

DYNAMIC MECHANICAL BEHAVIOR OF SWOLLEN POLY[2-(2'-HYDROXYETHOXY)ETHYL METHACRYLATE] IN THE RUBBERLIKE REGION*

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An investigation was carried out of the dynamic mechanical behaviour, in the rubberlike region, of networks of poly[2-(2'-hydroxyethoxy)ethyl methacrylate] obtained by crosslinking copolymerization with ethylene dimethacrylate (concentrations $0.33 \cdot 10^{-4}$ and $2.12 \cdot 10^{-4}$ mol cm^{-3}) and swollen with 2,2'-oxydiethanol to two extents (volume fraction of polymer v_2 0.56 and 0.34). The storage and loss shear compliances, J'_p and J''_p , were compared with those of poly(2-hydroxyethyl methacrylate) having half the length of the side chains, crosslinked and swollen to similar concentrations and investigated earlier.

Good agreement was observed between the results obtained for identical samples of swollen poly(2-hydroxyethyl methacrylate) by combining double transducer, torsion pendulum, and torsional creep data with those from a low-frequency forced vibration apparatus.

Increasing length of side chains is known to affect the viscoelastic behaviour of polymers similarly to an increased degree of swelling, with respect to both the position of the viscoelastic functions¹ and the glass transition temperature (ref.²). So far the question has remained unanswered as to the influence of side chains length on the viscoelastic functions in the rubberlike region, especially near the low-frequency part of the main maximum of the loss compliance J'' . Polymers suited for this purpose are those based on methacrylates or acrylates for which homologous series can be prepared containing side chains of various lengths¹. The effect of concentration of ethylene dimethacrylate as the crosslinking agent on the secondary losses of poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) swollen with 2,2'-oxydiethanol to various degrees was studied in our earlier paper³. This former study was carried out by combining data from double transducer, torsional pendulum and torsional creep measurements; the latter two devices gave information on the behaviour of systems under investigation in the rubberlike region.

In the present study we used poly[2-(2'-hydroxyethoxy)ethyl methacrylate-co-ethylene dimethacrylate] with a longer side chain $-\text{COOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$, which was investigated under conditions similar to those used for the copolymer of 2-hydroxyethyl methacrylate in the rubberlike region. Since we used a low-frequency

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forced vibration apparatus⁴ for this purpose, the same apparatus had to be used to repeat some data for crosslinked poly(2-hydroxyethyl methacrylate).

EXPERIMENTAL

Sample Preparation

The dynamic mechanical measurements were performed with two networks of poly[2-(2'-hydroxyethoxy)ethyl methacrylate-co-ethylene dimethacrylate] (*I*) obtained by crosslinking copolymerization in the presence of ethylene dimethacrylate in two concentrations (c) $0.33 \cdot 10^{-4}$ and $2.12 \cdot 10^{-4} \text{ mol cm}^{-3}$ and swollen with 2,2'-oxydiethanol to polymer volume fractions (v_2) 0.56 and 0.34. In order to compare data obtained earlier by combining three different methods³ and data measured using the low-frequency forced vibration apparatus⁴ we used a poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) (*II*) network with c $0.136 \cdot 10^{-4} \text{ mol cm}^{-3}$ swollen with 2,2'-oxydiethanol to v_2 0.37. The standard sample of *II* was the same as that used in ref.³ (designated there as sample A 2), swollen once again with 2,2'-oxydiethanol.

The procedure of crosslinking copolymerization was the same as earlier for *II* (ref.⁵): the polymerization took place in the presence of isopropyl percarbonate as initiator, concentration of $5 \cdot 10^{-3} \text{ mol/l}$, between two glass plates at 60°C for 4 hours. Two samples used in the measurements had a rectangular cross-section, were approximately $20 \cdot 10 \cdot 3 \text{ mm}$ in size, and were cut out from plates swollen with water to a low concentration.

