3 or ZrO_2 cells sealed with ceramic end caps fitted with two silicone O rings on each cap. Toluene was titrated into the opened cell with a 100-μL syringe. The cells were kept at room temperature by a constant flow of dry nitrogen gas. The swelling time was at least 6 h. No weight loss outside of weighing error of ±0.0002 g was observed over several days of cell use. The linear swell ratio, λ, was calculated as $(V/V_0)^{1/3}$. V_0 is the original network volume calculated from weight with densities.[15] $\rho(M_c\ 425) = 1.228$, $\rho(M_c\ 1000) = 1.112$, $\rho(M_c\ 2000) = 1.062$, and $\rho(M_c\ 3000) = 1.050$ g/cm^3 at 23 °C. V is the swollen volume. A series of experiments was performed comparing swelling in protonated toluene with those of deuteriated toluene in order to clarify the role of solvent in relaxation. Exactly parallel runs were made adding equal volumes to equal weights of M_c 2000 network.

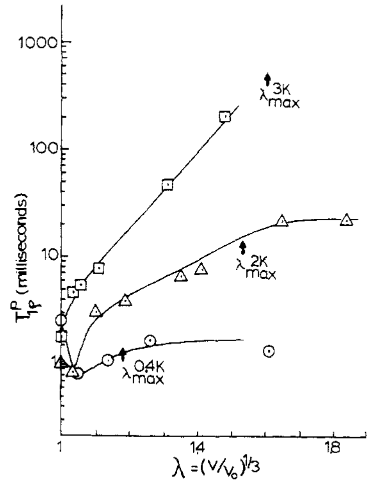

Figure 1. Phosphorus-31 spin–lattice relaxation times in the rotating frame, $T_{1\rho}{}^{P}$, versus extension ratio, $\lambda = (V/V_0)^{1/3}$ for networks with M_c of 425 (○), 2000 (△), and 3000 (□) λ_{max} for each network (designated by respective M_c = 0.4, 2, 3K) indicates maximum extension ratio based on a separate dimensional study.

All NMR spectra were obtained at 81 MHz on an IBM 200AF spectrometer with an IBM solids accessory and Doty solids probe. All spectra were obtained without spinning and with high power proton decoupling. Decoupling is beneficial for slightly swollen specimens but made little if any difference for highly swollen samples. Pulse sequences for measuring $T_{1\rho}{}^{P}$ were simply a ^{31}P 90° pulse followed by spin lock of time τ except for the low swell M_c 425 network where cross polarization was used to prepare ^{31}P spins. ^{31}P and ^{1}H 90° pulses were 5.0 μs and spin lock times ranged from 0.25 to 50 ms depending upon $T_{1\rho}{}^{P}$. Quadrature detection and phase alternation were used.

Results

Figure 1 shows $T_{1\rho}{}^{P}$ as a function of linear swelling ratio for networks with PPO molecular weights of 425, 2000, and 3000. At any given swell ratio above 1.05 there are dramatic differences in relaxation among the three samples. The M_c 425 sample shows a shallow minimum with short $T_{1\rho}{}^{P}$ values across the swelling range. The point of maximum swell, λ_{max}, based not on NMR but on simple measurement of volume change and solvent weight uptake,[15] is marked on Figure 1 for each network. It should be appreciated that the λ_{max} values were measured on a completely separate set of samples and some allowance must be made for some sample variation. Hence, it is expected that the λ_{max} values given in the figures only approximate the swell at which any changes in molecular relaxation should cease. Some increase in $T_{1\rho}{}^{P}$ for M_c 425 is seen for $\lambda > \lambda_{max}$. The network with M_c 2000 shows a minimum at $\lambda \approx 1.03$ and a linear increase in $T_{1\rho}{}^{P}$ in the range of λ = 1.1–1.6 followed by a plateau. The M_c 3000 $T_{1\rho}{}^{P}$ data in Figure 1 show no minimum. There is some curvature with a sharp increase of $T_{1\rho}{}^{P}$ for small increments of λ, followed by a linear change of the former with λ over the range 1.03–1.5. Measurements at higher λ were not feasible because of low signal to noise.

