Viscoelastic Properties of Polydimethylsiloxane Networks Prepared by Cross-Linking the Chains in Solution

R. E. Cohen,[1a] S. D. Severson,[1a] C. U. Yu,[1b] and J. E. Mark*[1b]

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and the Department of Chemistry and Macromolecular Research Center, The University of Michigan, Ann Arbor, Michigan 48109.

Received December 13, 1976

ABSTRACT: A total of 30 polydimethylsiloxane networks were prepared by γ irradiation of the polymer in the bulk (undiluted) state and in a series of solutions in cyclohexane. The volume fraction of polymer in the system being cross-linked ranged from 1.00 to 0.30, and radiation doses ranged from 0.80 to 72.1 Mrads. Values of the storage modulus and loss modulus obtained in shear at 110 Hz and at 175 °C by means of a Rheovibron Viscoelastometer were used to determine the possible effect of cross-linking in solution on the number of inter-chain entanglements in the resulting networks. It is first pointed out that in the case of networks prepared in solution, it is important to take into account the fact the network chains are not in their relaxed, reference state upon subsequent removal of the diluent. The present results, suitably interpreted in this regard, indicate that cross-linking in solution does not significantly reduce the viscoelastic losses generally attributed to inter-chain entanglements (involving segments of a chain which are relatively remote from its junction points). It is thus concluded that solution cross-linked networks do not have an unusually small number of such entanglements. They probably do have simpler topologies, but in the sense that the junction points which are *spatial* first neighbors are more likely also to be *topological* first neighbors than would be the case of a network prepared in the absence of diluent. Such a topological change would be of considerable importance since it would diminish the firmness with which the junctions are embedded in the network medium, and thus decrease the likelihood that the cross-links and chain vectors would transform affinely upon deformation of the network.

One of the most important goals in polymer science is the achievement of a detailed molecular interpretation of the long-range "rubberlike" elasticity exhibited by amorphous, unfilled polymer networks.[2–4] Although much has been accomplished in pursuit of this goal, almost nothing definitive is known about the dependence of elastomeric properties on network topology as characterized in part, for example, by the degree of entangling of the network chains.[2–6] One experimental approach showing considerable promise in this area is the cross-linking of polymer chains using techniques which would be expected to give networks having topologies simpler than those of networks prepared in the usual manner, which involves the random cross-linking of polymer chains in the bulk (undiluted) state.[7–10] The specific technique of this type which is of interest here is the cross-linking of chains in solution. A network thus prepared (and subsequently dried to the unswollen state) differs significantly from a network prepared by cross-linking the same polymer in the undiluted state in that it (i) approaches elastic equilibrium more rapidly, (ii) shows very little stress relaxation or irrecoverable flow, and (iii) has stress–strain isotherms in elongation which are much closer to the form predicted by the usual molecular theories of rubberlike elasticity.[7–10] These experimental observations have tentatively been attributed to differences in network topology, more specifically to a decrease in the number of chain entanglements in the case of a solution cross-linked network. Of relevance here are entanglements which are permanent or "trapped" in the sense of being extricable only by the rupture of chemical bonds; such entanglements would involve segments of a network chain which are relatively remote from the cross-links or junction points at its two ends. The solvent present during the cross-linking process is thus assumed to partially disentangle the polymer chains prior to their incorporation into the network structure. Removal of the solvent subsequent to the cross-linking would of course have no effect on the number of such permanent entanglements and any simplification of the network topology of this type would thus be preserved in the unswollen network.[7–10]

It is obviously of considerable interest to study other properties of such solution cross-linked networks, particularly those properties which would be sensitive to the degree of entangling of the network chains. Ideally suited for this purpose are measurements of dynamic mechanical properties in the temperature and frequency ranges where viscoelastic losses are generally attributed to rearrangement or "slippage" of chain entanglements.[5,6,11–14] The purpose of the present investigation was therefore to measure viscoelastic losses in solution cross-linked networks of polydimethylsiloxane (PDMS), in the unswollen state. Although a variety of polymers have been used in preparing solution cross-linked networks,[10] those prepared from PDMS are the ones which have been most thoroughly investigated with respect to their equilibrium elastomeric properties.[15–17] Additional information on their viscoelastic behavior should therefore provide important information on the topologies of these networks, and should help elucidate the effect of network topology on their mechanical properties in general.