The samples of *I* were water-extracted under reflux with a multiple water exchange for approximately eight hours. Samples with a lower concentration of the crosslinking agent were first partly dried at 100°C in saturated water vapor, then in a drying box at 50–60°C. The procedure outlined above was too drastic for samples with a higher concentration of the crosslinking agent, which in many cases led to their cracking. It was therefore necessary to deswell the samples over a saturated solution of ammonium sulfate at room temperature for about a week, and only later in a drying box over P_2O_5 at 50–60°C. The sample density determined by the method of double weighing under cyclohexane was 1.26 g cm^{-3} at 25°C. The reference samples of *II*, extracted earlier, were partly deswollen over saturated water vapor at 90–100°C for 3–4 hours, then in air for about 4 hours, after which they were dried in a drying box at 100°C over P_2O_5 to constant weight.

Swelling of samples. The samples of *I* were swollen with 2,2'-oxydiethanol in Petri dishes in a drying box at 50–60°C. On attaining the required concentration they were conditioned in closed weighing bottles at the same temperature. The sample of *I* was swollen and conditioned at 100°C. In both cases the samples had to be gradually additionally swollen, because conditioning in closed weighing bottles led to a slight decrease in the 2,2'-oxydiethanol content of the samples. Conditioning took up approximately two weeks in both cases; after this time the samples were assumed to be completely homogeneous. The density of the swollen samples was determined by a procedure described earlier⁵.

Measurement of Viscoelastic Properties

The samples were measured with a low-frequency forced vibration apparatus described elsewhere⁴. The predeformation of sandwich shear-stressed samples was 5–10%; the thickness of samples fixed between clamps was determined by a cavity micrometer. The sample thicknesses after installation and the changes in the degree of swelling during the measurements are given in Table I.

Measurements were made at 5 to 11 temperatures ranging approximately from -26 to 60°C on each sample; at each temperature, up to 20 frequencies were determined in the range from $2.5 \cdot 10^{-4}$ to 1 c.p.s. The temperature sequence was from the highest to the lowest. The weights used for sample deformation varied within a range from 1 to 2 kg. After completion of each series of measurements, a check was also made, by repeating several frequencies for one of the first temperatures measured.

Samples of I , $c = 0.33 \cdot 10^{-4} \text{ mol cm}^{-3}$, were measured at temperatures 54.7, 39.7, 25.0, 9.6, -4.7 , -10.5 , -17.0°C ($v_2 = 0.56$) and at temperatures 54.8, 25.0, 9.0, 2.3, -3.5 , -9.1 , -14.1 , -18.8 , -22.5 , -25.8°C ($v_2 = 0.34$).

Samples of I , $c = 2.12 \cdot 10^{-4} \text{ mol cm}^{-3}$, were measured at temperatures 52.7, 25.0, 13.9, 2.5, -2.7 , -8.7 , -13.8 , -18.5 , -21.8 , -24.4°C ($v_2 = 0.56$) and at temperatures 49.5, 25.0, 10.2, 4.6, -4.2 , -10.5 , -15.5 , -18.5 , -21.5 , -25.5°C ($v_2 = 0.34$).

The II sample ($c = 0.136 \cdot 10^{-4} \text{ mol cm}^{-3}$, $v_2 = 0.36$) was measured at temperatures 54.6, 25.0, 11.1, 4.7, -5.7 , -10.8 , -14.9 , -18.2 , -21.2 , -23.4°C .

An example of the dependence of J'_p on frequency, ω , for II measured at low temperatures is given in Fig. 1. Here J'_p is the storage compliance multiplied by Tq/T_0q_0 , where T and T_0 resp. are the temperatures of measurement and reference (298 K) and q and q_0 are the corresponding densities.

Treatment of viscoelastic data. The viscoelastic data were computed from the apparatus data by using an Elliot 4130 computer. The resulting J' and J'' values at different temperatures were reduced by the factor Tq/T_0q_0 to 25°C and empirically shifted on the logarithmic frequency scale to give the best fit. The temperature dependences of the empirical shift factors obtained from

TABLE I

Characterization of Poly[2-(2'-hydroxyethoxy)ethyl Methacrylate-co-ethylene Dimethacrylate]

c Concentration of crosslinking agent, G_z weight of swollen samples, d thickness of samples fixed in the apparatus, v_2 and v'_2 are the respective degrees of swelling before and after the experiment, α_1 coefficient of volume expansion, ρ_{25} sample density (25°C) calculated from the value for dry samples and density of 2,2'-oxydiethanol assuming additivity of volumes.

