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Communications to the Editor

Oligomers as Molecular Probes of Orientational Order in Strained Elastomeric Networks

In the past few years deuterium magnetic resonance (^2H NMR) has proven to be a valuable technique in the study of orientational order in elastomeric networks created by uniaxial strain. A measure of orientational order is the quadrupolar splitting of the ^2H NMR signal of a deuterated probe molecule generated by the orientational field in the strained network. This was first exploited by Deloche and Samulski,[1] who interpreted the quadrupolar splitting of deuterated solvent molecules used as swelling agents in terms of short-range orientational correlations between solvent molcules and polymer segments. The segmental order was probed directly by use of deuterated networks.[2-4] Gronski et al.[3] showed that in addition to the order parameter obtained from the quadrupolar splitting at maximum signal height characterizing the average segmental orientation, additional information can be obtained about the orientational behavior of the chain length distribution in the network by an analysis of the line shape of the ^2H NMR signal. The utility of selective deuteration was demonstrated for the case of chemically cross-linked networks[3] and thermoplastic elastomers.[4] Networks selectively deuterated at network junctions showed that chain segments attached to network junctions are oriented to a higher extent than the average. In a recent communication Samulski et al.[6] contrasted the quadrupolar splitting $\Delta\nu_s$ of deuterated solvent pobe molecules and the quadrupolar splitting $\Delta\nu_p$ of deuterated network chains at the same degree of swelling. The former was found to be smaller than the latter, which was explained by the structural dissimilarity between the probe and a hypothetical polymer segment. It was anticipated that $\Delta\nu_s/\Delta\nu_p \rightarrow 1$ if structurally similar molecules, i.e., oligomers of the same structure, were used as probe molecules. Using oligomers of increasing chain length, as the authors suggested, might provide a means of quantifying the ill-defined quantity of the hypothetical segment. In this communication we describe the main results of such an investigation.

The orientation behavior of four oligobutadienes with P_n = 10, 20, 40, and 80 (OB-10, OB-20, OB-40, and OB-80) in strained polybutadiene networks of various cross-link densities at different degrees of swelling was investigated. The oligomers were prepared by anionic polymerization from butadiene deuterated at the CH_2 groups in the 1,4 position and possess about equimolar 1,4 cis/trans structure and ca. 5–11% 1,2 monomer units. The networks were made from anionically prepared precursor chains by

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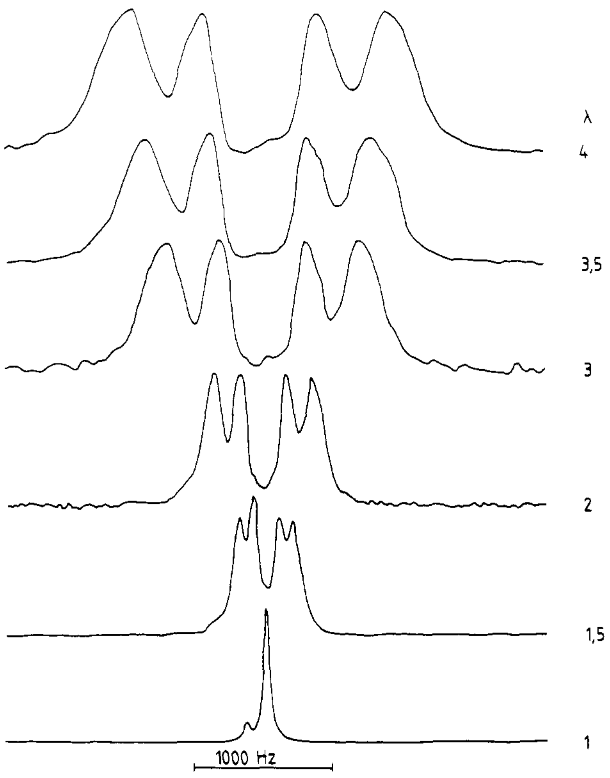

Figure 1. ^2H NMR spectra of the swelling agent 1,4-oligobutadiene-d_4 (P_n = 10) in a strained polybutadiene network as a function of extension ratio λ. The polymer volume fraction is 0.9 and the mean molecular weight of network chains, determined from $2C_1$ of the Mooney–Rivlin plot, is 16 400.