Experimental Section

Preparation of Networks. A total of 30 PDMS networks were prepared at 25 °C, using γ radiation, in exactly the manner described previously.[15,16] As in the previous studies, both undiluted PDMS and PDMS dissolved in cyclohexane were cross-linked in this way. The chosen values of the volume fraction $v_{2,S}$ of polymer in the system being cross-linked were 1.00, 0.75, 0.62, 0.55, 0.48, 0.40, and 0.30. Several networks were prepared at each of these values of $v_{2,S}$; radiation doses were varied from 0.80 to 72.1 Mrads in order to obtain networks covering a wide range in degree of cross-linking. The six networks prepared in the bulk (undiluted) state were designated B-1 through B-6. Similar designations were used for the other networks, which were prepared from the six cyclohexane solutions S1–S6. The preparative details for all the networks are summarized in the first three columns of Table I.

Extraction and Swelling Experiments. The techniques employed in both of these experiments are described in detail in the earlier studies of solution cross-linked PDMS.[15,16] In brief, each sample was placed into gently stirred benzene at room temperature; the weight of soluble (uncross-linked) polymer thus extracted and the pertinent value of $v_{2,S}$ were used to calculate the volume fraction $v_{2,C}$ of polymer in the solution which was successfully incorporated into the network structure. (This quantity represents the volume fraction $v_{2,S}$ corrected to account for the fact that the extractable polymer acts as solvent or diluent during the cross-linking proce-

Table I
Preparation of the Networks and Their Values of the Equilibrium Degree of Swelling, Cross-Link Density, and Viscoelastic Loss

Sample	$v_{2,\mathrm{S}}$[a]	Radiation dose, Mrad	$v_{2,\mathrm{C}}$[b]	$v_{2,\mathrm{N}}$[c]	$2C_1$, N mm^{-2}	$10^5\nu/2V$[d]	$-\log \tan \delta$[e]
B-1	1.00	0.80	0.672	0.0319	0.0060	0.315	0.752
B-2	1.00	0.98	0.810	0.0588	0.0155	0.720	0.743
B-3	1.00	1.49	0.883	0.0885	0.0320	1.40	0.853
B-4	1.00	2.04	0.930	0.109	0.0461	1.95	0.974
B-5	1.00	3.53	0.947	0.145	0.757	3.17	1.29
B-6	1.00	6.00	0.971	0.190	0.127	5.22	1.72
S1-1	0.75	1.35	0.635	0.0506	0.0080	0.437	0.755
S1-2	0.75	1.82	0.676	0.0756	0.0246	1.29	0.787
S1-3	0.75	2.91	0.700	0.0973	0.0415	2.12	1.09
S1-4	0.75	10.9	0.724	0.187	0.130	6.50	2.19
S2-1	0.62	1.31	0.538	0.0531	0.0060	0.366	0.687
S2-2	0.62	1.98	0.568	0.0759	0.0207	1.22	0.769
S2-3	0.62	3.63	0.580	0.104	0.0451	2.62	1.11
S2-4	0.62	12.6	0.596	0.163	0.120	6.84	2.05
S3-1	0.55	1.75	0.500	0.0693	0.0165	1.06	0.819
S3-2	0.55	2.77	0.514	0.0875	0.0327	2.06	0.961
S3-3	0.55	5.25	0.523	0.114	0.0622	3.87	1.28
S3-4	0.55	15.0	0.526	0.140	0.0975	6.04	2.00
S4-1	0.48	2.21	0.437	0.0817	0.0200	1.40	0.862
S4-2	0.48	4.13	0.445	0.0978	0.0404	2.80	1.10
S4-3	0.48	12.0	0.456	0.123	0.0745	5.07	1.75
S5-1	0.40	3.17	0.368	0.0772	0.0260	2.04	1.04
S5-2	0.40	14.5	0.380	0.107	0.0625	4.81	1.47
S5-3	0.40	21.8	0.382	0.112	0.0686	5.26	1.58
S5-4	0.40	44.1	0.386	0.148	0.126	9.59	2.30
S6-1	0.30	7.60	0.277	0.0740	0.0285	2.71	0.976
S6-2	0.30	27.4	0.280	0.0970	0.0535	5.04	1.53
S6-3	0.30	32.7	0.280	0.107	0.0673	6.34	1.61
S6-4	0.30	48.3	0.280	0.120	0.0920	8.67	1.80
S6-5	0.30	72.1	0.281	0.140	0.119	11.2	2.46