$c \cdot 10^4$ mol cm^{-3}	G_z g	d cm	v_2	v'_2	$\alpha_1 \cdot 10^4$ K^{-1}	ρ_{25} g cm^{-3}
0.33	0.4658	0.143	0.561	0.565	5.67	1.195
	0.4449	0.143	0.561	0.563		
2.12	0.3513	0.209	0.558	0.563	5.67	1.195
	0.4508	0.209	0.551	0.552		
0.33	0.6851	0.164	0.331	0.342	6.17	1.166
	0.5361	0.164	0.340	0.340		
2.12	0.5648	0.230	0.346	0.345	6.17	1.166
	0.4525	0.230	0.346	0.344		
0.136 ^a	0.7248	0.245	0.366	0.365	6.39	1.182

^a Sample of poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate)¹³.

low-temperature measurements (Fig. 2) satisfied Arrhenius' equation. The activation energy values, ΔH , calculated from these plots, are given in Table II; they were used for calculation of shift factors necessary for superposition of the data.

RESULTS AND DISCUSSION

Comparison of Results Obtained with Various Apparatuses

As has been pointed out earlier⁴, the low-frequency forced vibration apparatus permits high sensitivity measurements of the components of complex compliance in the rubberlike region. The example of the data for $\log J_p'$ vs $\log \omega$ given in Fig. 1 shows that the scatter of data thus obtained is, in a suitable range of compliances, very small.

Since the reference poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) samples having approximately the same degree of swelling as poly[2-(2'-hydroxyethoxy)ethyl methacrylate-co-ethylene dimethacrylate] (I) had already been measured, we found it necessary to compare older data obtained by combining the double transducer-torsion pendulum-torsional creep with new measurements with the low-frequency forced vibration apparatus on the same material. Comparison of the reduced data of the poly(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) samples (II), crosslinking agent concentration (c) $0.136 \cdot 10^{-4} \text{ mol cm}^{-3}$, swollen to polymer

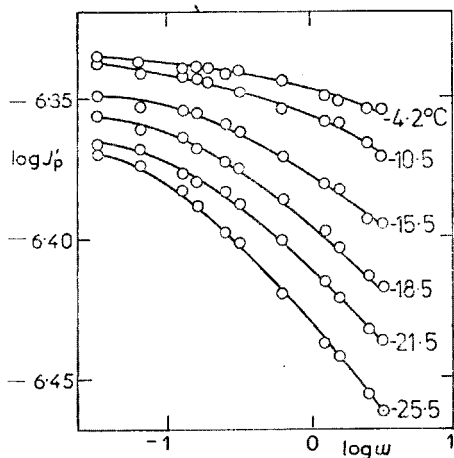


FIG. 1

Dependence of Storage Compliance (J_p') on Frequency (ω) for I4 (Table II)

Measured with the low-frequency forced vibration apparatus.

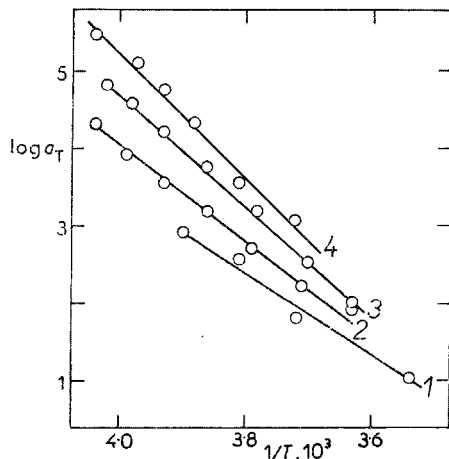


FIG. 2

Temperature Dependence of the Empirical Shift Factors a_T Plotted in the Arrhenius Form and Used for Calculations of ΔH