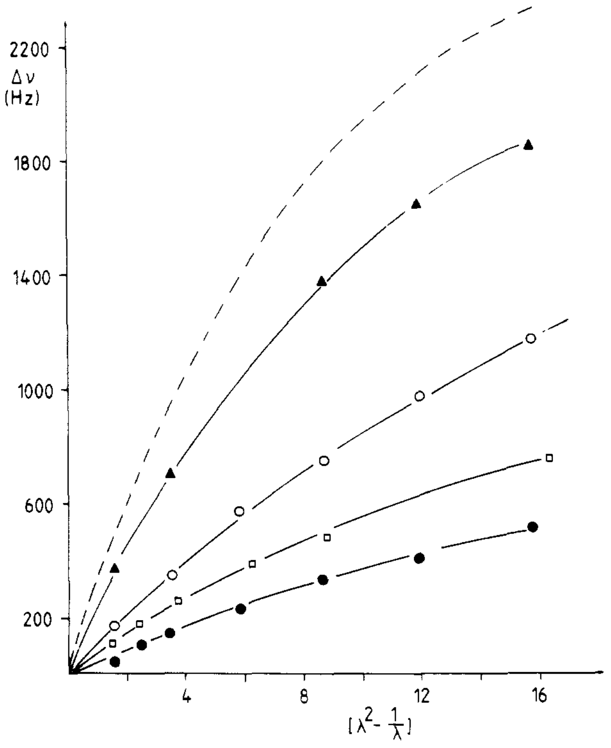

Figure 2. Quadrupolar splitting of the trans CD_2 groups of the swelling agent 1,4-oligobutadiene-d_4 (P_n = 10) for various polymer volume fractions: (▲) 0.9, (○) 0.7, and (●) 0.5 in a polybutadiene network (M_c = 16 400). The upper curve (- - -) represents the quadrupolar splitting extrapolated to the dry state. (□) Quadrupolar splittings of a deuterated network (M_c = 15 900) in the dry state (from ref 3).

cross-linking in solution.[7] The synthesis and characterization of the oligomers are described elsewhere.[8] ^2H NMR spectra were obtained with a CXP-300 Bruker spectrometer. The direction of the field B_0 was parallel to the principal axis of strain **d**.

In the following we describe the main features of the investigation concerning conformational effects and the magnitude of oligomer vs. segmental orientation. A detailed analysis with additional material, e.g., concerning effects of oligomer chain lengths, will be presented in a later publication. In Figure 1 the ^2H NMR spectra of OB-10 are presented at various extension ratios with respect to the swollen unstrained length. The volume fraction of the oligomer is 0.1, and the cross-link density is characterized by a mean molecular weight M_c = 16 400 of the network chains obtained from the Mooney–Rivlin constant $2C_1$ from stress–strain measurements. As in the case of low molecular weight solvents,[1] the deuterium resonance showing a single line in the isotropic state exhibits a quadrupolar splitting increasing with strain. The new result is the unusual magnitude of these splittings for a low molecular weight molecule dissolved in a strained rubber network. Another new result is that a splitting of the resonance into two pairs of signals instead of one is observed. The ratio of the intensities of the outer and inner doublet was shown to be identical with the ratio of trans and cis double bonds in the oligomer as measured by ^{13}C NMR. The analysis of the methine carbon resonances with known assignment[9] shows that the trans content decreases from 55% to 47% with increasing molecular weight of the oligomers OB-10 to OB-80.[8] The same change is observed for the relative intensity of the outer doublet of the deuterium resonances of the oriented samples. The splitting of the outer doublet increases from 380 Hz at λ = 1.5 to 1940 Hz at λ = 4,0. In Figure 2 the quadrupolar splittings of the trans pair are plotted vs. the strain function $\lambda^2 - \lambda^{-1}$ for various volume fractions of OB-10. As observed earlier in the case of the deuterated networks,[3] the quadrupolar splittings become saturated at high strain after an initial linear increase. The upper curve in Figure 2 represents the splittings obtained by extrapolation to zero oligomer content. The magnitude of this splitting is in sharp contrast to the much lower quadrupolar splitting of a deuterated network (PB$_d$-3–5 of ref 3) also included in Figure 2. Both networks have approximately the same M_c values (ca. 16 000). To appreciate the significance of these results one must recall the origin of the quadrupolar splitting. It arises because in an anisotropic medium like a strained rubber the molecular motion is also anisotropic. Consequently the fluctuating anisotropic quadrupolar interaction between the deuterium quadrupole moment and the electric field gradient directed along the C–D bonds is not averaged on the time scale of the quadrupolar interaction frequency (10^6 Hz) even for small highly mobile solvent molecules.[1] The degeneracy of the Zeeman energy levels is removed and a quadrupolar splitting is observed proportional to the time-averaged orientation of the C–D bonds with respect to the direction of the magnetic field. In the fast-motion limit, valid for rubbers, the quadrupolar splitting can be expressed by