The line shapes of M_c 425 as they vary with swell ratio are given in Figure 2. The line shape does not change for $\lambda > 1.44$. This is somewhat larger than λ_{max}, but this may arise from the imprecision discussed in the previous paragraph. For the M_c 2000 network there are line-shape changes between λ = 1.0 and 1.08 (Figure 3), but there is little further change beyond λ_{max}. The small shoulder on the line shape past full swell possibly implicates some degradation. The change in line shape between no swell and full swell for M_c 3000 is slight, there being only a 30% decrease in apparent half-width at half-height for the λ

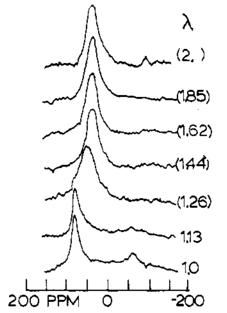

Figure 2. 81-MHz ^{31}P NMR line shapes as a function of extension ratio for network M_c 425. Values in parentheses are for solvent addition beyond λ_{max} to show that NMR properties do indeed change little past λ_{max}, as expected.

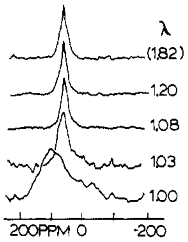

Figure 3. 81-MHz ^{31}P NMR line shape for network M_c 2000 as a function of extension ratio. Parentheses indicate solvent addition past λ_{max}.

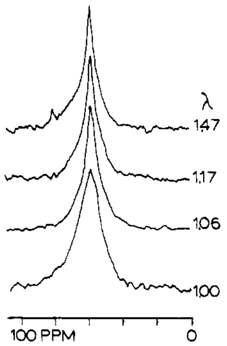

Figure 4. 81-MHz ^{31}P NMR line shapes for network M_c 3000 as a function of extension ratio. Parentheses indicate solvent addition past λ_{max}.

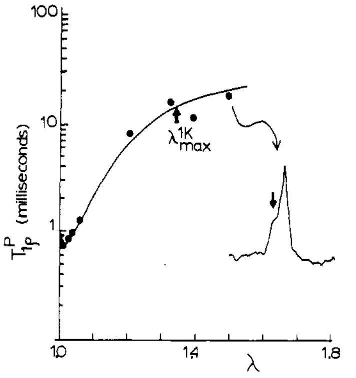

Figure 5. Phosphorus-31 spin–lattice relaxation, in the rotating frame, $T_{1\rho}^P$, versus extension ratio, λ, for M_c 1000 network. Inset shows spectrum of $\lambda = 1.49$ case with a shoulder indicating deterioration of phosphorus junction molecular structure and narrower central line feature than is seen for the higher M_c cases.

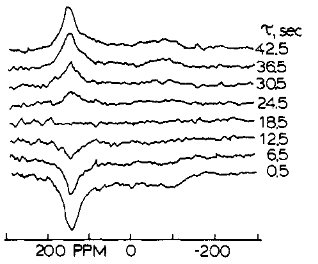

Figure 6. Phosphorus-31 spin relaxation, T_1^P, spectra of M_c 425 network showing uniformity of relaxation across the spectrum.

Table I
Relaxation Data for Deuteriated and Protonated Toluene Swelling

λ	$T_{1\rho}^P$(toluene), MS	$T_{1\rho}^P$(toluene-d_8), MS
1.03	1.68	1.88
1.06	3.27	3.88
1.09	6.09	5.41
1.25	14.7	13.4

= 1.48 sample compared to $l = 1$. However, as shown in Figure 4 there is a significant gradual sharpening of the central peak region with increased swelling.

The M_c 1000 sample behaved anomalously. The $T_{1\rho}^P$ versus λ plot (Figure 5) shows a very shallow minimum with steeper rise at increasing λ than is expected on the basis of the results from the other three samples. These longer than expected $T_{1\rho}^P$ values may well result from dangling ends or free chains. At highest swell the line shape was narrower than that for the M_c 2000 line, and the shoulder at ~80 ppm was much more prominent than for the M_c 2000 spectrum. These effects may result from the deterioration of the M_c 1000 network sample.

As a test of heterogeneity in the network samples a T_1^P relaxation at room temperature was performed on the M_c 425 sample as shown in Figure 6. Although signal to noise is not so good, there appears to be no dispersion of relaxation across the spectrum. This is particularly apparent in the 18.5-s delay spectrum, demonstrating that all line-shape positions zero at the same delay.