[a] Volume fraction of polymer in the solution being irradiated. [b] Volume fraction of polymer in the solution which was successfully incorporated into a network structure. [c] Volume fraction of polymer in the network at swelling equilibrium in cyclohexane at 25 °C. [d] Cross-link density in mol of cross-links/cm^3 of the unswollen network. [e] Measured at 175 °C and 110 Hz.

dure.)[15] The resulting values of $v_{2,\mathrm{C}}$ are given in the fourth column of Table I. After drying, the extracted samples were placed into cyclohexane at 25 °C and permitted to reach maximum (equilibrium) swelling. The value of the volume fraction $v_{2,\mathrm{N}}$ of polymer in each network under these equilibrium conditions was calculated from the weights of the sample in the unswollen and swollen states, assuming additivity of volumes of diluent and polymer. These results are given in column five of the table.

Viscoelasticity Measurements. Dynamic mechanical properties were determined on a Rheovibron DDV-II-C instrument using a twin specimen, shear-sandwich geometry similar to that described recently by Murayama.[18] Specimens suitable for these shear measurements were obtained by fastening each sample to the bench of a milling machine using mounting tape with adhesive on both sides; perpendicular vertical cuts were then made with a rotating knife blade mounted in the chuck of the apparatus. The resulting specimens had a square cross section (0.432 cm) and thicknesses ranging from about 0.160 to 0.094 cm. In order to determine accurately the thickness of each shear specimen, the total thickness of the slightly precompressed shear sandwich (specimens and grips) was measured with a micrometer and the thickness of the metal grips was determined separately. The precompression, required to eliminate slippage of the specimens (particularly at lower temperatures), was always less than 10% of the original sample thickness. Using these techniques it was possible to obtain with sufficient precision the specimen shape factor[5] required for calculation of the individual components of the complex modulus G^*.

Measurements were conducted at a constant frequency of 110 Hz, over temperatures ranging from about −50 to 200 °C.[19] (The lower limit of −50 °C was dictated by a marked stiffening of the specimens below this temperature; since PDMS has a melting point of ca. −40 °C,[20] this was presumably due to network crystallization.) The viscoelastic data were taken in a continuous fashion as the temperature was slowly increased. The temperature itself was continuously recorded via thermocouple output on a strip-chart recorder; the rates of temperature increase were always less than 2 °C/min. Care was taken to ensure that oxidative degradation did not influence the results at the higher temperatures. The Rheovibron environmental chamber was periodically swept with nitrogen in some runs and numerous runs were repeated over various regimes of temperature after reaching the upper limit of 200 °C. Reproducible results were always observed and no visual changes suggesting degradation were noticed in any of the samples studied.

Results and Discussion

The values of $v_{2,\mathrm{N}}$ characterizing the degree of swelling in cyclohexane at 25 °C were used to establish a connection between the present PDMS samples and those studied earlier[15] with regard to their equilibrium elastomeric properties in elongation at 25 °C, in the unswollen state. Both series of samples were identically prepared at the same values of $v_{2,\mathrm{S}}$, and their swelling properties were determined in exactly the same way. In the earlier study,[15] the networks were characterized using the "reduced stress" defined by

$$[f^*] \equiv f/[A^*(\alpha - \alpha^{-2})] \qquad (1)$$

where f is the elastic force, A^* is the cross-sectional area of the undeformed deswollen sample, and the elongation $\alpha = L/L_i$ is the length of the deformed sample relative to its initial, undeformed length. The experimental values of $[f^*]$ were

