# Notes

## Reconsideration of Deuterium NMR Observations of Orientational Coupling in Polymer Networks in Light of Motional Heterogeneity in Styrene-$d_8$–Styrene Block Copolymers

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*Received December 16, 1991*
*Revised Manuscript Received May 5, 1992*

### Introduction

Short-range orientational coupling has been observed in networks and melts by various optical techniques[1–3] and deuterium nuclear magnetic resonance ($^2$H-NMR).[4,5] To gain information about intermolecular interactions in bulk polymers, oligomers with chemical structure identical to that of the network or highly entangled melt chains have been used as probe molecules. For various degrees of macroscopic deformation of the matrix, the steady orientation distribution in the network (or quasi-steady in the melt) and of the probe molecules is measured. The ratio of the order parameter observed for the probe to that of the matrix is a measure of the degree of local orientational coupling and is defined as the coupling constant, $\epsilon$. The optical measurements of the coupling constant, $\epsilon$, have given values between 0.3 and 0.7 for polyethylene and poly(ethylene–propylene).[2,3] For polymer networks, $^2$H-NMR spectroscopic results have been interpreted as demonstrating a value of $\epsilon = 1$ for both polybutadiene and poly(dimethylsiloxane).[4,5]

If the coupling constant for these polymers is indeed unity, then the network chains, which experience both the intermolecular orientational coupling and the extensional force acting at their ends, are oriented to exactly the same degree as the free probe chains, which experience only the intermolecular coupling.[6,7] For this to be the case, the intermolecular coupling must be much stronger than the extensional force that drives the overall orientation. This is difficult to accept in the two polymers for which it is reported, since neither offers hydrogen bonding, dipole–dipole interaction, or stiff monomer units to provide strong intermolecular coupling.[4,5] Here an alternate interpretation of the $^2$H-NMR line shapes is proposed that eliminates this paradox.

The $^2$H-NMR spectra of networks show that the quadrupolar interaction is heterogeneously averaged. This can be attributed either to a distribution of motional rates for segmental reorientation[8] or to a distribution of quadrupolar interactions that are averaged by a single reorientational process.[9] Here we adopt the former view and suggest that the average rate of segmental reorientation is substantially higher for dangling chains than it is for true network chains. Therefore the dangling chains dominate the narrow component of the spectrum, and it is their order parameter that determines the peak splitting of the network line shape. To test the plausibility of substantial dynamic heterogeneity between dangling chains and true network chains, we characterize the difference in mobility between the ends and the center of an entangled linear polymer using styrene-$d_8$–styrene block copolymers.

### Previous Results

The general appearance of the observed $^2$H-NMR line shapes is shown in Figure 1. In an isotropic network (extension ratio $\lambda = 1$), line shapes like those in the top row of Figure 1 are observed for the labeled oligomer (in an unlabeled network) and for the labeled network. The labeled oligomer shows a narrow line (~20-Hz width at half-height in Sotta et al.[5]), decaying to zero at the baseline. In contrast, the network shows a line shape that seems to be a narrow line (~30-Hz width) superimposed on a broader one (~230-Hz width). Upon extension both the oligomer and network spectra show splitting due to the anisotropic orientation distribution of the carbon–deuterium bonds (lower two rows, Figure 1). The magnitude of the splitting, $\Delta\nu$, is quantitatively related to the orientational order parameter. Comparison of the splitting observed between the peaks of the spectra of the oligomer and the network as a function of the extension ratio shows the two to be equal. From this it was concluded that the order parameter of the oligomers is equal to that of the network chains.[5]

### Alternate Interpretation

It is known that these networks contain dangling chains. Molecular motion of the dangling chains is on average somewhat more hindered than that of free oligomers and somewhat less restricted than that of the true network chains (i.e., chains connected at both ends to the network). Since molecular motion largely controls the line width in the reported spectra and since the line width varies inversely as the correlation time of molecular motion,[10] it is reasonable that three effective line widths may be present:[11] the narrowest line is expected for the oligomer, an intermediate width for the dangling chains, and the greatest width for the true network chains.

On the basis of this simplified view, we approximate the oligomer line shapes (Figure 2 of ref 5) by a single Lorenzian line that is split by anisotropic orientation, and the network line shapes (Figure 6 of ref 5) by a superposition of two Lorenzian lines with a weighting based on a fraction of dangling chains of 18% (within the range 10–20% estimated for the PDMS networks) and with the two line widths evident in the observed network spectra. The results are shown in Figure 1. Although the narrow component of the network line shape accounts for a relatively small fraction of the total spectral intensity, it dominates the central portion of the spectra (right side, Figure 1). Consequently only the orientation of the most mobile segments can be inferred from the splitting of the peak when the network is deformed.