$T_{1\rho}^P$ measured in networks swollen in toluene-d_8 as compared to toluene do not differ significantly as shown in Table I. At low swell the deuteriated solvent gives slightly longer $T_{1\rho}^P$ values, and at higher swell the protonated solvent gives longer $T_{1\rho}^P$, but the differences are only on the edge of experimental accuracy of ±7%.

Discussion

The overall spectral changes in ^{31}P NMR line shapes as a function of λ and M_c give a clear measure of the motion of the ^{31}P cross-links and the influence of chain motion upon junction motion for these networks. The "powder spectrum" as shown for $\lambda = 1$ in Figure 2 indicates the expected axial symmetry based on the structure around the ^{31}P atom. The axial powder spectrum spans 278 ppm (22 KHz). Upon swelling the parallel and perpendicular features shift toward $\sigma_{iso} = \mathrm{Tr}(\sigma)$ when the axially bonded phosphorus junction moiety begins to move at a frequency greater than 22 KHz and the local molecular axis motions displace an angle ≥90°. For the M_c 425 sample this type of motion is not without constraints and is on the slow side of 22 KHz because the line shape at full swell although at σ_{iso} has a breadth much greater than the sharper feature of the unswelled case. This broader line shape is then a consequence of the fewer configurational states available to chains due to cross-link constraints.

In the simplest interpretation of $T_{1\rho}$ as a function of correlation time, τ, the minimum is reached at $\omega\tau = 1$ for observation at frequency ω.[16,17] In our case $\omega = \tau^{-1} \approx 50$ KHz at $\lambda \approx 1.04$. This near agreement of correlation time from line shape and from $T_{1\rho}$ considerations is encouraging and should improve with detailed line-shape calculations now under way. There is some change in line shape and $T_{1\rho}^P$ with swelling of the M_c 425 network beyond the λ_{max} = 1.14. This effect may be due to contributions from

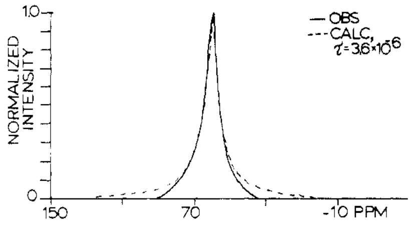

Figure 7. Comparison of calculated and observed line shapes for swollen networks: (—) observed line shape for M_c 3000, $\lambda = 1.17$; (---) line shape computed for hard collision exchange model, three sites with $\sigma_{\parallel}$ along mutually perpendicular axes at jump rate $\tau - 1 = 2.8 \times 10^5$ s^{-1} and $T_2 = 3 \times 10^{-3}$ s with $\sigma_{\parallel} = -127.3$ ppm and $\sigma_{\perp} = 154.7$ ppm.

defects such as loose ends in these samples. The uniform relaxation shown in Figure 6 argues against nonuniform ^{31}P environments in these networks. It is of keen interest that for M_c 425 the final line shape ($\lambda \geq 1.44$) is much broader ($\Delta\nu_{1/2} = 4000$ Hz) than the high λ shape attained for the M_c 3000 case (1200 Hz). This clearly indicates that the short chain lengths restrict the motion of the junction point so that the correlation time for its motion is considerably longer than for the higher M_c cases. This restriction is also seen, though less dramatic, in the M_c 2000 case where the line width at full swell is 2000 Hz, again broader than the M_c 3000 case. These broader lines and shorter $T_{1\rho}{}^{\mathrm{P}}$ values should reflect the constraints or number of rotational isomeric states accessible in the lower M_c networks.