$$\Delta\nu_i = \tfrac{3}{2}\delta\langle P_2(\cos\phi_i)\rangle\langle P_2(\cos\theta)\rangle P_2(\cos\psi) \qquad i = c, t \quad (1)$$

where $\delta = e^2qQ/h$ is the static quadrupolar coupling constant (δ = 164 kHz for polyethylene[10]) and $\langle P_2\rangle$ the time-averaged second-order Legendre function specifying the average orientation (ϕ_i) of the CD bonds near cis (c) and trans (t) double bonds with respect to a chain direction (e.g., the end-to-end vector of a statistical chain segment), the average orientation (θ) of the chain vector with respect to the principal axis of strain, and the fixed orientation ψ of the strain direction with respect to the magnetic field. The latter orientation factor is 1.0 because $\mathbf{d}\|\mathbf{B}_0$.

The fact that two quadrupolar splittings are observed, one for CD_2 groups at double bonds in cis configuration and another in trans configuration, can be explained by different constraints imposed by the combined influence of configuration and conformation leading to different conformational order parameters $\langle P_2 \cos (\cos \phi_i)\rangle$ with respect to the orientation of a statistical segment. In fact different quadrupolar splittings have been observed for CD_2 spacer groups in main-chain liquid crystalline polymers,[11] and it was shown by RIS calculations that different conformational order parameters with respect to the rigid mesogenic groups account for these splittings.[12] From the spectra in Figure 1 it can be seen that the ratio of trans and cis quadrupolar splittings increases with strain from 2.0 to 2.3. Slightly lower ratios are found for higher oligomer volume fractions. These effects are attributed to conformational changes during stretching or dilution, respectively. Monte Carlo simulations of stretched elastomer chains are currently in progress to explain the observed splittings. The knowledge of the ratio of the cis/trans quadrupolar splittings will serve to determine the length of the statistical segment which has to be consistent with the observed ratio. At large strain ($\lambda \geq 2.5$) the cis/trans doublets are split further, probably because the conformational order parameters $\langle P_2 \cos (\phi_i)\rangle$ in eq 1 depend not only on the configuration of the double bond in the immediate neighborhood but also on the configuration of the double bond separated by two single bonds on the other side. It has be left to conformational calculations whether this is a consequence of the selection of specific conformations of the bond triplets between the double bonds by the imposed strain or whether the enhanced segmental orientation merely acts as a "resolution enhancement" of conformations which are already present in the undeformed state. Because of the greater line width different cis/trans quadrupolar splittings and their relative changes cannot be observed in the spectra of the networks. Therefore the oligomers represent ideal probes to monitor conformational changes not only in the oligomer molecules but also in the polymer chains by virtue of their identical structure.

In recent calculations of the ^{2}H NMR line shapes of strained polybutadiene networks[3] it was shown that a segment length of 10 monomer units had to be chosen under the assumption that the conformational equilibrium was not disturbed by strain. Therefore one expects that the quadrupolar splitting of oligomer guest molecules of a length of 10 monomer units or more is indistinguishable from the splitting of the host network whereas for smaller lengths the oligomer splittings due to increased overall mobility and diminished orientational coupling should be smaller. Unexpectedly, one finds that the quadrupolar splittings of OB-10 in a network of a given cross-link density, if extrapolated to zero oligomer content, are considerably greater than the splitting of a nondiluted network of the same cross-link density. The quadrupolar splittings in Figure 2 can be directly compared because the data of the network taken from ref 3 and measured for perpendicular orientation of the principal axis of strain ($P_2(\cos \psi) = -0.5$) to the magnetic field have been corrected for parallel orientation ($P_2(\cos \psi) = 1$) by multiplication by a factor 2. Assuming that the observed splitting of the network is the arithmetic mean of the cis and trans splittings and considering that the trans is about twice the cis splitting, one should correctly compare 3/4 of the extrapolated value of the trans splitting of the oligomer in Figure 2 with the quadrupolar splitting of the network. The corrected value of the oligomer is still greater by a factor of 2 than the polymer quadrupolar splitting.

