Viscoelastic Properties of Cross-Linked Solutions of Poly(β-hydroxyethyl methacrylate) in Diethylene Glycol. III. Dynamic Measurements. Dependence on Concentration in the Transition Zone

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ABSTRACT: From a dilute network of poly(β-hydroxyethyl monomethacrylate) cross-linked by 0.136×10^{-4} mol cm^{-3} of ethylene glycol dimethacrylate, four solutions in diethylene glycol were prepared with different degrees of swelling; the volume fractions of the polymer were $v_2 = 0.606$, 0.495, 0.319, and 0.168. Measurements of dynamic mechanical properties were performed with a Fitzgerald transducer in the frequency range from 30 to 1600 cps and a temperature range of -73 to $+55°$; also with a torsion pendulum in the frequency range from 0.2 to 2 cps and temperatures from -10 to $55°$. Data corresponding to lower frequencies were obtained by converting creep data from previous studies. The influence of swelling degree on the shapes of the retardation and relaxation spectra and on the monomeric friction coefficient was studied. The magnitude of the low-frequency secondary losses in the rubberlike state was evaluated and the contribution to the equilibrium compliance was calculated. The possibility of the time–concentration superposition was discussed in comparison with the time–temperature superposition, with special attention to the influence of the high-frequency secondary relaxation, known from isochronal modulus–temperature measurements. The relaxation (H) and retardation (L) spectra, calculated for the main transition, were similar for $v_2 = 0.606$ and 0.495, and also for the dry sample studied previously. An indication of a low-frequency secondary relaxation of the entanglements was found in the L spectra. This part of the spectrum shifts toward shorter times with dilution, as does the main maximum in L. With increasing swelling degree, the contribution to the secondary maximum decreases, while the spectrum near the main maximum becomes broader; at $v_2 = 0.319$, the secondary peak disappears into the right side of the main maximum. With increasing concentration of diluent, an indication of the high-frequency secondary dispersion of side chains, known from isochronal low-temperature measurements, appears. The superimposed values of the glass–rubber transition are somewhat influenced, at high reduced frequencies, by this secondary effect. The superimposed curves and the spectra, which can be calculated only to a first approximation, have therefore higher slopes in this range than expected. The free volume parameters, calculated from the c_1 and c_2 values of the WLF equation and obtained from the superimposed data in the glass–rubber transition, were in full agreement with those obtained from time–concentration superposition of the creep curves in the rubberlike state. The time–concentration superposition gives similar results to the time–temperature superposition, as far as the generalized compliance is concerned, if the differences in the swelling degrees are not large. The effects both of entanglements and of other long-range motions and of the secondary dispersion due to the side chain–diluent motions can seriously influence the long and short time portions of the spectra. Time–temperature and time–concentration superposition of viscoelastic data can therefore be applied only in limited ranges of temperature and concentration.

The frequency and time dependence of linear viscoelastic functions and the form of the associated relaxation and retardation spectra have been studied in this laboratory for various rubbers and many other polymers,[2–5] including a series of polymethacrylates.[2a] Solutions of some of these polymers in various solvents have also been studied, especially poly(methyl methacrylate)[6] and poly(n-butyl methacrylate)[7] in diethyl phthalate.

Visoelastic behavior of hydrophilic polymethacrylic acid esters in the main transition region and in the rubberlike state have been studied by transient experiments only.[8–12] In some studies involving creep measurements in torsion and simple elongation, the influence of cross-linking by ethylene glycol dimethacrylate in the presence of an inert diluent was investigated. Recently the time–temperature superposition of creep curves of poly(β-hydroxyethyl monomethacrylate) prepared in the presence of 40 parts of water by volume and cross-linked to various degrees was studied.[11] Also, the time–concentration superposition of the generalized creep curves, obtained for the main transition region of the same samples, was performed[12] for two concentrations (C) of cross-linking agent and ranges of volume fraction of polymer (v_2): $C = 0.086 \times 10^{-4}$ mol cm^{-3} and $v_2 = 0.78$–1; and $C = 1.241 \times 10^{-4}$ mol cm^{-3} and $v_2 = 0.56$–1.

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In the present study, these hydrophilic polymers prepared in the absence of a diluent during polymerization have been investigated by the dynamic methods previously applied to other systems. The advantages of this approach are, first, that more exact data can be obtained in the rubbery state, where the changes of the static compliance are often very small. Second, samples with a great range of diluent concentrations can be used in contrast to transient methods where the time scale becomes too short at high dilution. Third, the losses, which are especially interesting in the rubberlike region, can be measured directly.

This paper describes the viscoelastic behavior of four solutions of poly(β-hydroxyethyl monomethacrylate) in diethylene glycol covering a wide concentration range. The combination of double transducer, torsion pendulum, and creep data provides conclusions about the influence of diluent on the shapes of viscoelastic spectra over a wide range of time scale.