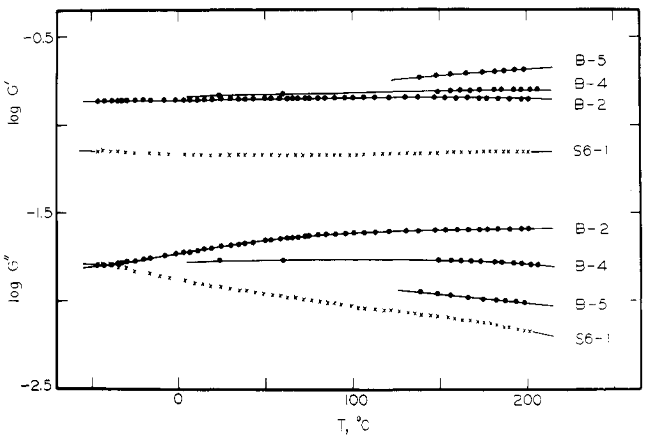

Figure 1. Semilogarithmic plots of the storage modulus G' and loss modulus G'' against temperature for some typical polydimethylsiloxane networks prepared in the bulk (undiluted) state (●) and in a solution (×) having a volume fraction of polymer of 0.30. Networks B-2 and S6-1 are similar with regard to their degree of equilibrium swelling in cyclohexane at 25 °C, whereas B-4, B-5, and S6-1 have similar cross-link densities; see Table I. Measurements were carried out at 110 Hz, and both G' and G'' are in units of N mm^{-2}.

represented in the usual manner, in terms of the phenomenological equation[21]

$$[f^*] = 2C_1 + 2C_2\alpha^{-1} \tag{2}$$

where $2C_1$ and $2C_2$ are constants independent of α, with $2C_2$ serving as a measure of the difference between the form of the observed stress–strain isotherm and that indicated by the usual molecular theories of rubberlike elasticity.[2-4] The quantity of primary interest at this point is the constant $2C_1$, since it is directly related to the cross-link density of the network.[10,22-25] The values of $2C_1$ for the previous samples were therefore calculated, using tabulated values[15] of $[f^*]$ (at α = 1.300) and the corresponding values of $2C_2$. They were then plotted against $v_{2,\mathrm{N}}$ for each chosen value of $v_{2,\mathrm{S}}$. The values of $2C_1$ for the PDMS samples presently under investigation were then obtained from this series of curves by means of interpolation and limited extrapolation. The results are given in column six of the table. They were interpreted using the equation[24-26]

$$2C_1 = C(\nu kT/V)(V/V_0)^{2/3} = C(\nu kT/V)v_{2,\mathrm{C}}^{2/3} \tag{3}$$

derived for networks of Gaussian chains, in which ν is the number of network chains, k is the Boltzmann constant, and T = 298.2 K is the absolute temperature. Since V is the volume of the unswollen network and V_0 is the volume at which the network was formed, the ratio V/V_0 is simply the volume fraction $v_{2,\mathrm{C}}$ of polymer in the system during the cross-linking process.[7,27] The coefficient C has the value ½ in the case of a network in which the cross-links do not follow the deformation "affinely" (i.e., in direct proportionality with changes in the macroscopic dimensions).[24] This is expected to be the case at very large deformations, such as would be associated with the constant $2C_1$ since it represents the reduced stress at the limit $\alpha^{-1} = 0$. The PDMS networks under investigation would have cross-links of functionality four, and the density of cross-links in the unswollen network is therefore given by the quantity $\nu/2V$.[2] Its values (in mol of cross-links/cm^3) were calculated from eq 3 and are given for each of the networks in column seven of the table. The alternative quantity, the molecular weight M_c between cross-links, is a direct measure of the average length of the network chains and is related to $\nu/2V$ by the simple equation[2]