This unexpected behavior might be explained in accordance with eq 1 by assuming that the mean segmental orientation of the network is matched by the segmental orientation of the oligomer but with a correspondingly higher conformational order. However, this appears to be highly unlikely in view of the structural and conformational identity of the oligomers and the polymer. The discrepancy between the quadrupolar splittings of the network and the oligomers is explained more convincingly by the presence of a distribution of segmental orientations as a consequence of the distribution of elastically effective chain lengths in the network. The success of calculations of the ^{2}H NMR line shapes of strained networks has shown that this assumption is realistic.[3,13] According to this model long chains near the weight average of the distribution correspond to small quadrupolar splittings near the maximum height of the doublet, i.e., to the quantity ordinarily measured and plotted in Figure 2, whereas short chains of the distribution give rise to quadrupolar splittings twice as large, or even greater at very high strain,[3] contributing to the intensity in the wings of the resonances. The observation of oligomer quadrupolar splittings twice as large as the splitting at maximum signal height of the polymer spectrum can therefore naturally be explained by assuming that the orientation of the short oligomer chains is coupled to the orientation of the short chains of the chain length distribution in the network. The existence of orientational intersegmental correlations has been inferred from the enhancement of optical anisotropies[14] and fluorescence polarization[15] in the dry state as compared to swollen networks. The possibility that such correlations may be affected by the chain length distribution in the network has apparently not been envisaged before. The results presented here give first evidence of this effect and, moreover, corroborate the previously given interpretation of the ^{2}H line shape changes of strained networks in terms of a distribution of segmental orientations.

The results presented in this communication demonstrate that deuterated oligomers represent ideal molecular probes by which information about conformational changes, orientation distributions, and orientational correlations in strained networks can be investigated on a local scale. Questions concerning the extent of conformational changes and the nature of orientational couplings remain to be answered.

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Low-Angle Light Scattering Study of Polyelectrolyte Behavior of Ionomers in Polar Solvent

Ionomers are a new class of ion-containing polymers which have ions in concentrations up to 10–15%, randomly distributed in nonionic backbone chains, and have been widely studied in the solid state.[1-3] Recently, the solution properties of ionomers have begun to be studied[4-10] because of their unique properties: (1) in nonpolar solvents, ionomers show aggregation behavior due to dipole–dipole attractions between ion pairs; (2) in polar solvents, they show polyelectrolyte behavior due to the repulsion between fixed ions in polymer chains. Even ionomers with only a few percent of ions show characteristic polyelectrolyte behavior. Lundberg et al.[5] studied this polyelectrolyte behavior using viscosity measurements; the reduced viscosity increased remarkably with decreasing polymer concentration. MacKnight et al.[10] studied the polyelectrolyte behavior using neutron scattering; the scattering curves exhibit a broad single maximum. Here, we study the polyelectrolyte behavior of an ionomer (lightly sulfonated polystyrene) in a polar solvent (DMF) using light scattering measurements.

Although much work has been done to elucidate the structure of salt-free polyelectrolytes in aqueous solution, the exact structure of polyelectrolytes is still not clear.[11] One of the reasons is the difficulty in obtaining reliable data for salt-free polyelectrolyte solutions. For example, only a few light scattering data are available.[12-14] One of the reasons for the scarcity of data is that the scattered intensity from salt-free polyelectrolyte solutions is very small: the excess scattering from a salt-free polyelectrolyte in aqueous solution over that of water is only 10–100%; i.e., the reduced scattered intensity, $R_\theta = (0.1\text{–}1) \times 10^{-6}$.[13] Therefore, it is very difficult to obtain reliable data for this system. Another reason is that optical clarification is difficult for aqueous solution systems.