Numbers of curves correspond to samples of I listed in Table II.

volume fractions (v_2) 0.34, is given in Fig. 3. The same shift factors as in ref.³ were used for the reduction of the results. The agreement is quite good and the low frequency forced vibration apparatus overlaps all of the three methods used earlier. However, such comparatively good agreement was obtained only for the case described above; in some others (not quoted here) low frequency forced vibration data had to be shifted towards lower compliances by about 0.1 log decade to agree with the values in ref.³. So far no satisfactory explanation of these differences could be offered; in principle, however, they are not too large, if we bear in mind that the measurements were carried out with samples having different shape factors and different compression, and that also the degrees of swelling could differ to some extent.

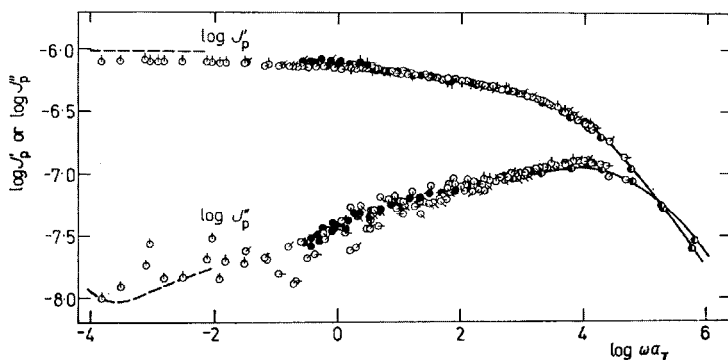


FIG. 3

Plot of J'_p vs ωa_T and J''_p vs ωa_T for a Swollen Poly(2-Hydroxyethyl Methacrylate-co-Ethylene Dimethacrylate) (II) Sample (Data Reduced to 25°C)

Sample A2 of ref.⁵, $c = 0.136 \cdot 10^{-4} \text{ mol cm}^{-3}$; $v_2 = 0.34$. Data: \circ low-frequency forced vibration apparatus, \bullet torsional pendulum (from³), \ominus Fitzgerald's apparatus (from³), - - - - torsional creep (from³). Rotation of pips starting at 0° means gradual decrease in temperatures from the highest given in the text (Experimental, Measurement of Viscoelastic Properties).

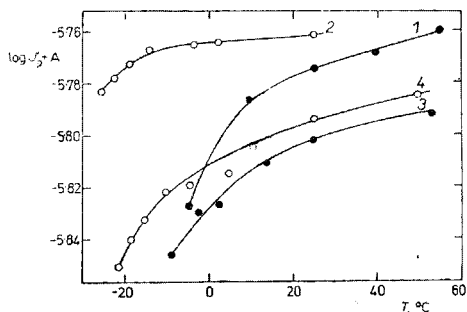


FIG. 4

Plots of J'_p vs T for samples of I corresponding to a measurement frequency 0.005 c.p.s.

Numbers of curves correspond to samples listed in Table II; values of A . 1 0.164, 2 0, 3 0.574, 4 0.516.

Temperature Dependence of J'_p

The temperature dependence of $\log J'_p$ corresponding to a frequency 0.005 c.p.s. is given in Fig. 4. In each case the reduced compliance increases with temperature without reaching a constant value. As expected, a greater rate of increase is observed for samples swollen to a lower degree (samples 1 and 3) which are somewhat farther from the equilibrium than samples 2 and 4. Also the faster increase in compliance with the temperature of sample 1 having a lower degree of crosslinking compared to sample 3 is easy to understand; on the other hand, such an expected tendency does not appear in the case of sample 2 compared to sample 4.