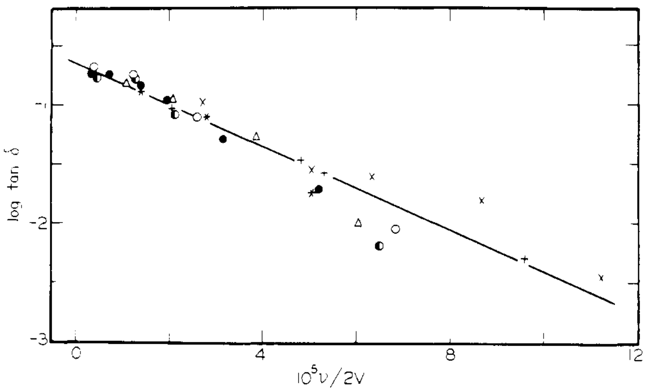

Figure 2. The logarithm of the loss tangent at 175 °C shown as a function of the cross-link density for all of the networks investigated. Values of the volume fraction $v_{2,\mathrm{S}}$ of polymer in the system being cross-linked were 1.00 (●), 0.75 (◐), 0.62 (○), 0.55 (△), 0.48 (*), 0.40 (+), and 0.30 (×).

$$M_\mathrm{c} = \rho/(\nu/V) \tag{4}$$

where ρ is the density of the unswollen polymer network.

The viscoelastic properties of the networks were characterized in terms of the two components of the complex modulus, namely the storage modulus G' and the loss modulus G''. Typical results obtained on several of the PDMS samples are shown in Figure 1. At the chosen frequency of 110 Hz, the high-temperature region is of greatest interest with regard to molecular motions which might be attributed to inter-chain entanglements. In addition, the differences between the observed values of the loss modulus for different samples are seen to be maximized in this region. A temperature of 175 °C was therefore chosen for the desired comparisons of viscoelastic losses among the networks prepared at various degrees of dilution. These comparisons are most conveniently carried out through the use of the "loss tangent" tan δ = tan (G''/G'). It is the decrease in this quantity which has been attributed[11] to a decrease in the number of such entanglements. Values of the negative logarithm of this quantity are given in the final column of the table. In order to investigate the possible dependence of the loss tangent on the amount of diluent present during cross-linking, all of the values of log tan δ were plotted against the degree of cross-linking, as shown in Figure 2. It is thus immediately possible to determine the effect of varying diluent concentration on tan δ at constant $\nu/2V$, which is of course equivalent to comparing the networks at constant average length of the network chains. The results in the right-hand portion of the figure are seen to scatter somewhat, because of the inherent difficulties in measuring very small values of tan δ. Nonetheless, all of the results, for the entire range $v_{2,\mathrm{S}}$ = 1.0–0.3, are very well represented by the single line shown, which was located by least-squares analysis. A more limited set of data obtained near room temperature similarly showed no systematic decrease in tan δ with decrease in $v_{2,\mathrm{S}}$.[28]

The viscoelastic results pertaining to 175 °C are further analyzed in Table II, where 17 of the 30 samples have been placed into three groups in which the networks are arbitrarily designated as having low, moderate, or high degree of cross-linking, on the basis of their relative values of $\nu/2V$. The specific value of $\nu/2V$ for each sample, and the average value for each group of samples, is given in column three of the table. Column four gives the concentration of polymer in the system in which the network was prepared, and column five lists the values of the negative logarithm of the storage modulus G' for each of the networks. At (approximately) constant degree of cross-linking, G' itself is seen to decrease with decrease in $v_{2,\mathrm{S}}$

Table II
Viscoelastic Properties of the Networks at Approximately Constant Values of the Cross-Link Density

Rel deg of cross-linking	Sample	$10^5\nu/2V$	$v_{2,S}$	$-\log G'$	$-\log \tan \delta$	$10^3 \mathrm{d} \log G'/\mathrm{d}T^a$	$10^3 \mathrm{d} \log \tan \delta/\mathrm{d}T^a$
Low	B-1	0.315	1.00	0.812	0.752	−0.080	0.54
	S1-1	0.437	0.75	0.931	0.755	−0.19	0.13
	S2-1	0.366	0.62	0.963	0.687	−0.57	0.21
		Av. 0.373 ± 0.043					
Moderate	B-4	1.95	1.00	0.804	0.974	0.21	−0.71
	S1-3	2.12	0.75	0.924	1.09	0.27	−1.13
	S2-3	2.62	0.62	0.941	1.11	0.44	−1.14
	S3-2	2.06	0.55	0.979	0.961	0.20	−0.82
	S4-2	2.80	0.48	1.00	1.10	0.58	−1.28
	S5-1	2.04	0.40	0.993	1.04	0.15	−1.20
	S6-1	2.71	0.30	1.15	0.976	0.23	−1.62
		Av. 2.33 ± 0.33					
High	B-6	5.22	1.00	0.619	1.72	0.97	−3.19
	S1-4	6.50	0.75	0.650	2.19		
	S2-4	6.84	0.62	0.747	2.05		
	S3-4	6.04	0.55	0.833	2.00		
	S4-3	5.07	0.48	0.886	1.75	0.62	−3.29
	S5-3	5.26	0.40	0.991	1.58	0.62	−3.27
	S6-3	6.34	0.30	1.07	1.61	0.83	−4.25
		Av. 5.90 ± 0.61					