By using ionomers dissolved in polar solvents to study polyelectrolyte behavior, we can overcome these problems. In ionomer solutions, the excess scattered intensity is twenty to several hundred percent of that from solvent; i.e., $R_\theta = (1\text{–}20) \times 10^{-6}$. Therefore, the scattered intensity from ionomer/polar organic solvent solutions is more than 10 times larger than that from polyelectrolyte/water solutions. Also, optical clarification is easier due to the low viscosity of the ionomer solution. Therefore, we can obtain reliable light scattering data for polyelectrolyte behavior in the absence of salts. The purpose of the present work is to study the characteristics of salt-free polyelectrolytes by using ionomers in polar solvents. It should be mentioned that even though the characteristic polyelectrolyte behavior is smaller for ionomer solutions than for polyelectrolytes, they maintain the essential features.

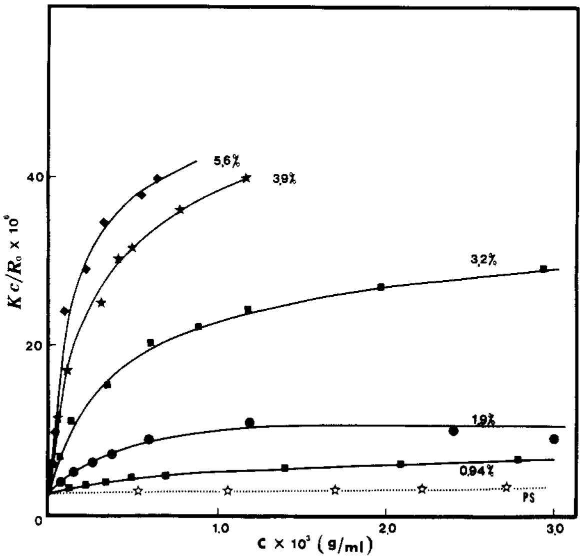

Figure 1. Reciprocal reduced scattered intensity at zero angle, Kc/R_0, against c for S-xSSA-Na of various ion contents as well as PS in DMF.

Lightly sulfonated polystyrene (S-SSA) was prepared by the sulfonation of polystyrene, using acetyl sulfate as a sulfonating agent.[15] The starting polystyrene was a polystyrene standard (Pressure Chemical Co.) with a narrow molecular weight distribution ($M_w = 4.0 \times 10^5$, $M_w/M_n < 1.06$). The acid content, which was controlled by changing the amount of acetyl sulfate, was 0.94, 1.9, 3.2, 3.9, and 5.6 mol %. The acid copolymers were converted to ionomers by adding the proper amount of methanolic sodium hydroxide in benzene/methanol (90/10), freeze-drying, and drying at room temperature under vacuum. The ionomers were easily dissolved in dimethylformamide (DMF). Light scattering measurements were conducted with a KMX-6 low-angle light scattering photometer (Chromatix-LDC/Milton Roy) at a wavelength of 633 nm at 25 ± 0.5 °C, and the specific refractive index increment, dn/dc, was measured with a KMX-16 differential refractometer (Chromatix/LDC-Milton Roy) at 25 ± 0.1 °C.

Figure 1 shows the results of light scattering for S-xSSA-Na in DMF for various ion contents. Again, ionomers show typical polyelectrolyte behavior;[16] the reciprocal reduced scattered intensity (Kc/R_0) rises steeply from the intercept at zero concentration, bends over, and becomes nearly horizontal at higher concentration. From the intercept, the weight-average molecular weight, M_w, is obtained as 4.0×10^5 for all ionomers. Therefore, the ionomers are molecularly dispersed in DMF.

In order to analyze the light scattering data from the ionomers in a polar solvent, we used a simple effective potential model with an effective diameter. This model, which treats the macroions as if they were neutral but have an effective size, was originally introduced by Doty and Steiner[16] for their analysis of light scattering data from macroions and then used by Benmouna et al.[17] for their explanation of the origin of the peak observed in X-ray and neutron scattering curves obtained from salt-free polyelectrolytes. Doty and Steiner[16] derived the following equation for macroions in water by considering the long-

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