Experimental Section

Materials. Sample A2 from our previous study,[13] a copolymer of poly(β-hydroxyethyl monomethacrylate) with 0.136×10^{-4} mol cm^{-3} of ethylene glycol dimethacrylate, was used for the measurements. Four solutions in diethylene glycol were prepared as described previously,[13] with v_2 = 0.168, 0.319, 0.495, and 0.606. The lowest concentration was near swelling equilibrium, and the highest was near the maximum in hardness which could be measured by the torsion pendulum at room temperature. The samples were measured in both the Fitzgerald double transducer[14] and the Plazek torsion pendulum.[15] Similar samples were used in both instruments as well as for the creep measurements reported elsewhere.[13,16] The values of the creep compliance $J_p(t)$ found previously[13,16] were converted by well-known approximation methods[2a] into the components of the complex dynamic compliance J' and J'' for consideration with the dynamic data obtained by direct measurement.

Double Transducer Measurements. The measurements were performed using a standard procedure described elsewhere.[14] The details of temperature sequences are as follows.

v_2 = **0.606.** The initial swelling degree was v_2 = 0.594 and 0.602 for the twin samples. Measurements at frequencies between 45 and 1000 cps were performed at 21 temperatures in this sequence: 23.9, 15.6, 6.7, −4.8, −16.9, 36.3, 41.0, 45.1, 50.4, 28.8, 33.1, 18.5, 21.1, 24.7, 32.3, 35.5, 40.7, 49.3, 25.2, 14.1, and 5.1°. The values found for the first nine measurements (before and including the high-temperature runs) gave somewhat higher values of compliances; we think this is due to slight deswelling, since the swelling degrees after the measurements were found to be 0.601 and 0.610. Although this difference may seem rather small, the concentration dependence of the frequency scale is considerable as will be seen below. Therefore, the mean value of v_2 found after the experiment (v_2 = 0.606) was considered a standard value and the values obtained for the first nine measurements were shifted empirically[16] (log a_c = −0.36) to match the data measured later; this correction was quite reasonable. The measurements at the three last temperatures were not used.

v_2 = **0.495.** Two pairs of samples swollen to v_2 = 0.495 were measured in the double transducer at the same time. The samples on both sides of the transducer had exactly the same swelling degree but differed somewhat in weight and installed height; one was compressed about 3% and the other about 10%. The two pairs of samples were first measured at 22.8°. Next a pair on just one side was subjected to sinusoidal vibrations in the measuring cell at 100 cps continuously for 3 days at the amplitude normally used for measurements, and both pairs were measured once more at 23.7°. Afterward a third measurement was made at 22.7° after the same pair of samples had been oscillated at 100 cps for 3 days at 50° while the other pair remained at rest at 50°. The reason for this procedure was to determine the influence of compression, vibration, or preliminary heat treatment on the data. The influence of the vibration was negligible. The pairs compressed to 3 and 10% of their initial height gave the same results. On the other hand, the preliminary heating of the samples to 50° caused a shift of the storage and loss compliance J' and J'' toward lower values because of a slight deswelling.

v_2 = **0.319.** The v_2 values were 0.318 and 0.322 before, and 0.316 and 0.321 after the measurements, which were performed at 21 temperatures in the following sequence: 23.4, 14.6, 4.4, −5.6, 34.6, 45.4, 55.5, −1.6, −11.6, −15.3, −20.2, −25.1, −31.6, −36.7, −42.1, −49.7, −54.5, −67.0, −71.5, −61.1, and 23.0° (check run). The three lowest temperatures showed too much scatter and were not used.

v_2 = **0.168.** The v_2 value was 0.163 before and 0.174 after the measurements, performed at 17 different temperatures in the following sequence: 27.8, 36.7, 45.4, 52.8, −18.8, −57.6, −48.7, −45.0, −34.0, −38.0, −33.4, −72, −59.5, −64.5, −67.1, −73.6, −55.7. Since the samples were very soft, measurements could be carried out only at low frequencies (24 to about 160 cps), though at very low temperatures the range was extended to 600 cps. The data exhibited much scatter, and J'' could be reliably measured only at −59.5° and below; at higher temperatures, only J' was obtained. The results shown for this solution can be considered only as first approximations.

The data from all double transducer measurements were calculated by a computer to obtain values of J' and J'', with a Fortran program prepared by Mr. C. P. Wong. The values were reduced to 25,° making use of the calculated densities of the samples under the assumption of volume additivity.[13]

Torsion Pendulum Measurements. All the calculations of the torsion pendulum data were made with a Varian Data Machines 620i computer, programmed by Mr. C. P. Wong. Details of temperature sequences are as follows.

v_2 = **0.606.** The sample was swollen to v_2 = 0.595 but the v_2 value changed during the measurement to 0.584; this latter value was taken as a basis and the data were shifted to higher frequencies corresponding to v_2 = 0.606 by the free volume parameters calculated earlier from concentration shifts of the creep curves.[13] Measurements at five to seven different frequencies were performed at 24.4, 24.2, 49.7, 45.0, 38.3, 31.9, and 24.7° (check run).

v_2 = **0.319.** The sample was swollen to v_2 = 0.326, which dropped to 0.317 during the measurement. Measurements of five to seven different frequencies were performed at the temperatures 24.1, 29.7, 34.1, 14.2, 9.6, 4.5, −5.8, and 24.4° (check run).