[a] Temperature coefficients refer to an average temperature of 175 °C.

(or $v_{2,C}$); this is consistent with eq 3 in that G' decreases with decrease in reduced stress, and $2C_1$ is simply the value of the reduced stress in the limit of large deformation. The following column presents values of the negative logarithm of the loss tangent. At constant degree of cross-linking, there is no significant dependence of $\tan \delta$ on $v_{2,S}$ in any of the three groups of samples. The last two columns of the table give values of the temperature coefficients $\mathrm{d} \log G'/\mathrm{d}T$ and $\mathrm{d} \log \tan \delta/\mathrm{d}T$ determined over the range 150–200 °C and thus pertaining to an average temperature of 175 °C. Again, neither of these coefficients, at constant degree of cross-linking, shows any systematic dependence on the concentration $v_{2,S}$ of polymer in the system used to prepare the networks.

From the above evidence it is concluded that PDMS networks formed in solution do not have viscoelastic properties significantly different from those prepared in the undiluted state, when the comparisons are properly carried out (at constant degree of cross-linking).[29] To the extent that the observed viscoelastic losses may be attributed to the presence of inter-chain entanglements, as is generally assumed,[11] it is also concluded that the solution cross-linked networks do not have an unusually small number of such entanglements.[30]

It is of course important to compare the present results on dynamic mechanical properties with the previously reported results[15] on the equilibrium elastomeric properties of some identically prepared PDMS networks. One interesting result of the earlier study which is relevant here is the observation that PDMS networks prepared in solution come to elastic equilibrium relatively rapidly and show very little stress relaxation and "permanent set" (irrecoverable flow). Since increase in degree of cross-linking is known to decrease these nonequilibrium effects,[15] their decrease with decrease in $v_{2,S}$ at constant $2C_1$ may be largely due to the associated increase in the cross-link density. The other important result reported earlier[15] was the observation that cross-linking in solution greatly decreases the constant $2C_2$ appearing in eq 2. This is not explicable in terms of the increase in $\nu/2V$ with decrease in $v_{2,S}$ at constant $2C_1$, since $2C_2$ *increases* with increase in cross-link density.[10,15] The effect may be understood, however, using recent theoretical arguments advanced by Flory,[24,25] which associate $2C_2$ with the firmness with which the cross-links are embedded in the network medium. As is obvious from eq 2, $2C_2$ is simply the decrease in $[f^*]$ from its maximum value, at a reciprocal elongation α^{-1} of 1.0, to its minimum value $2C_1$, at $\alpha^{-1} = 0.0$. At relatively small stresses, corresponding to small α, the cross-links are assumed to remain firmly embedded in the network medium because of entanglements between the chains *and the cross-links or network junction points.* For relatively small elongations, therefore, the cross-links and chain vectors would be transformed affinely. At higher elongations, however, the stress level would be sufficient to overcome some of the constraints on the cross-links, they would become less firmly embedded, and the deformation would become nonaffine. According to these arguments, the coefficient C in eq 3 is predicted to decrease significantly with increasing elongation.[24,25] It is these molecular changes, giving rise to a change from an affine to nonaffine deformation, which explain the decrease in $[f^*]$ with α^{-1} which has long been characterized by the constant $2C_2$.[10]

These recent theoretical developments, shown to be consistent with the dependence of $2C_2$ on a number of experimental variables,[10,25] suggest that solution cross-linked samples may be topologically simpler than those prepared in the undiluted state, but in the sense of having fewer chain-junction entanglements rather than fewer inter-chain entanglements. Specifically, the solvent present during the cross-linking would give a cross-link distribution in which cross-links which are *spatial* neighbors would be more likely also to be *topological* neighbors than would be the case for networks prepared in the undiluted state. This simplification would persist after removal of the solvent, and the cross-links would be less firmly embedded in the sense that they would be less enmeshed with the surrounding chain molecules. Deformation of such a network may be markedly nonaffine over *the entire range of elongation,* with $[f^*]$ as a consequence showing little of the dependence on α^{-1} characterized by the constant $2C_2$.

