sults[19] cover the range 325-1050 Å for *p*-BA and 113-650 Å for *p*-PT.

Acknowledgment. Financial support by the Bundesministerium für Forschung und Technologie, Projekt "Steife Makromoleküle", is gratefully acknowledged. We also thank Prof. G. Wegner for many helpful discussions.

Registry No. PHB (homopolymer), 30729-36-3; PHB (SRU), 26099-71-8.

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Notes

Segmental Orientation in Networks Cross-Linked in Solution

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Received February 22, 1988;
Revised Manuscript Received May 31, 1988

Introduction

Two of the most important new techniques for studying segmental orientation in strained polymers are fluorescence polarization[1-3] and nuclear magnetic resonance (NMR) spectroscopy.[4-7] Deuterium NMR in particular has now been used to investigate some important general issues regarding rubberlike elasticity, but reliable analysis of such results requires proper account of polymer reference volumes. An analysis of data of this type[7] is the subject of the present communication.

Specifically, deuterium NMR spectroscopy was recently used to study quadrupolar splitting, $\Delta\nu$, and the chain orientation function, S, in elongated poly(dimethylsiloxane) (PDMS) networks having either deuterated chain segments or swollen with a deuterated solvent.[7] Some networks had been prepared by end-linking PDMS chains in solutions with toluene, which was then removed prior to the elasticity measurements. Both $\Delta\nu$ and S were found to decrease substantially with a decrease in the volume fraction, v_{2C}, of polymer present during network formation. The decreases were attributed to decreased trapping of inter-chain entanglements due to the presence of diluent.[7] Apparently neglected in the analysis, however, was the fact that the reference volume, V_0, of the network (during cross-linking) was not the same as its volume, V, during the elasticity measurements. For example, $V < V_0$ means that the chains are "supercontracted"[8] at the beginning of the elasticity measurements. Qualitative consideration suggested that this difference could well account for the experimental observations, and the quantitative elasticity calculations described below were therefore undertaken.

Theory

The effects of the differences in volumes are more easily analyzed through the polymer volume fractions

$$v_{2C} = V_d/V_0 \tag{1}$$

$$v_2 = V_d/V \tag{2}$$

where V_d is the volume of the dry polymer network, V_0 is its reference volume, and V is the volume of the network during the elasticity measurements. The volume fraction v_{2C} thus characterizes the system during cross-linking, and v_2, in this case,[7] characterizes it during the elongation-NMR measurements.

The orientation function, S, for a phantom network, in which junction fluctuations are not constrained by chain interpenetrations,[3] is given by[1,2]

$$S = D[\Lambda_x^2 - (\Lambda_y^2 + \Lambda_z^2)/2] \tag{3}$$

where D is a configurational factor, and Λ_x^2, Λ_y^2, and Λ_z^2 are components of the microscopic deformation tensor. These three latter quantities are given by

$$\Lambda_t^2 = (1 - 2/\phi)\lambda_t^2 + (2/\phi) \qquad t = x, y, z \tag{4}$$

where ϕ is the junction functionality. The λ_t's are extension ratios relative to the unstretched network in its reference volume, V_0, and for elongation along the x axis can be written

$$\lambda_x = (v_{2C}/v_2)^{1/3}\alpha \tag{5}$$

$$\lambda_y = \lambda_z = (v_{2C}/v_2)^{1/3}\alpha^{-1/2} \tag{6}$$

where the elongation, α, is now relative to the unstretched network at its volume, V. Thus, for a phantom network,

$$S = (1 - 2/\phi)(v_{2C}/v_2)^{2/3}D(\alpha^2 - \alpha^{-1}) \tag{7}$$

The critical point is that the ratio v_{2C}/v_2 cannot be ignored when networks are studied at a degree of swelling significantly different from that at which they were prepared.

Since the phantom network model is generally appropriate only at very high elongations or very high degrees of swelling,[3] it is useful also to consider the more realistic

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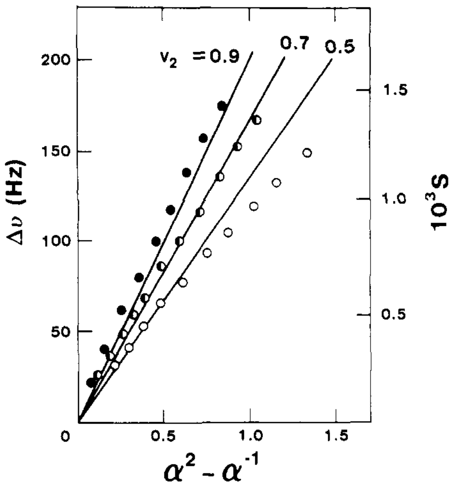