Other Diluent Concentrations. Six measurements were performed on one sample swollen to various degrees of v_2 = 0.491–0.605 at five to seven frequencies near room temperature. The concentrations used were as follows: v_2 = 0.605 (24.8°), 0.586 (23.7°), 0.562 (24.2°), 0.544 (23.9°), 0.517 (26.1°), and 0.491 (24.4°). The sample was always swollen to the desired degree by immersing it to ethylene glycol for a short time; it was then allowed to equilibrate at room temperature for 2 days at least. The compression during the measurements was 2–5%. The sample swollen to

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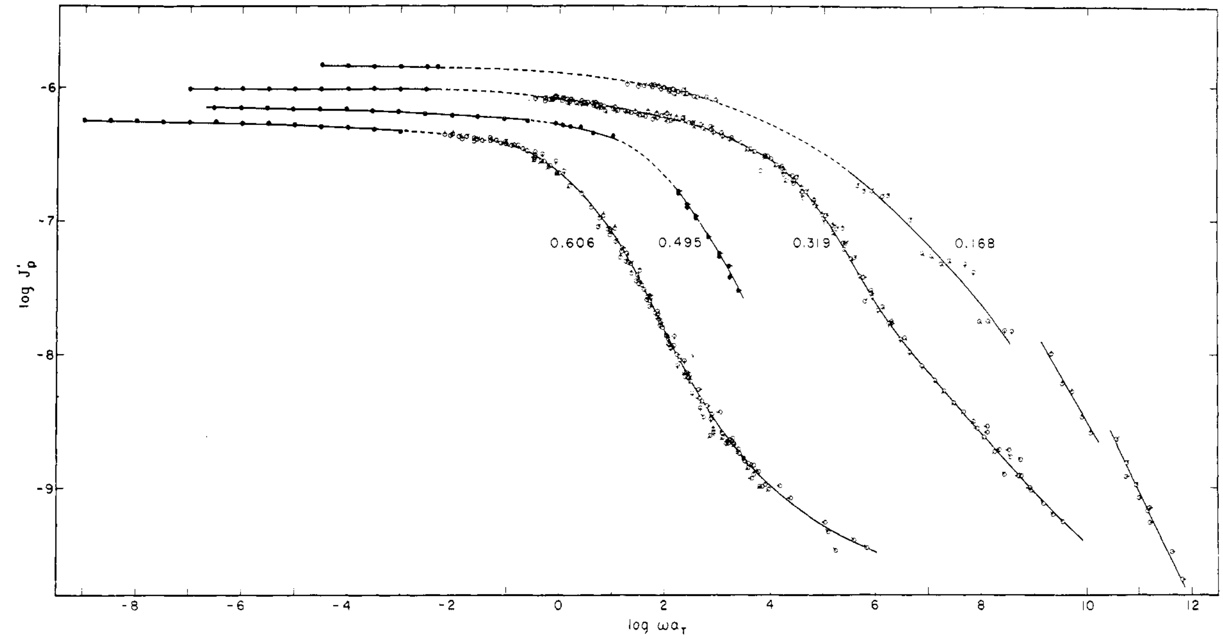

Figure 1. Log J_p' plotted against log ωa_T for cross-linked poly(β-hydroxyethyl monomethacrylate) solutions in diethylene glycol, at various temperatures reduced to 25°, and four concentrations identified as shown. In each series pip up denotes highest temperature and successive 45° rotations clockwise denote successively lower temperatures listed in text: $v_2 = 0.606$, two series of Fitzgerald double transducer apparatus data from 50.4 to $-4.8°$ in eight steps and from 49.4 to 18.5° in eight steps, and torsion pendulum data from 49.7 to 24.4° in seven steps; $v_2 = 0.495$, double transducer at 22.7° and torsion pendulum at 24.4°; $v_2 = 0.319$, double transducer from 55.5 to $-54.5°$ in 16 steps and torsion pendulum from 34.1 to $-5.8°$ in seven steps; $v_2 = 0.168$, double transducer from 52.8 to $-67.1°$ in 10 steps; ⊗, calculated from creep data in ref 13 and 16.

$v_2 = 0.491$ was used to match with the data from the double transducer.

Results

The original data before temperature reduction are omitted to save space. The data obtained from the double transducer for $v_2 = 0.606$ and 0.319 were empirically superimposed to find the log a_T values for each curve. The constants c_1^0 and c_2^0 of the WLF equation[2a]

$$\log a_T = \frac{-c_1^0(T - T_0)}{c_2^0 + T - T_0} \tag{1}$$

were then calculated, using the well-known procedure, for the reference temperature 25°; they were $c_1^0 = 12.2$ and $c_2^0 = 159.4$ for $v_2 = 0.606$ and $c_1^0 = 6.345$ and $c_2^0 = 164.8$ for $v_2 = 0.319$. Using these constants, the shift factors log a_T were calculated for every temperature used and the superposition of the data was performed. The same constants c_1^0 and c_2^0 were used for the superposition of the torsion pendulum data for the corresponding solutions.

A sample swollen to $v_2 = 0.495$ was measured by both the double transducer and the torsion pendulum at only one temperature near 25°. The constants c_1^0 and c_2^0 found for $v_2 = 0.606$ were used for the shifting of the $v_2 = 0.495$ data to 25°. The c_1^0 and c_2^0 constants for $v_2 = 0.319$ were used for the concentration $v_2 = 0.168$. This procedure, which was necessary because no reliable c_1^0 and c_2^0 data could be obtained for $v_2 = 0.495$ and 0.168 solutions, could influence to some degree the shape of the superimposed curve.