Temperature Dependence of Shift Factors

The activation energies for *I* in Table II vary from 24 to 37 kcal mol⁻¹ and increase with increasing degree of swelling and increasing concentration of crosslinking agent. They are similar in magnitude to those calculated earlier for *II* from the constants c_1 , c_2 of the WLF equation³. The low values of the latter for highest diluent concentration are associated with the fact that the constants c_1 , c_2 of the WLF equation were calculated for *II* from the main transition region, while for *I* the data of the main transition were not available. It has been found earlier^{1,8} that for polymethacrylates the agreement between the shift factors calculated from the viscoelastic measurements in the main transition region and in the rubberlike region is not too good; important

TABLE II

Activation Energies and Equilibrium Compliances for Copolymers of 2-(2'-Hydroxyethoxy)ethyl (*I*) or 2-Hydroxyethyl (*II*) Methacrylate, resp. with Ethylene Dimethacrylate
Definition of c and v_2 are in Table I, J_e is the equilibrium compliance.

Sample	$c \cdot 10^{-4}$ mol cm ⁻³	v_2	ΔH kcal mol ⁻¹	$\log J_e$	$\frac{d \log J_e}{d \log v_2}$	
<i>I</i>	1	0.33	24.0	-5.92 ₄	0.89	
	2		28.5	-5.73 ₅		
	3	2.12	0.56	33.3	-6.36 ₆	0.31
	4		0.34	36.8	-6.29 ₈	
<i>II</i> ^a	1'	0.136	0.55	31.1 ^b	-6.38 ₃	0.88
	2'		0.34	15.5 ^b , 20.6 ^c	-6.20 ₀	
	3'	2.058	0.55	—	-6.88 ₄	-0.16
	4'		0.34	—	-6.91 ₇	

^a Values in ref.^{3,5}. ^b Calculated from expression $\Delta H = 2.303 R c_1^0 T^2 / c_2^0$ using constants c_1^0 and c_2^0 given in Table II and ref.⁶. ^c Calculated from constants c_1^0 and c_2^0 given in ref.³.

differences were found for poly(butyl methacrylate) networks even at glass transition temperature, T_g , + 50°C (ref.⁸).

Time and Concentration Dependence of J'_p

For both *I* networks, J'_p increases with increasing concentration of 2,2'-oxydiethanol (Fig. 5a). For the higher concentration of crosslinking agent, J'_p was inversely proportional to $v_2^{1/3}$ in accordance with the kinetic theory of elasticity for the equilibrium

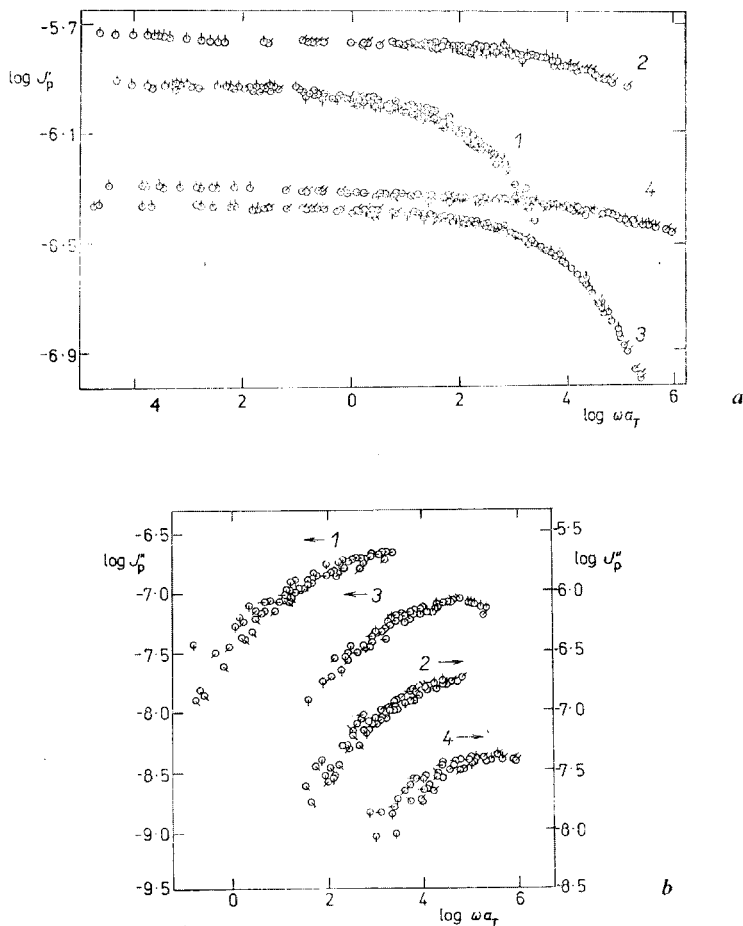


FIG. 5
Reduced Data for *I* Networks Swollen to Two Different Degrees (Referred to 25°C): (a) $\log J'_p$ vs $\log \omega a_T$, (b) $\log J''_p$ vs $\log \omega a_T$