Upon extension (at steady state), we expect the true network chains to orient under the combination of the

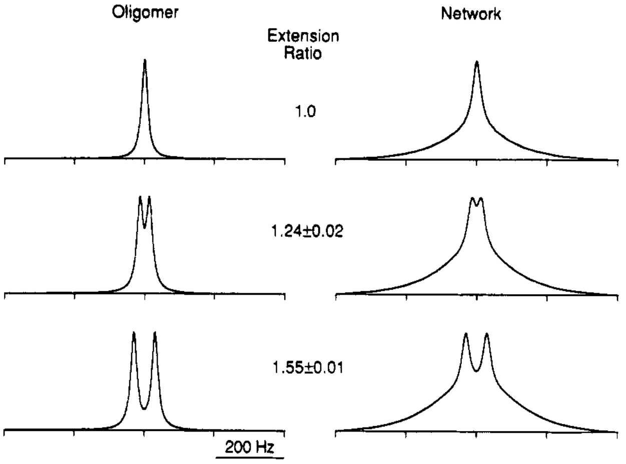

**Figure 1.** Simulated line shapes for oligomers (left column) and network (right column). The extension ratios indicated are those at which the corresponding spectra were observed by Sotta et al.[5]

force at the network junctions and the local intermolecular coupling, and we expect the dangling chains to orient only under the influence of the short-range orientation coupling. Therefore, let the two components of the network line shape undergo different degrees of splitting at a given extension, $\Delta\nu_d$ for the dangling chains and $\Delta\nu_n$ for the network chains. In particular, results are shown for $\Delta\nu_d = 0.5\Delta\nu_n$. This corresponds approximately to the case $\epsilon = 0.5$, a value in the middle of the range indicated by optical measurements. We assume the order parameter of the oligomers equals that of the dangling chains, because both are oriented only due to orientational coupling. Line shapes suggested by this simple model for $\Delta\nu_d = 14$ and 30 Hz (corresponding to $\lambda \approx 1.24$ and 1.55, in ref 5) are in good agreement with the observed spectra. This indicates that the $^2$H-NMR spectra actually are consistent with values of the coupling coefficient observed by optical techniques.[12]

## Experimental Section

Our interpretation depends upon the greater mobility of dangling chains dramatically reducing their $^2$H-NMR line width relative to that of true network chains. To determine the plausibility of ascribing the narrow line to the dangling chains, we consider an entangled polymer melt as a model system. Entangled linear polymers are used because their partially motionally averaged line shapes show line width heterogeneity like networks and because we can control the length and location of labeled blocks in the chains.

In particular, we measure the $^2$H-NMR line width as a function of temperature for deuterated end blocks and center blocks. Four differently labeled, nearly monodisperse polystyrenes were used for these experiments. Three of the polymers are triblocks with $M_w \approx 68\,000$ g/mol: one with short end blocks deuterated [PS-SE, (1.3k-$d_8$-S)–(63k-S)–(1.3k-$d_8$-S)], another with a short center block labeled [PS-SC, (34k-S)–(3k-$d_8$-S)–(34k-S)], and one with a long center block labeled [PS-LC, (31k-S)–(7k-$d_8$-S)–(31k-S)]. The fourth sample is a 100 000 g/mol diblock polymer with a long end block labeled [PS-LE, (90k-S)–(10k-$d_8$-S)]. The polymers were prepared by sequential addition of purified monomers using living anionic polymerization. The polydispersities were $M_w/M_n \leq 1.07$ as determined by GPC. The reported molecular weights of the blocks were determined from the monomer feed ratios and the overall molecular weight as determined by GPC.

The pulsed deuterium NMR (30.72 MHz) spectra were obtained with a Bruker MSL-200 NMR spectrometer equipped with a B-VT-1000 temperature control unit. Spectra were acquired using the solid echo sequence[13] $[(\pi/2)_x–\tau_1–(\pi/2)_y–D0]$ with phase cycling. The 90° pulse length was 2 $\mu$s, and data were acquired during the $D0$ period and accumulated. The number of scans (200–16 000) was adjusted to obtain an adequate signal to noise ratio. The delay time $\tau_1$ was 20 $\mu$s and $D0$ was 0.5 s. Data (1024 points) were acquired with spectral width from 50 to 625 kHz, depending on the time required for complete decay of the signal.