The creep curves from our previous study were converted into J'_p and J''_p data by approximation procedures described elsewhere.[2a] For the concentrations $v_2 = 0.606$ and 0.495, the creep curves were obtained from the concentration-reduced superimposed creep curve (Figure 4 of ref 16) using vertical log shifts of 0.22 and 0.31, respectively (Figure 7 of ref 16), and log a_c = 0.49 and -1.96 from the log a_c function (Figure 5 of ref 16). For example swollen to $v_2 = 0.319$ a superimposed curve found for two different temperatures was taken as a basis (Figure 1 of ref 16). For $v_2 = 0.168$, the creep curve obtained for the equilibrium swollen sample A2 (Figure 2 of ref 13) was taken as a basis.

The data recalculated from the creep curves and taken from the torsion pendulum measurement fitted very well as can be seen in Figure 1 where the superimposed curves of all four samples are given. On the other hand, the data obtained by the double transducer had to be systematically shifted to agree with those from the torsion pendulum; this shift was identical for both log J'_p and log J''_p, being -0.10 for $v_2 = 0.606$, 0.495, and 0.168 and -0.11 for $v_2 = 0.319$. The necessity of such a correction, often found previously, was ascribed to the uncertainty in detemining the height of samples in the double transducer.

Furthermore, a horizontal shift was necessary to correct for a concentration difference for one sample which had $v_2 = 0.606$ in the double transducer and $v_2 = 0.584$ in the torsion pendulum. The former was taken as reference and a shift of log $a_c = 0.57$ was applied to the latter. For the other samples ($v_2 = 0.495$ in transducer, 0.491 in torsion pendulum; $v_2 = 0.319$ in transducer, 0.317 in torsion pendulum), the concentrations were so close that no correction was necessary.

In Figure 1, the curves extending for 21 logarithmic decades have the usual shapes. Increasing concentration of diluent shifts the log J'_p curves toward higher frequencies. The shapes of the curves for $v_2 = 0.606$ and 0.495 are much the same; however, the curves are

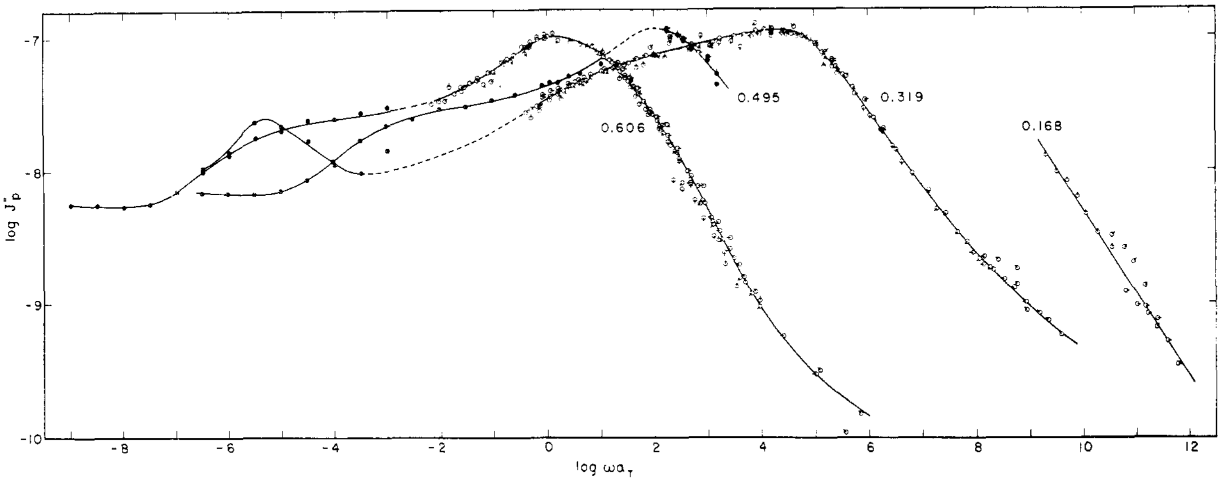

Figure 2. Log J_p'' plotted against log ωa_T for poly(β-hydroxyethyl monomethacrylate) solutions in diethylene glycol. The data correspond to those shown in Figure 1; the values corresponding to the temperatures −48.65 and higher were omitted for the sample swollen to v_2 = 0.168.

steeper in the high-frequency range for $v_2 = 0.319$; this effect is quite marked for the highly swollen sample with $v_2 = 0.168$. The behavior of the latter sample in the region of $\log J'_p = -8$ to -9.5 will be discussed below.

In Figure 2, log J''_p for samples swollen to four different concentrations is plotted against log ωa_T. Starting with the concentration $v_2 = 0.606$, the maximum of the loss compliance becomes more diffuse with increasing degree of swelling; this can be very clearly seen when comparing the samples swollen to $v_2 = 0.606$ and 0.319. The shape of the maximum is nearly symmetrical for $v_2 = 0.606$; however, for $v_2 = 0.319$, the left branch drops very slowly. A secondary small loss maximum arises at low frequencies for $v_2 = 0.606$ and 0.495. When the diluent concentration is increased, the separation between the secondary relaxation peak and the main peak disappears. It follows that the main broad maximum of the $v_2 = 0.319$ solution corresponds to the secondary peak joined with the main maximum.