The above analysis, although tentative,[31] does provide a consistent interpretation of both the equilibrium elastomeric behavior and the viscoelastic properties of solution cross-linked networks of PDMS.

Acknowledgments. It is a pleasure to acknowledge the financial support provided by the National Science Foundation (to R.E.C. and to J.E.M.) and by the Petroleum Research Fund, administered by the American Chemical Society (to R.E.C.).

References and Notes

(1) (a) Massachusetts Institute of Technology; (b) University of Michigan.

(2) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.

(3) K. Dušek and W. Prins, *Adv. Polym. Sci.*, **6**, 1 (1969).

(4) L. R. G. Treloar, "The Physics of Rubber Elasticity", 3rd ed, Clarendon Press, Oxford, 1975.

(5) J. D. Ferry, "Viscoelastic Properties of Polymers", 2nd ed, Wiley, New York, N.Y., 1970.

(6) W. W. Graessley, *Adv. Polym. Sci.*, **16**, 1 (1974).

(7) J. E. Mark, *J. Am. Chem. Soc.*, **92**, 7252 (1970).

(8) C. Price, G. Allen, F. de Candia, M. C. Kirkham, and A. Subramaniam, *Polymer*, **11**, 486 (1970).

(9) J. E. Mark, *J. Polym. Sci., Part C*, **31**, 97 (1970).

(10) J. E. Mark, *Rubber Chem. Technol.*, **48**, 495 (1975).

(11) N. R. Langley, R. A. Dickie, C. Wong, J. D. Ferry, R. Chasset, and P. Thirion, *J. Polym. Sci., Part A-2*, **6**, 1371 (1968).

(12) R. E. Cohen and N. W. Tschoegl, *Int. J. Polym. Mater.*, **2**, 49 (1972); **2**, 205 (1973); **3**, 3 (1974).

(13) J. W. M. Noordermeer and J. D. Ferry, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 509 (1976).

(14) C. R. Taylor, R. Greco, O. Kramer, and J. D. Ferry, *Trans. Soc. Rheol.*, **20**, 141 (1976).

(15) R. M. Johnson and J. E. Mark, *Macromolecules*, **5**, 41 (1972).

(16) C. U. Yu and J. E. Mark, *Macromolecules*, **6**, 751 (1973).

(17) C. U. Yu and J. E. Mark, *Polym. J.*, **7**, 101 (1975).

(18) T. Murayama, *J. Appl. Polym. Sci.*, **19**, 3221 (1975).

(19) S. D. Severson, M.S. Thesis in Chemical Engineering, Massachusetts Institute of Technology, 1976.

(20) J. Brandrup and E. H. Immergut, Ed., "Polymer Handbook", Wiley, New York, N.Y., 1975.

(21) M. Mooney, *J. Appl. Phys.*, **19**, 434 (1948); R. S. Rivlin, *Philos. Trans. R. Soc. London, Ser. A*, **241**, 379 (1948).

(22) P. J. Flory and Y. Tatara, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 683 (1975).

(23) G. Ronca and G. Allegra, *J. Chem. Phys.*, **63**, 4990 (1975).

(24) P. J. Flory, *Proc. R. Soc. London, A*, **351**, 351 (1976).

(25) P. J. Flory, submitted to *J. Chem. Phys.*

(26) J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, **66**, 1006 (1977).