Numbers of curves correspond to samples given in Table II. The meaning of pips see Fig. 3.

compliance J_e , which can be assumed to hold also for data measured in the rubberlike region and near equilibrium. For the lower concentration of crosslinking agent, J_p' was inversely proportional to v_2^3 with a approaching 0.9; an identical value was found for a similar network of *II* measured earlier³, while for a *II* network crosslinked to a still higher degree the experimentally determined exponent was even negative.

In Fig. 6*a*, all equilibrium compliance values of the samples of *I* are seen to be higher than those of the samples of *II*. These differences have been found earlier⁹; they are connected with the lower crosslinking efficiency in copolymerization of *I* (with the same concentration of crosslinking agent), and also with a non-zero C_2

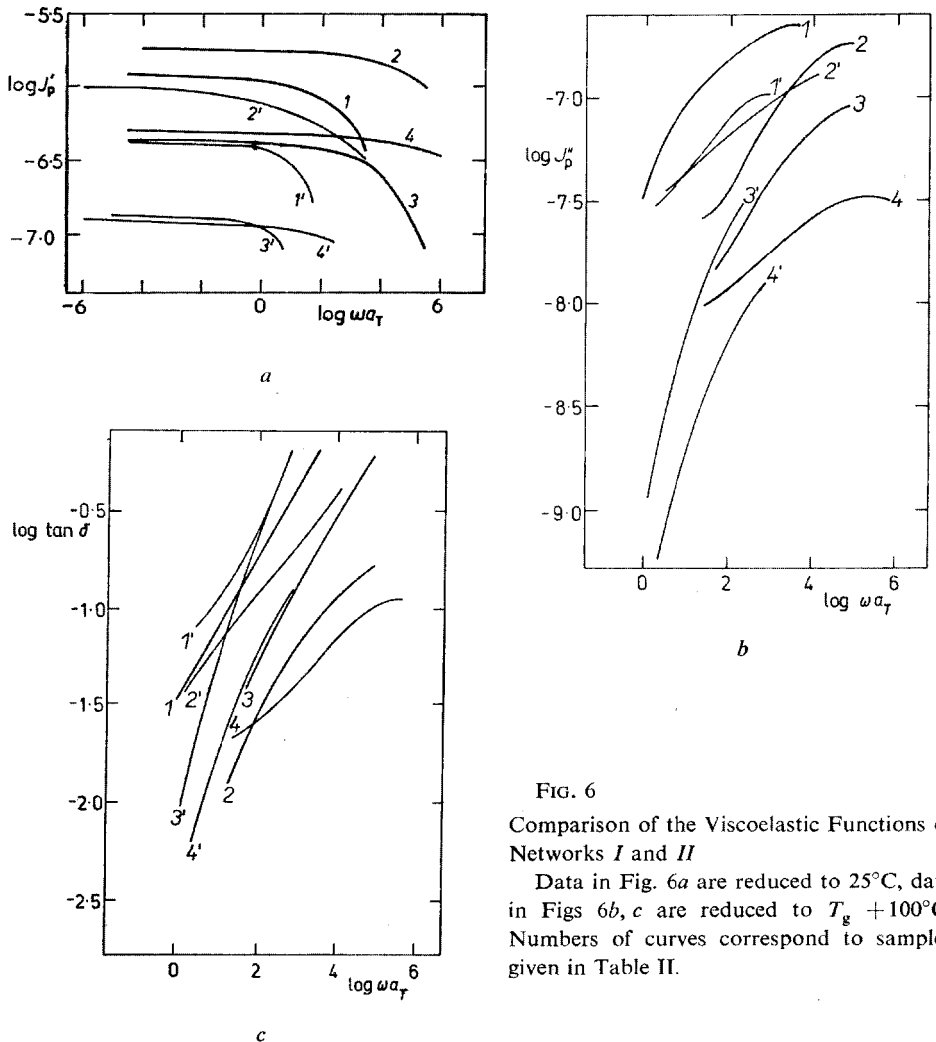


FIG. 6
Comparison of the Viscoelastic Functions of
Networks *I* and *II*

Data in Fig. 6*a* are reduced to 25°C, data in Figs 6*b*, *c* are reduced to $T_g + 100^\circ\text{C}$. Numbers of curves correspond to samples given in Table II.

constant of the Mooney–Rivlin equation for *II* (ref.⁵) (C_2 is zero for *I*). For lightly crosslinked networks, the dependence of J' on swelling approaches proportionality to v_2^{-1} as previously found¹⁰ for *II*; differences between the two polymers in this respect appear only for more highly crosslinked networks, where the finite extension of the network¹⁰ chain plays a more prominent role in *II* than in *I*.

Time and Concentration Dependence of J''_p

While a relatively good temperature-frequency superposition was found over the whole temperature and frequency range for J' , J'' exhibited a comparatively large scatter in the region of low reduced frequencies; these results were therefore not taken into account. The reduced J'' data for sample 1 (for temperatures 9.6°C and lower), sample 2 (for -3.5°C and lower), sample 3 (for -2.7°C and lower) and sample 4 (for -4.2°C and lower) are given in Fig. 5*b*. They correspond to a range of about four logarithmic decades on the left-hand branch of the main maximum of J_p . To compare the losses of *I* with *II*, the J'' and $\tan \delta$ values of the low-frequency branch of the primary maximum were recalculated to $T_g + 100^\circ\text{C}$ by using ΔH values of Table II (*I*) and/or c_1 and c_2 values of ref.