The sharp peak in Figure 2 found for the concentration $v_2 = 0.319$ at log $\omega a_T \cong -5$ was calculated from the creep curve as shown in Figure 1 of ref 16 and will be discussed later. Only low-temperature data are shown for $v_2 = 0.168$. The plot of J'' is steeper, and the superposition of the data is not quite perfect.

Discussion

Low-Temperature Behavior. From isochronal measurements it is known that poly(β-hydroxyethyl monomethacrylate) in the swollen state, like many other hydrophilic polymers swollen by polar diluents, exhibits a large secondary maximum of losses, extremely sensitive to the swelling degree.[17-19] This maximum ($\beta_{(\mathrm{sw})}$ peak as proposed previously[19]) was ascribed to relaxation motions of the side chains in the diluted state and is hardly perceptible in the dried polymer; on the other hand it is already quite significant for samples having less than 1% of diluent. For higher concentrations of diluent, the decrease of the storage modulus with temperature is realized in two discernible steps;[20] the first corresponds to the $\beta_{(\mathrm{sw})}$ peak, the second to the main transition. With increasing concentration of diluent, the glass–rubber transition shifts toward low temperatures faster than the $\beta_{(\mathrm{sw})}$ peak; if the concentration of the diluent is very high, the temperature of the main transition is not too different from that of the $\beta_{(\mathrm{sw})}$ peak, and only one single sharp decay of the storage modulus is seen in this region.[20] A comparison of the characteristic temperatures of the G'' maxima corresponding to the α and $\beta_{(\mathrm{sw})}$ peaks of the system poly(β-hydroxyethyl monomethacrylate)–ethylene glycol, taken from ref 20, is shown in Table I. For a better comparison of the high-frequency areas, we converted the J'_p and J''_p values from Figures 1 and 2 to G'_p and G''_p by the equation $\log J'_p = -\log G'_p - \log(1 + \tan^2 \delta)$. The result is shown in Figure 3. For the sample swollen to $v_2 = 0.606$, the log G'_p curve has its usual shape, except in the neighborhood of log ωa_T = 4–5; here a plateau is seen corresponding to lower values of moduli (log $G'_p < 9$) than usually expected. This plateau is an evidence of a two-step decay of the storage modulus of the samples swollen to lower degrees, where both the main transition and the secondary transition are still well separated. As this effect is included only within the values corresponding to the highest reduced frequencies, it is not surprising that this indication is not important for G''_p.

TABLE I
CHARACTERISTIC TEMPERATURES CORRESPONDING TO THE α AND THE SECONDARY $\beta_{(\mathrm{sw})}$ PEAKS OF THE SYSTEM POLY(β-HYDROXYETHYL MONOMETHACRYLATE)–ETHYLENE GLYCOL[a]

v_2	T_α, °C	$T_{\beta(\mathrm{sw})}$, °C
0.667	−9	−88
0.531	−31	−95
0.369	−57	−100
0.241	(−70)	−102
0.155	*b*	−110

[a] Values taken from isochronal G''–temperature measurements at the frequency 1 cps, from ref 20. [b] α peak merged into $\beta_{(\mathrm{sw})}$ peak.

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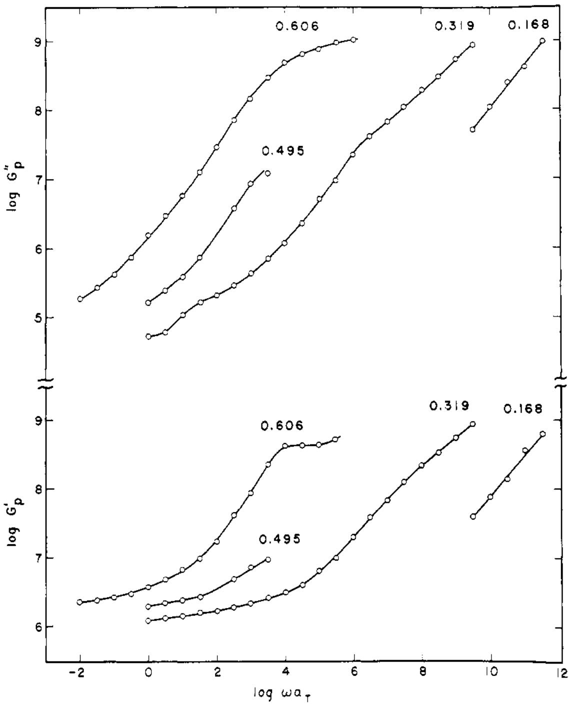

Figure 3. Log G_p'' and log G_p' plotted against log ωa_T for four solutions of poly(β-hydroxyethyl monomethacrylate) in diethylene glycol, identified by values of v_2 as shown.

With increasing concentration of diluent, the main and secondary transitions approach each other. The effect on the shape of G'_p is evident for $v_2 = 0.319$; the inflection disappears, but the high-frequency part of the curve is steeper than that of the sample swollen to $v_2 = 0.606$. An indication of two relaxation mechanisms is, however, better seen in log G''_p; the low-frequency part of the curve corresponds to the glass–rubber transition, the high-frequency part is already modified by the secondary relaxation.

From comparison of G' and G'' corresponding to concentrations $v_2 = 0.606$ and 0.319 it can be seen that the simple time–concentration shift is no longer valid. The steepness of the high-frequency part of both superimposed curves increases with dilution, an effect attributable to increasing influence of the secondary dispersion.