(27) It is obviously essential to include the factor $v_{2,\mathrm{C}}^{2/3}$ in interpreting the mechanical properties of any network prepared in solution since, under these conditions, it may be considerably less than unity. Values of the reduced stress or storage modulus uncorrected for this effect should therefore not be used as a measure of effective cross-link density in comparisons[11,15] between samples prepared at different values of $v_{2,\mathrm{S}}$. In simple, physical terms, the polymer chains are cross-linked at a volume V_0 characterizing the polymer solution. Subsequent removal of the solvent collapses the chains into a type of compressed or "super-contracted" state in which their configurational distribution is obviously very different from that associated with the state in which the cross-links were introduced. Under these conditions, the chains, and the entire polymer network, are much easier to deform than would be the case had the same number of cross-links been introduced in the undiluted state. The factor $v_{2,\mathrm{C}}^{2/3} < 1$ must therefore be introduced to take account of the fact that the reference state for an unswollen network prepared in solution is not identical to the state of zero imposed stress in any subsequent study of its mechanical properties.

(28) As can be seen from Figure 2 and Table I, cross-linking in solution provides a convenient way of changing the viscoelastic loss of a polymer network independently of its modulus. For example, a network having a very small value of tan δ can be prepared by cross-linking it to a relatively large value of the cross-link density $\nu/2V$. If the cross-links are introduced in the presence of relatively large amounts of solvent, however, the large value of $\nu/2V$ would not give a large value of the modulus or reduced stress because it would be largely offset by the factor $v_{2,\mathrm{C}}^{2/3} \ll 1$ appearing in eq 3.

(29) Langley and co-workers,[11] in a study of the dynamic mechanical properties of natural rubber, have reached the opposite conclusion, namely that cross-linking in solution does decrease the viscoelastic loss, and have attributed this decrease to a decrease in the number of inter-chain entanglements. They, however, compared solution and bulk cross-linked samples essentially at equal values of G' uncorrected by the important factor $v_{2,\mathrm{C}}^{2/3}$ discussed above. We would therefore attribute the smaller values of tan δ which they report for the solution cross-linked samples (at constant G') simply to an increase in degree of cross-linking, unrecognized because of its being offset by decrease in the factor $v_{2,\mathrm{C}}^{2/3}$.

(30) The expectation that cross-linking in solution would reduce the number of inter-chain entanglements implicitly assumes that such entanglements are rather numerous in a typical, bulk cross-linked network [see, for example, N. R. Langley and K. E. Polmanteer, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1023 (1974)]. The present experimental results and recent theoretical arguments,[24] however, suggest that such entanglements may be less numerous or less important than is widely thought to be the case.

(31) If one arbitrarily abandons the idea put forward here, that the observed viscoelastic losses are due to permanent entanglements, it may be possible to rationalize the present results in terms of network chain ends or untrapped entanglements (W. W. Graessley and N. R. Langley, private communications). At the present time, however, this interpretation would seem to be less plausible than the analysis presented here.

Temperature Dependence of Orientation Correlations in *n*-Alkane Liquids

G. D. Patterson,* A. P. Kennedy, and J. P. Latham

Bell Laboratories, Murray Hill, New Jersey 07974. *Received February 1, 1977*

ABSTRACT: The depolarized Rayleigh intensities of *n*-hexadecane and *n*-docosane are measured as a function of temperature above the melting point. A parameter directly proportional to the magnitude of the orientation correlations is determined from the intensities. The results are then analyzed in terms of the general theory of orientation correlations in isotropic fluids developed by deGennes. We conclude that near their melting point the *n*-alkanes are far above a hypothetical rotational ordering transition comparable to an isotropic–nematic phase transition.

It is known[1,2] that the depolarized Rayleigh scattering intensities of *n*-alkane liquids indicate that there are orientation correlations between the chains for the higher alkanes. It has also been reported[3–6] that the intensities decrease with increasing temperature near the melting point. It has recently been suggested[7] that such effects are due to a near second-order transition comparable to the isotropic–nematic transition in liqud crystals which would occur below the melting point of the *n*-alkanes. This transition was predicted[7] to occur at 270 K for *n*-hexadecane. In the present work, new measurements of the depolarized Rayleigh ratio R_{HV} are reported as a function of temperature for *n*-hexadecane and *n*-docosane. The various contributions to R_{HV} are discussed in detail and evaluated either theoretically or experimentally. The results are discussed in terms of the general theory of orientation correlations in fluids developed by deGennes.[8]