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Solvent vs. Segment Orientation in Strained Swollen Elastomeric Networks

Deuterium NMR (DMR) has emerged as a valuable technique for investigating orientational order generated in uniaxially strained rubbers. The methodology exploits the observation of residual quadrupolar interactions (usually in the form of a resolved, quadrupolar splitting) which may be related to the degree of induced order in the rubber. In 1981 Deloche and Samulski[1] used deuterated swelling agents at low concentrations (solvents such as benzene-d_6, chloroform-d_1, etc.) as DMR probes in elongated rubbers and inferred that *both* the solvent probe and the polymer segments experience short-range orientational correlations.[2] Solvent quadrupolar splittings unequivocally demonstrate the existence of the orientational coupling between solvent molecules and ordered segments of the deformed chains. Extensions of such DMR measurements to labeled networks enabled direct studies of the chain segment behavior.[3,4] More recently, investigations of segment (and probe) quadrupolar interactions have been shown to be related to network cross-linking density and to be attenuated by swelling the networks.[5] This dependence on network characteristics strongly supports the initial proposal that short-range segment–segment (and solvent–segment) correlations must be included in a comprehensive description of elastomeric networks.[1] Here we use DMR to contrast segmental and solvent probe orientational order in well-defined poly(dimethylsiloxane) networks. This study gives direct insights into the nature of the orientational field that both probe molecules and chain segments experience in deformed networks.

Identical tetrafunctional end-linked poly(dimethylsiloxane) networks were prepared as described previously[6,7] (the molecular weight between crosslinks $M_n = 23000$; the molecular weight distribution is 1.6). Network formation was carried out at a polymer volume fraction of $V_c = 0.71$. One network, PDMS(D), contains a known fraction (~20%) of perdeuterated chains: $(\text{-Si(CD}_3)_2\text{-O-})_n$. The second network, PDMS, is unlabeled. These two samples, PDMS(D) and PDMS, were swollen with benzene and benzene-d_6, respectively. Network swelling and elongation were performed as indicated earlier.[1,3,5] DMR spectra were obtained with a CXP-90 Bruker spectrometer operating at 2 T; the field $\mathbf{B}_0$ is normal to the principal strain direction $\mathbf{d}$ of the uniaxially deformed network.

Typical quadrupolar splittings for benzene-d_6 and PDMS(D) are shown in the DMR spectra in Figure 1 at the same extension ratio $\lambda = L/L_0 = 1.42$. The volume fraction of polymer in the swollen networks is $\phi = 0.92$. The resolved doublet of the solvent probe is characteristic of that obtained with a variety of labeled swelling agents in various elastomer networks.[1,5] One of the primary sources of the lack of resolution in the PDMS(D) spectrum can be attributed to a superposition of spectra originating from a distribution of chain lengths between junctions:[4,8] For a given λ, classical descriptions[9] of rubber elasticity indicate that higher orientational segmental order will be exhibited by the shorter chains.

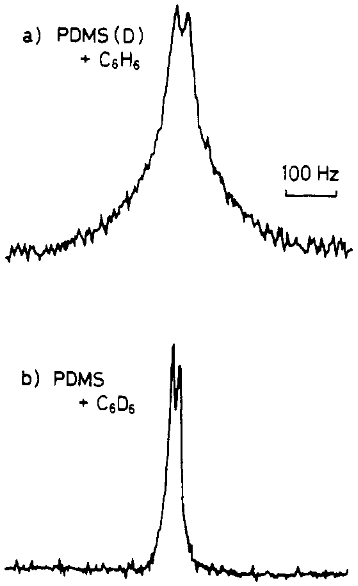

Figure 1. DMR spectra of (a) perdeuterated poly(dimethylsiloxane) chains in a network PDMS(D) swollen with benzene and (b) benzene-d_6 in an unlabeled PDMS network. In both samples the polymer volume fraction $\phi = 0.92$ and the elongation ratio $\lambda = 1.4$.

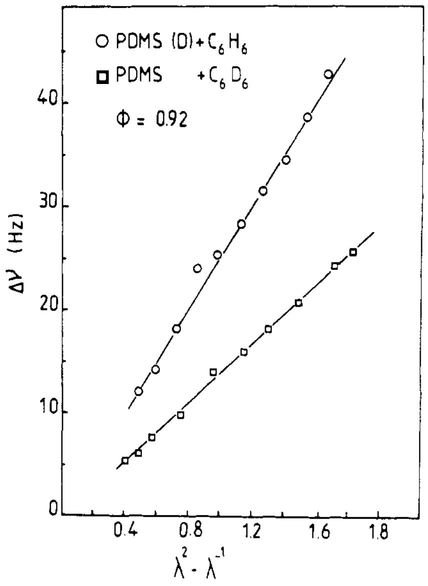

Figure 2. Solvent probe and polymer quadrupolar splittings $\Delta\nu$ vs. $\lambda^2 - \lambda^{-1}$.

Figure 2 shows the quadrupolar splittings of the solvent, $\Delta\nu_s$, and of the polymer, $\Delta\nu_p$, vs. $\lambda^2 - \lambda^{-1}$ for both networks in the small deformation limit ($\lambda \leq 2$). As reported earlier,[1,3] both $\Delta\nu_s$ and $\Delta\nu_p$ are linear in this strain function; at the same λ the observed ratio $\Delta\nu_s/\Delta\nu_p = 0.56$. In the following we examine the implications of the order of magnitude equivalence of solvent and chain segment quadrupolar splittings in comparable networks at the same degree of swelling.