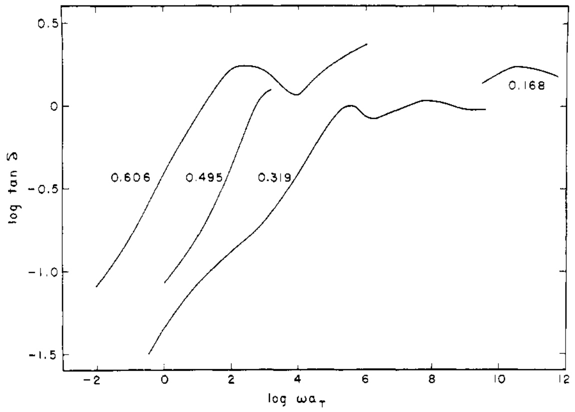

Figure 4. Log tan δ plotted against log ωa_T for four solutions of poly(β-hydroxyethyl monomethacrylate) in diethylene glycol.

The same mechanism can be seen even more clearly in Figure 4 where log tan δ is plotted against log ωa_T for the four solutions; there is indication of a high-frequency dispersion for $v_2 = 0.606$ and 0.319. For $v_2 = 0.168$, only the high-frequency peak is seen. Although the exact shapes and positions of the high-frequency peaks can be subject to some error because of the superposition of the data, the qualitative conclusions are in full agreement with our previous observations taken from isochronal measurements.[17–19]

Retardation Spectra. Retardation spectra (L) calculated by the Williams–Ferry approximation methods[2a] are shown in Figure 5. The black points correspond to the calculations from the generalized creep curve of sample A2 (Figure 4 of ref 16) shifted to corresponding concentrations. Open circles shown for the concentrations $v_2 = 0.319$ and 0.168 are calculated from the actual creep measurements (as shown when discussing Figure 1). The values calculated from the superimposed creep curves and the dynamic data fit very

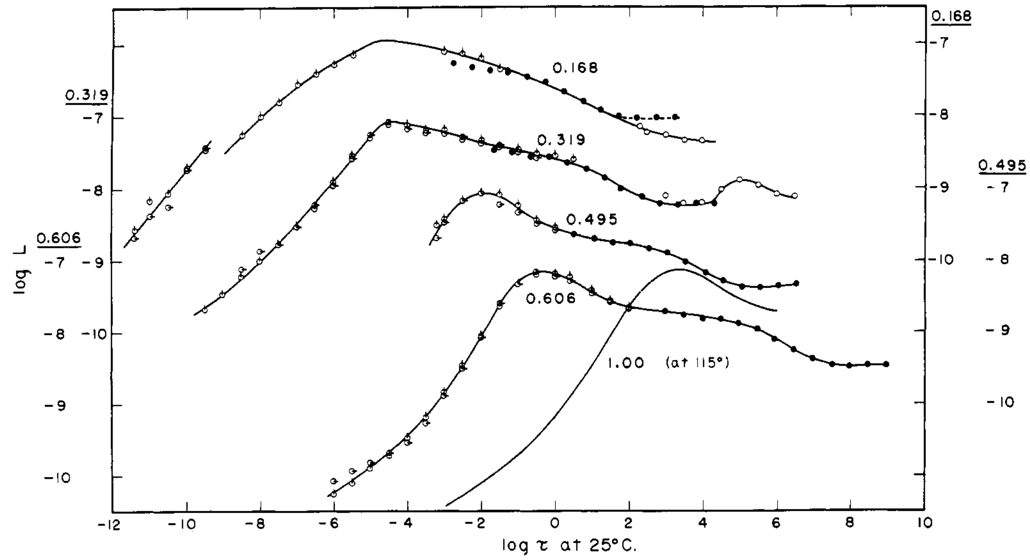

Figure 5. Retardation spectra of the samples of Figures 1 and 2 reduced to 25°. The curve for the dry sample ($v_2 = 1$), reduced to 115°, is taken from ref 10. Black points, $L(\tau)$ data calculated from the generalized curve (Figure 4 of ref 16).

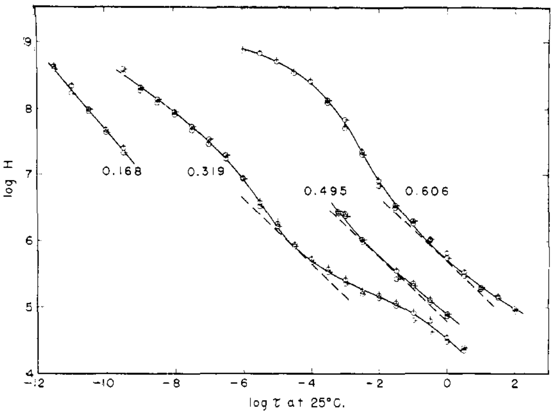

Figure 6. Relaxation spectra calculated for the samples of Figures 1 and 2. Slopes of $-1/2$ are indicated.