³ (*II*). The T_g values of *II* were estimated as -38° and -68°C ($v_2 = 0.55$ and 0.34) and as -70° and -85°C ($v_2 = 0.56$ and 0.34) (Eq. 1 of ref.¹¹ with T_g of 2,2'-oxydiethanol taken as -100°C (ref.¹²), T_g (*II*) = 98°C (ref.¹³), T_g (*I*) = 11°C (ref.^{13,14}), k_α (*II*) = 2.7 (ref.¹¹), k_α (*I*) = α_{fd}/α_{fp} = 8.2/2.55 = 3.25 (ref.^{7,14})). The results are given in Fig. 6*b* (J'') and 6*c* ($\tan \delta$).

The position of the left-hand branch of the maximum in J'' on the frequency scale depends primarily on the monomeric friction coefficient, ζ_0 , and the average molecular weight of a chain between crosslinks, M_c ; in the framework of the Mooney modification of the Rouse theory¹, the relevant relaxation times should be proportional to $\zeta_0 M_c^2$ for a network whose strands have a Gaussian distribution of configurations. Even in a swollen network, this branch of J'' may be expected to shift to lower frequencies with increase in either ζ_0 or M_c . Comparisons at different degrees of swelling suggest that the reduction to $T_g + 100^\circ\text{C}$ does not account for all the dependence of ζ_0 on v_2 . Comparisons at different degrees of crosslinking show the expected effect of M_c . For comparison of the two polymers, the only useful pair is 1' and 3, which have the same swelling and also the same actual degree of crosslinking as gauged by the values of J_c . Apparently poly[2-(2'-hydroxyethoxy)ethyl methacrylate-co-ethylene dimethacrylate], with longer side chains, has a ζ_0 smaller than that of poly-(2-hydroxyethyl methacrylate-co-ethylene dimethacrylate) by about three orders of magnitude, even when compared at $T_g + 100^\circ\text{C}$ for both systems. A similar, but less marked, effect of side chain length is observed in undiluted methacrylate polymers¹.

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