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Received December 6, 1989
Revised Manuscript Received March 5, 1990

On a Controversy about Interpretation of Nuclear Magnetic Resonance Observations in Poly(dimethylsiloxane) Networks Cross-Linked in Solution

The use of deuteron magnetic resonance (^{2}H NMR) to study chain segment orientation in strained rubbers has increased in recent years.[1-4] Three years ago we published results concerning segmental orientation in elongated poly(dimethylsiloxane) (PDMS) networks prepared by an end-linking reaction in solution at different precursor polymer volume fractions, V_{2c}.[5] The experiments were performed either on deuterated solvent molecules used as NMR probes of unlabeled networks or directly on deuterated networks. In both cases we observed that, for a given elongation ratio, α, the segmental degree of order, S (related to the quadrupolar splitting $\Delta\nu$), increases with increasing values of the concentration, V_{2c}, the molecular weight of the precursor chains being held constant. This dependence of S was suggested to be related to an increase of chain entanglements trapped during the end-linking reaction carried out at high V_{2c}. Cooperative diffusion constant measurements by light scattering on polystyrene[6] and PDMS[7] networks, swelling and elastic properties of PDMS networks,[8] elasticity measurements on polyurethane networks[9] and NMR studies of the swelling process of PDMS networks[10] all support this interpretation.

Recently this interpretation was considered "erroneous" by Erman and Mark.[11] These authors argued that the observed effects are only due to the fact that the reference volume of the network during cross-linking is different from its volume during the NMR experiments. They reinterpreted our results in terms of the polymer volume fractions V_2 (during NMR experiments performed on dry samples, i.e., $V_2 = 1$) and V_{2c} (during cross-linking) so that the observed behavior of the segmental order, S, would be attributed to the so-called "memory term", $(V_{2c}/V_2)^{2/3}$, as indicated in relation 7 of the ref 11.

In our opinion, one cannot be totally categorical concerning the existence and the role of the "memory term". To the best of our knowledge to date, there are no decisive experiments showing that chains are "supercontracted" when $V_2 > V_{2c}$. We may also add that no influence of cross-linking on the chain dimensions has been detected; in particular, small-angle neutron scattering experiments carried out on dry networks prepared at different concentrations V_{2c} have not revealed any influence of V_{2c} on the chain dimensions, while the Young modulus was noticeably affected.[12] Moreover, various experiments do not lead to the expected V_{2c} dependence resulting from the "memory effect". For instance, it is found that the polymer volume fraction at swelling equilibrium[8] goes like $V_{2c}^{3/4}$, while the expected dependence would be $V_{2c}^{2/5}$. Also, the shear modulus of dry PDMS networks[13,14] does not scale as the expected law $V_{2c}^{2/3}$. However, the main purpose of this note is to show that, even if such a "memory term" does exist, this effect is not sufficient to explain all the NMR results reported in ref 5.

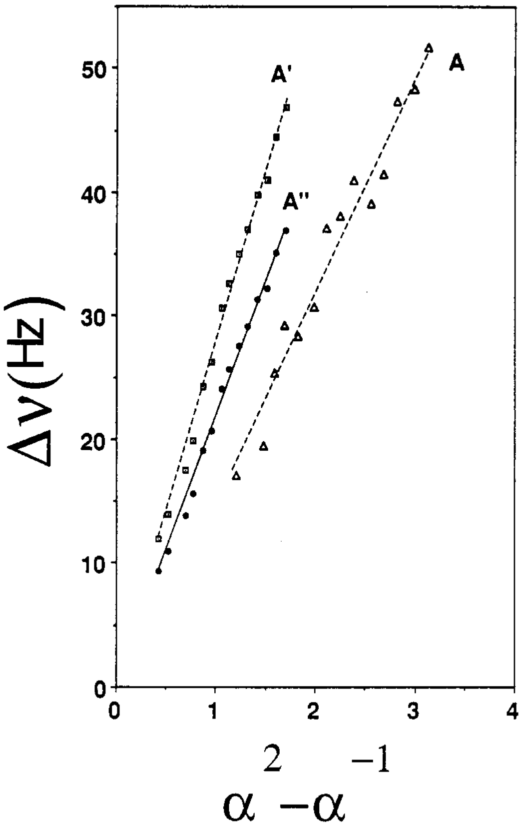

Figure 1. Quadrupolar splitting $\Delta\nu$ vs $\alpha^2 - \alpha^{-1}$ for two end-linked PDMS networks (M_n = 25 000) synthesized in the dry state (sample A′) and in solution at a concentration V_{2c} = 0.7 (sample A); these data have already been reported in Figure 3 of ref 5. The full line (A″) is obtained by multiplying the experimental data of curve A′ by the "memory term" $(V_{2c}/V_2)^{2/3}$ = 0.79. The elongation ratio, α, is relative to the unstretched volume V_2 during the NMR experiments.

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In their note Erman and Mark have analyzed the order parameter variation, $S(V_{2c})$, observed for the probe solvent molecules using either a phantom theory ($S \sim V_{2c}^{2/3}$) or a constrained junction theory. The best fit of the data is obtained with the latter one by adjusting the parameter κ, which depends on V_{2c}. As for the results observed in deuterated networks, Erman and Mark claimed without showing any details that good agreement is obtained between the theory and the experiments. Therefore, we have reanalyzed our data to test the hypothesis that the differences observed in labeled networks, synthesized at different concentrations V_{2c}, may be simply ascribed to the "memory effect" and therefore are consistent with a factor of $V_{2c}^{2/3}$. Good agreement is observed in two PDMS networks of low molecular weight (i.e., the samples B′(V_{2c}=1) and B(V_{2c}=0.7) in ref 5). However, as shown in Figure 1, a large discrepancy is observed in networks of higher molecular weight (A′(V_{2c}=1) and A(V_{2c}=0.7)). It appears that the full line A″, calculated from the curve A′ by multiplying by the "memory factor", has a slope that differs by about 25% from the experimental one (dotted line A) obtained for $V_{2c} = 0.7$; such a discrepancy cannot be due to the error bar on slopes, which is estimated to ∓2 Hz. This test demonstrates that the variation of the chain orientation function, S, is not merely related to a change in the reference state of the network when V_{2c} varies. Thus an interpretation including chain entanglements must be considered herein.

From the above discussion, it is clear that the term $(V_2/V_{2c})^{2/3}$ is not sufficient to reproduce the variation $S(V_{2c})$ observed on long chains. No decisive arguments exist to exclude an interpretation of our NMR results based on chain entanglements. We consider that our conclusions in ref 5 are still relevant. Now the basic issue that should be resolved is the role of entanglements on the chain conformation: topological constraints either reducing the freedom of the chemical cross-links[15] or acting along the chain contours.[16] Further experiments sensitive to the behavior of network chains are necessary in this field.

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Received July 5, 1989
Revised Manuscript Received March 2, 1990