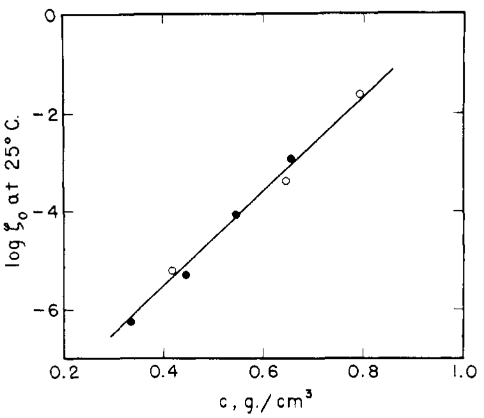

Figure 7. Concentration dependence of the friction coefficient ζ_0 at 25° for three solutions of poly(β-hydroxyethyl monomethacrylate). ●, data for solutions of poly-*n*-butyl methacrylate in dibutyl phthalate (Figure 16-3 of ref 2a).

well, though for the higher diluent concentrations there is a slight disagreement. The diffuse maximum on the long time side, shown for the sample swollen to $v_2 = 0.319$, was discussed earlier. From Figure 5 similar conclusions can be made as from Figure 2; the spectra become broader with increasing concentration of diluent.

Deviations in slope begin to be apparent for the sample swollen to $v_2 = 0.319$. Similarly as shown above for G' and G'', the secondary high-frequency dispersion begins to influence more and more the shape of the left side of the spectrum; on the other hand a broader distribution of retardation times makes the peak corresponding to the secondary relaxation less apparent. The indication of the secondary relaxation in the L spectrum, found for $v_2 = 0.606$ near $\log \tau = 5$, shifts with increasing concentration toward lower times. This shift is of similar direction and magnitude to that of the main peak of the L spectrum. An indication of another secondary peak, shifted to still longer times, is shown for the solution $v_2 = 0.319$. It was ascribed previously to a slight heterogeneity of the network structure, resulting in some very long retardation times. Also this effect was found to be concentration dependent and there was an indication of its shifting toward longer times with increasing dilution (Figure 6 of ref 13). It means that perhaps two long-range mechanisms having long retardation times occur, and are influenced by dilution in opposite directions. One may be due to entanglements, and the other to long-range motions of large cross-linked areas.

The retardation spectrum of the dry polymer, taken from ref 10, is shown in the same figure; no conclusions can be made for the time position of this spectrum, because the sample measured was prepared in the presence of an inert diluent and the L values correspond to the reference temperature 115°.[10] However, the shapes of the spectrum of the sample swollen to $v_2 = 0.606$ and $v_2 = 0.495$, and of the dry sample are very similar.

Relaxation Spectra. The H spectra (Figure 6) were calculated by usual approximation methods.[2a] The influence of the secondary, high-frequency relaxation is seen in the upper portions where the slopes differ. Nevertheless, the points calculated from G' and G'' are in good agreement. (The same was found for the L values, and can be explained by the fact that the time-temperature superposition of the storage and loss compliances was quite successful also in the high-frequency range.)

The H and $\log \tau$ values were read from individual spectra at the points where the slope had the theoretical value $-1/2$. The monomeric friction coefficient ζ_0 was then calculated from the equation

$$\log \zeta_0 = 2 \log H + \log \tau + \log (6/kT) + 2 \log (2\pi M_0/acN_0)$$

where M_0 is the monomer molecular weight, c the polymer concentration in grams per cubic centimeter, and N_0 Avogadro's number; a^2 is the mean square molecular length per monomer unit. Here a was taken[12] as 7×10^{-8} cm. The values of $\log \zeta_0$ at 25° are listed in Table II and plotted against the concentration of the polymer in grams per cubic centimeter in Figure 7. In the same figure the values found for four solutions of poly(*n*-butyl methacrylate) in dibutyl phthalate (Figure 16-3 of ref 2a) are also reported. Fortuitously, they fall on the same line. At least the slopes of $\log \zeta_0$ plotted against concentration of a diluent are the same.

Relaxation spectra reduced to corresponding states are shown in Figure 8. The values of $a^2\zeta_0 kT$ for the sample swollen to $v_2 = 0.168$ were calculated using the ζ_0 value found by extrapolation to the corresponding concentration. Using this plot our previous conclusions are more clearly seen: with increasing dilution the H spectra are growing steeper on their short-time ends, less steep on their long-time ends.

Equilibrium Compliance. The relationship between

TABLE II
SOME PARAMETERS FOR SOLUTIONS OF POLY(β-HYDROXYETHYL MONOMETHACRYLATE) IN DIETHYLENE GLYCOL

v_2	Log ζ_0 at 25°	$c_1{}^0$	$c_2{}^0$
0.606	−1.66	12.2	159.4
0.495	−3.38		
0.319	−5.20	6.35	166.8
0.168	−7.49[a]		

[a] Extrapolated value from Figure 7.

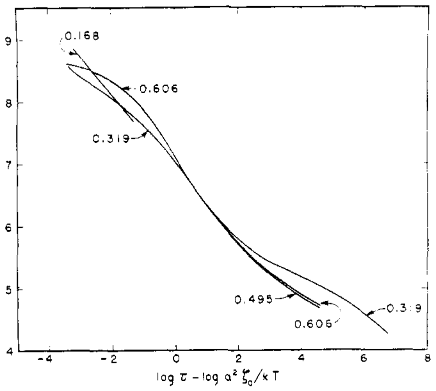

Figure 8. Plot of log H − log Tc/M_0 *vs.* log τ − log $a^2\zeta_0/kT$ for four solutions of poly(β-hydroxyethyl monomethacrylate) in diethylene glycol.