A quantitative description of the change in correlation time and distribution of jump or diffusion angles with swelling would greatly enhance our understanding of the dynamic role of the cross-link point in elastic materials. Line shapes presented in this work, especially those with partially averaged chemical shift anisotropy, are sensitive to this quantitative information; however, data reduction are rather model dependent. We have computed spectra based on Mehring's multiple site molecular reorientation formula[17] as programmed by Wemmer.[18] In the jump rate, $\tau^{-1} \gg \gamma H_0(\sigma_{\perp} - \sigma_{\parallel})$, case the specific geometry of the jump interrelationship between sites does not show up in the narrowed line shape. We adopted a simple three-site model with $\sigma_{\parallel}$ respectively along x, y, and z axes. For $\tau < 2 \times 10^{-5}$ s the computed line shapes are narrow and isotropic and are somewhat similar to our observed high-swell shapes. However, as shown in Figure 7 the calculated line shape has much broader wings than the observed M_c 3000, $\lambda = 1.17$ shape even though the upper 80% of the line shape matches well to the observed shape. This incongruity of line shape is more dramatic for lower λ. For higher λ there is little if any line-shape change even though $T_{1\rho}{}^{\mathrm{P}}$ changes dramatically as shown in Figure 1. The absence of sensitivity of line shape to τ might be explained by some flexibility in the phosphorus molecular framework which gives a range of chemical shifts, thus smearing the isotropic line. For $\tau > 2 \times 10^{-5}$ the model leads to extra humps in the calculated shape similar to those seen in P_4.[19] The broad line shapes such as for M_c 425, $\lambda = 1.26$ in Figure 2, and for M_c 2000, $\lambda = 1.00$ in Figure 3, show no such features so any precision in correlation times and angles based on line shapes must await work on further simulation models. It is reasonable and exciting to expect that 2D exchange NMR[20] will soon yield the details of jump versus diffusion motion and the distribution function of angular motion of the cross-link point.

It is also difficult to unambiguously interpret NMR relaxation times in terms of correlation times; the difficulties apply also to the present case of $T_{1\rho}{}^{\mathrm{P}}$ relaxation as a function of swelling ratio. The exact form of $T_{1\rho}(\tau)$ depends upon the mechanism postulated. In these networks ^{31}P–^{31}P dipolar interaction is unlikely if there is regular >20 Å spacing between ^{31}P nuclei expected in these networks although aggregation of cross-link points through phase separation is not ruled out. The ubiquitous proton bath from the network chain, aromatic cross-linking agent, and the toluene swelling agent each may contribute heteronuclear dipolar decoupling. In addition, up to some point of rapid motion, modulation of the chemical shift anisotropy clearly is the major contribution to the relaxation. These mechanisms could be sorted out by use of appropriate deuteriated species and relaxation studies at a series of NMR frequencies. The comparative data in Table I for protonated and deuteriated toluene relaxation conclusively show that solvent protons contribute less than 10% to the relaxation rate. An additional factor to consider in the relaxation interpretation is that the importance of separating the amplitude and frequency modulation of motions has been shown to be important.[21] Both heteronuclear dipole–dipole (HDD) interaction and chemical shift anisotropy (CSA) contributions to $T_{1\rho}$ follow the same spectral density,[17] so one expects

$$\left(\frac{1}{T_{1\rho}}\right)_{\mathrm{obsd}} = (K_{\mathrm{CSA}}{}^2 + K_{\mathrm{HDD}}{}^2)\,\frac{\tau}{1 + \omega_1{}^2\tau^2}$$

to describe the fluctuation dependence of $T_{1\rho}$, assuming the same correlation time for each mechanism. It is expected that the relative contribution of each relaxation mechanism may change with λ, but on a simplest model keeping the K^2 constant we may convert $T_{1\rho}$ values to τ values based on the $\omega\tau = 1$ value. On the short τ side of the minimum we may plot ln ($T_{1\rho}$) versus λ to get a kind of energy per unit of linear swell. From the slopes of Figure 1 one sees that the energies M_c 3000 and 2000 are in the ratio of about 2:1, implying that it requires twice the energy to stretch the 2K network as the 3K network in the linear region.

The increase in orientational mobility with swelling is in agreement with the fluorescence experiments and theory of Erman and Monnerie,[11,12] who observed in labeled polyisoprene a linear increase of main chain segmental mobility by a factor of about 2.5 between $\lambda = 1$ and 1.05, which is about the same as our $T_{1\rho}$ change over that swell range. Our $T_{1\rho}{}^{\mathrm{P}}$ values pertain to the orientational mobility of the junction point directly. Its relationship with the motion of chain segments will be discussed below.

The failure of the M_c 1000 case to follow the trend for the M_c 425, 2000, and 3000 samples is ascribable to sample heterogeneity as shown in the high-swell spectrum inset to Figure 5. The sample still possessed network properties in that it was an elastic solid and swelled, but clearly for detailed motional analysis the sample is entirely unsatisfactory. The overall trend with swelling to show a minimum followed by a relatively sharp rise in $T_{1\rho}$ with a subsequent leveling off is the same as for the other networks but apparently increased freedom of some of the chains through degradation shortens the correlation time and lengthens $T_{1\rho}{}^{\mathrm{P}}$

As a *caveat* it should be pointed out that these networks include a rather bulky cross-linking agent which will influence the relaxation picture. Although reorientation of the phosphorus moiety is quite certain, the particular λ at which this sets in and the value of τ at a given λ may be influenced by the presence of the aromatic rings in the vicinity of the ^{31}P atom as well as the possibility of some hydrogen bonding between urethane linkages. Research is underway to produce networks with ^{31}P at the junction point but with simpler linkage to the polymer chain.