The quadrupolar interaction (resulting from the electric field gradient at the deuterium nucleus) is averaged along the principal strain direction **d** by all molecular motions that are rapid on the DMR time scale, i.e., motions characterized by frequencies larger than the quadrupolar interaction ($\sim 10^6$ Hz). In the case of benzene-d_6, rotational and translational reorientation of the probe are relevant; for PDMS(D), methyl group rotation, chain isomerization, and larger scale chain reorientation average the quadrupolar interaction. In this rapid motion limit, the quadrupolar splitting may be expressed in frequency units as

$$\Delta\nu_{\mathrm{i}} = \frac{3}{2} q_i P_2(\cos\alpha_{\mathrm{i}}) S_{C_n} P_2(\cos\Omega) \qquad \mathrm{i} = \mathrm{s,p} \qquad (1)$$

where q_{i} is the quadrupole coupling constant ($q_{\mathrm{s}} = 190$ kHz for benzene-d_6[10] and $q_{\mathrm{p}} = 175$ kHz for the methyl deuterons in PDMS(D)[11]). The angles of the second Legendre polynomials characterize the internal molecular structure and the experimental geometry, respectively: α_{i} is the angle between the C–D bond vector and the local molecular symmetry axis, C_n, and Ω is the angle between **d** and $\mathbf{B}_0$. In the present experiments $\Omega = 90°$. For benzene-d_6, the C_6 axis makes an angle $\alpha_{\mathrm{s}} = 90°$ with the C–D bonds; for the PDMS monomer the local C_3 axes of the CD_3 groups involve the tetrahedral angle $\alpha_{\mathrm{p}} = 70.5°$. $S_{C_n} = \langle P_2(\cos\theta_{C_n})\rangle$ is the average orientation of the C_n axis relative to **d**; the brackets indicate an average over the rapid molecular motion. With these definitions we find, for example, at $\lambda = 2$ ($\Delta\nu_{\mathrm{s}} = 21$ Hz and $\Delta\nu_{\mathrm{p}} = 38$ Hz), the order parameters $S_{C_6} = 3 \times 10^{-4}$ and $S_{C_3} = 9 \times 10^{-4}$ for the solvent probe and polymer, respectively.

In principle it is possible to refine the comparison of the factor of 3 difference between the solvent and polymer order parameters. However, it is necessary to address the question of the orientation of the local C_3 symmetry axis in the monomer relative to a hypothetical segment axis l in the PDMS chain. In such an analysis $S_{C_3} = P_2(\cos\beta)S_{\mathrm{l}}$, where β is the angle between the C_3 axis and l and S_{l} is the order parameter defining the orientation of the segment relative to **d**. If we define a segment as a single monomer unit (for example, l connects two adjacent oxygens in the PDMS chain), $\beta = 90°$. In this case $S_{C_3} = (-1/2)S_{\mathrm{l}}$ and so the two order parameters which should be contrasted, S_{C_6} and S_{l}, differ by a factor of 6. When a more realistic segment axis is defined—a "hypothetical segment" containing w monomers—$P_2(\cos\beta)$ must be averaged over the intrasegmental isomerization. This may be readily accomplished via an equilibrium statistical mechanical average over all segment conformations with the rotational isomeric state approximation. For example, when w is increased from 1 to 6, $\langle \bar{P}_2(\cos\beta)\rangle$ decreases from $-1/2$ to $\sim -1/5$.[12] This further increases the disparity between S_{C_6} and the value of S_{l} extracted from $\Delta\nu_{\mathrm{p}}$.

In spite of the numerical uncertainties in deriving an order parameter for the polymer, the order of magnitude ($\sim 10^{-4}$) and the similarity between S_{C_6} and S_{l} is in itself very striking. In contrast with thermotropic liquid crystals the magnitude of the order parameters characterizing strained elastomeric networks are a factor of 10^3 smaller. However, as in liquid crystals, the guest probe and the host matrix reflect similar orientational order. The fact that both of our observed order parameters exhibit the same strain dependence suggest that the orientational diffusion of the solvent is strongly coupled to the ordering of the chains. Hence labeled solvents may be confidently used to probe orientational order generated in deformed, swollen elastomeric networks. By (sample) definition, this is a nonperturbative probe technique. Clearly routine use of solvent probes that are devoid of specific interactions with the elastomer (e.g., hydrogen bonding) will facilitate the examination of short-range orientational correlations in a variety of rubbers, correlations which may strongly influence macroscopic properties.[13]

Optimally, a probe that is structurally similar to the polymer chain will be most informative. In this case we anticipate that $\Delta\nu_{\mathrm{s}}/\Delta\nu_{\mathrm{p}} \rightarrow 1$. Moreover, a systematic study of the type described here using oligomers of increasing degree of polymerization to probe short-range orientational correlations may provide a straightforward way to quantify the size (w) of the "hypothetical segment", a heretofore ill-defined entity that has been conceptually very valuable in polymer physics.

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References and Notes

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