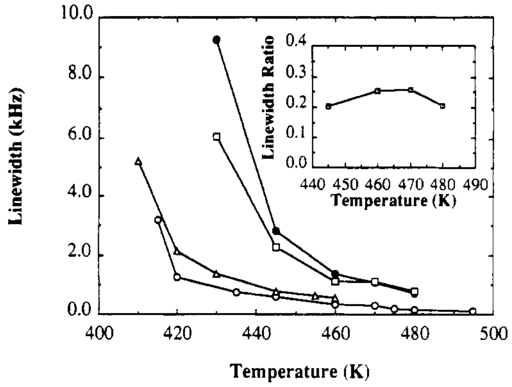

**Figure 2.** Temperature dependence of the $^2$H-NMR line width of the deuterated block in the following linear polystyrenes: (○) PS-SE; (△) PS-LE; (□) PS-LC; (●) PS-SC. Insert: Ratio of the line width of PS-SE to that of PS-SC.

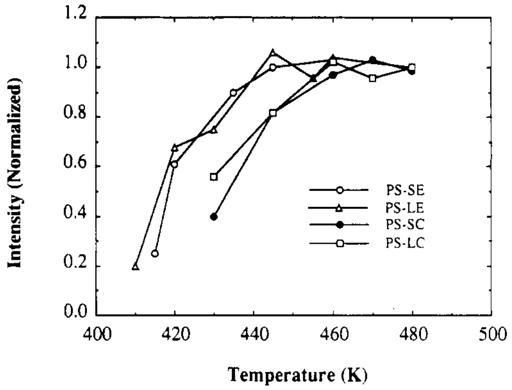

**Figure 3.** Temperature dependence of the normalized intensity of the spectra of the deuterated block in the linear polystyrenes.

## Results

The one-dimensional $^2$H-NMR line shapes clearly show the effect of position along the chain. In contrast to the heterogeneous line width observed for perdeuterated polymers, the line shapes for the labeled blocks are all nearly Lorenzian. The increase of mobility with temperature results in progressive narrowing of the line width (Figure 2) and saturation of the signal intensity[14] (Figure 3). The line width and intensity curves are shifted to higher temperature for the center-labeled blocks compared to the end-labeled blocks. At any given temperature, the line width is much greater for the center blocks than the end blocks (Figure 2). In particular, at temperatures where both the end and center blocks appear to be in the fast motion limit (i.e., above roughly 450 K; see Figure 3), the ratio of the line width of PS-SE[15] to that of PS-SC becomes nearly independent of temperature with a value of 0.23 ± 0.03 (insert, Figure 2). The line width and intensity depend much more on the position of the labeled block than on its length for blocks from 1300 to 10 000 g/mol.

## Conclusion

We have demonstrated that in an entangled melt at temperatures well above $T_g$ ($T > T_g + 60$ °C) the $^2$H-NMR line width of a deuterated end block of length $M_e/10$ is roughly one-fifth to one-fourth that of a center block of comparable length. This difference is a manifestation of the greater motional freedom of segments near a free end compared to segments in the interior of an entangled chain.

We expect qualitatively similar dynamic heterogeneity to exist between dangling chains and true network chains. Therefore, it is reasonable to attribute the intensity in the narrow component of the line shape of a deuterated network to the dangling chains.

With this interpretation of the $^2$H-NMR line shapes, the splittings that are found to be equal[5] are those of the dangling chains and the free oligomer. This eliminates the paradox that appeared to exist, because the steady-state orientation of both the dangling chains and the free oligomers is driven only by intermolecular orientational coupling to the mean field of chains.

**Acknowledgment.** This work was supported by the NSF Presidential Young Investigator Program (J.A.K.).

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(11) Actually there is a distribution of correlation times for each of the three types of chains, but here a simplified treatment with a single effective $T_2$ is used to illustrate the new interpretation of the line shapes.
(12) Careful analysis of the network line shapes would be required to determine the magnitude of the splitting of the broad component because $\Delta\nu_n$ is much less than its line width.
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(15) At temperatures above 470 K, the line width of the end-labeled polystyrenes was small enough that the difference in the chemical shift of the alkyl and aromatic deuterons could be observed. The line widths of the two individual peaks were determined by an optimal fit of two Lorenzian peaks to the observed line shape. The width of the aromatic deuteron line was consistently somewhat narrower than that of the alkyl deuterons (roughly 75–80%). The average of the two values is shown in Figure 2.

**Registry No.** (d-PS)(PS) (block copolymer), 108592-10-5.