There is consistency between this ^{31}P junction point data and the previous ^{13}C, segmental motion data.[13,14] For the segmental motion in networks with $M_c > 2000$ the ^{13}C relaxation pattern showed little network influence as evidenced by the close resemblance to the ^{13}C relaxation in long linear chains. This threshold is also shown in the ^{31}P line shapes and $T_{1\rho}{}^{\rm P}$ of this work in that the M_c 425 and M_c 2000 networks show definite limitations to motion at full swell; i.e., the network chain constrains the cross-link motion. Even though we were unable to observe the high λ case for M_c 3000, it is clear from Figure 4 that little line-shape change will ensue with higher λ but the $T_{1\rho}{}^{\rm P}$ would be of keen interest.

The origin of junction mobility is from the segmental motion and the interrelationship between the two is a topic of basic interest in understanding real networks. Further experiments in which simple extension of networks is followed by ^{31}P NMR are in progress. Comparison of dielectric measurement, ^{13}C NMR relaxation, and ^{31}P NMR relaxation on this system of networks shows that the ^{13}C $T_{1\rho}$ minimum is near the T_g from DSC and dielectric relaxation but that the ^{31}P junction point motion of the unswollen polymers begins at a much higher temperature than the segmental T_g. This strongly suggests coupling between the junction point motion and segmental motion suffers a lag, presumably because of the anchoring effects of multiple chains emerging symmetrically from each junction point.

In assigning particular motions to the large and rapid change in $T_{1\rho}{}^{\rm P}$ with linear swell ratio (Figure 1), it is of interest to compare the changes in $T_{1\rho}{}^{\rm P}$ with temperature in the unswelled networks.[14,22] Between room temperature and 310 K $T_{1\rho}{}^{\rm P}$ for the M_c 3000 sample increases by only 1 order of magnitude. That swelling in toluene by a linear swelling ratio of only 1.5 increases by $T_{1\rho}{}^{\rm P}$ 3 orders of magnitude dramatizes the motional freedom or rotational isomeric states made accessible by solvent. These differences should be theoretically calculable and could reflect a number of factors including inter- and intrachain limitations on available rotational isomeric states in networks.

In summary, this work shows that ^{31}P NMR is a powerful tool for examining the specific motion of the junction point in the networks. $T_{1\rho}{}^{\rm P}$ is very sensitive to M_c, swell ratio, and defects in the network. $T_{1\rho}{}^{\rm P}$ changes by several orders of magnitude between $\lambda = 1$ and 1.5 for M_c 3000 but hardly changes for M_c 425. ^{31}P line shapes for $M_c \leq 2000$ at maximum swell reflect the constraints placed on the junction point by the network chains. These orientational mobility results are in agreement with previous theories of Erman predicting linear variation of log (mobility) with λ within the range studied.[11]

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Registry No. (PO)(tris(4-isocyanatophenyl) thiophosphate) (copolymer), 115678-76-7; (PPO)(tris(4-isocyanatophenyl) thiophosphate) (copolymer), 115678-77-8.

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Small-Angle Neutron Scattering of Cross-Linked Polystyrene Networks

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ABSTRACT: Small-angle neutron scattering experiments have been performed on polystyrene networks labeled with deuterium. Changes in molecular dimensions of the polymer chains upon swelling and upon stretching in the rubbery state were derived from these measurements. The experimental observations were compared with predictions from classical theories, and areas of agreement and disagreement were discussed.

Introduction

The elasticity of rubbery materials results from the uncoiling of flexible molecular chains in the rubber network. Theoretical models of this phenomenon relate macroscopic variables such as the modulus of elasticity, thermodynamics of deformation, and swelling in solvents to the elongation of these molecular chains. Only in the past 15 years with the development of small angle neutron scattering (SANS) has it become possible to make direct measurements of macromolecular dimensions. By com-