Figure 1. Quadrupolar splitting, $\Delta\nu$, and orientation function, S, for PDMS networks, shown plotted against the strain function $(\alpha^2 - \alpha^{-1})$.[7] The networks were prepared at the specified values of the volume fraction, v_{2C}, of polymer present during cross-linking and contained approximately 10 wt % $CDCl_3$ during the deuterium NMR measurements used to obtain $\Delta\nu$ and S. The experimental results are shown by the circles and the results calculated for phantom networks by the curves.[3,9]

constrained junction model.[3,9] This requires simply including the term $2B_x/\phi$ on the right-hand side of eq 4, where

$$B_x = (\lambda_x - 1)(\lambda_x + 1 - \zeta\lambda_x^2)/(1 + g_x)^2 \qquad (8)$$

with

$$g_x = \lambda_x^2[\kappa^{-1} + \zeta(\lambda_x - 1)] \qquad (9)$$

The two parameters κ and ζ characterize the severity of the constraints on the junctions and the nonaffineness of the transformations of the constraint domains, respectively.[3,9]

Results and Discussion

Typical experimental values of $\Delta\nu$ and S reported by Deloche et al.[7] for undeuterated polymer are shown by the circles in Figure 1. They are shown plotted against the strain function appearing in eq 7 for three representative values of v_{2C}. The curve from the phantom network theory can be fit to the data for $v_{2C} = 0.7$ and $v_2 = 0.90$ by the choice $D = 3.36 \times 10^{-3}$, as is shown in the figure. Recalculations of S from eq 7 for $v_{2C} = 0.9$ and 0.5 (with $v_2 = 0.90$) then give the other two curves. They are seen to give good representations of the two corresponding sets of experimental data, thus demonstrating that the observed dependence of S on v_{2C} can be simply accounted for by proper definition of the extension ratios. Explanations in terms of trapped entanglements[7] are thus clearly unnecessary, and in fact erroneous.

Although the issue involving reference volumes is of primary importance, the agreement is found to be even better if the same analysis is used with the constrained junction theory. The experimental data for $v_{2C} = 0.9$, 0.7, and 0.5 (with $v_2 = 0.90$) are fitted by $D = 2.37 \times 10^{-3}$ and the v_{2C}-dependent expression for PDMS[10]

$$\kappa = \kappa_0 v_{2C}^{4/3+m} \qquad (10)$$

with $m = 8/9$. Using these parameters and $\kappa_0 = 3$ and $\zeta = 0$ (the usual value)[3] in eq 9, 8, 4, 5, 6, and 3 then gives the curves shown in Figure 2. There is now nearly perfect agreement between experiment and theory. Similarly good agreement is obtained for the experimental results[7] reported for the deuterated polymer.

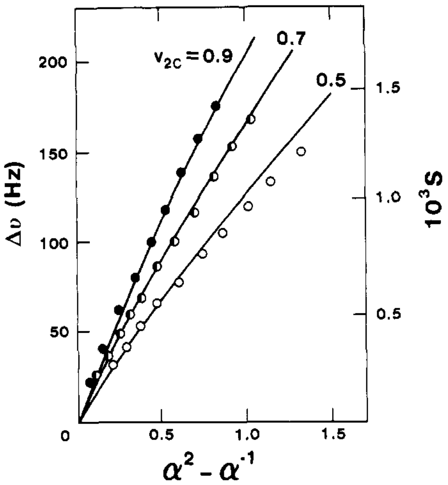

Figure 2. Same experimental results[7] as in Figure 1 but theoretical curves calculated from the constrained junction theory of elastomeric networks.[3,9]

Acknowledgment. We acknowledge the financial support provided J.E.M. by the National Science Foundation through Grant DMR 84-15082 (Polymers Program, Division of Materials Research).

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Infrared Laser-Induced Reactions of Difluorocarbene with 1,2-Polybutadiene

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Received March 29, 1988;
Revised Manuscript Received May 18, 1988

Laser-induced gas–solid heterogeneous reactions are important because they provide insight into mechanisms of heterogeneous processes and hold promise of technical innovations for practical applications.[1] Most work has involved metal and metal oxide surfaces (e.g., Pt, Zn, TiO_2, ZnO) or non-metal and non-metal oxide surfaces (e.g., Si, Ge, SiO_2); however, little effort has been expended to study the analogous reactions involving polymers. Alterations of polymer surfaces without affecting the bulk of the

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