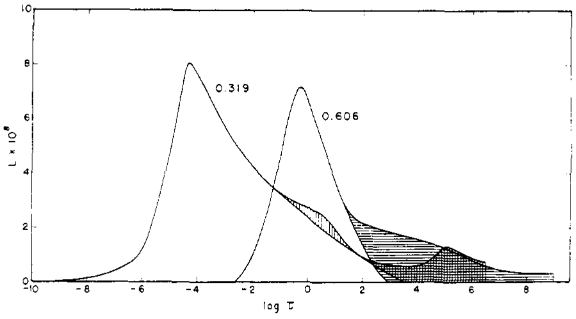

Figure 9. Example of determination of J_e and J_{eN} for the samples swollen to v_2 = 0.606 and v_2 = 0.319.

the equilibrium compliance, J_e, and the retardation spectrum can be written in the form

$$J_e = \int_{-\infty}^{\infty} L\, d\ln\tau + J_g \qquad (2)$$

For the polymer in the rubberlike state $J_g << J(t)$ so J_g can be neglected. The function L is plotted with a nonlogarithmic scale against log τ in Figure 9 for the two solutions: v_2 = 0.606 and v_2 = 0.319. An attempt was made to separate the main transition region from the secondary relaxation. In Figure 9 the sample having v_2 = 0.606 has a greater contribution of the secondary relaxation than that swollen to v_2 = 0.319. The distribution of relaxation times of the latter solution is, however, more asymmetric than that of the sample swollen to v_2 = 0.606.

We calculated J_e from the integrals for all four samples used, and separated the contributions of the main mechanism (J_{eN}) and the secondary relaxation ($J_e - J_{eN}$) with a procedure previously described.[4,20] The results are given in Table III and plotted in Figure 10 against v_2. The upper line shows the equilibrium compliance J_e obtained directly from the creep measurements of ref 13. It decreases with increasing swelling degree, as discussed previously.[16] The J_e values obtained from the two methods differ by 10–15%, which is fairly good agreement. The largest difference was found for the sample swollen to v_2 = 0.168; the J_e value obtained from the integration of the L area is subject to more error as seen from Figure 5. After an empirical separation of the main and secondary relaxation, the contribution of the long-time relaxation to the equilibrium compliance $J_e - J_{eN}$ could be calculated. This contribution is one-fourth of J_e for the sample swollen to v_2 = 0.606, but quickly drops to one-tenth for v_2 = 0.319 and still less for v_2 = 0.168. The secondary relaxation mechanism is highly sensitive to the swelling degree; with increased swelling this effect loses its importance. On the other hand the increased degree of swelling gives rise to an asymmetry of the relaxation time distribution toward longer times; that is, in the direction of the secondary relaxation. It is therefore a question if the separation of the long-time secondary relaxations is for both cases objective and whether the physical meaning of an asymmetrical distribution of relaxation times, corresponding to the solution v_2 = 0.319, is not the same as that of a separate peak of the solution v_2 = 0.606.

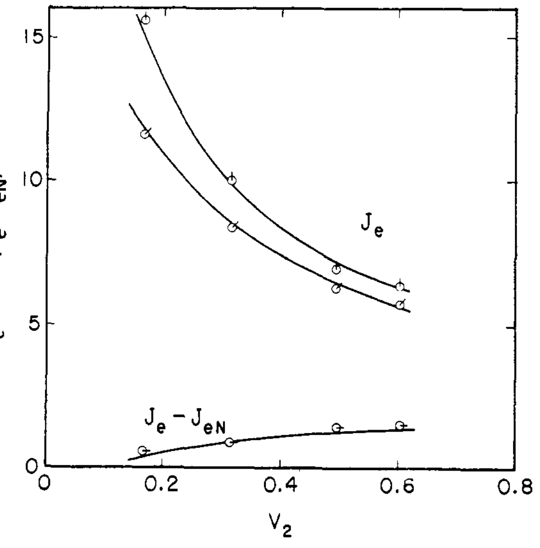

Figure 10. Concentration dependence of the equilibrium compliance J_e and the secondary relaxation contribution to J_e.

Free Volume Parameters. From the concentration dependence of log ζ_0, the free volume parameters can be calculated for three of the four solutions. Choosing v_2^0 = 0.606 as a reference concentration, we made use of the Fujita equation[21] in the form

$$\frac{v_2^0 - v_2}{-\log a_c} = \frac{2.303f^2(v_2^0)}{\beta} + 2.303f(v_2^0)(v_2^0 - v_2) \quad (3)$$

TABLE III
CONTRIBUTIONS TO THE EQUILIBRIUM COMPLIANCE AS CALCULATED FROM EQUATION 2

v_2	$J_{eN} \times 10^8$ dyn^{-1} cm^2	$(J_e - J_{eN}) \times 10^8$, dyn^{-1} cm^2	$J_e \times 10^8$ dyn^{-1} cm^2	$J_e \times 10^8$ from creep[13] dyn^{-1} cm^2
0.168	11.02	0.62	11.64	15.48
0.319	7.57	0.81	8.38	10.00
0.495	4.82	1.42	6.24	6.92
0.606	4.24	1.52	5.76	6.31

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(20) R. G. Mancke and J. D. Ferry, *Trans. Soc. Rheol.*, **12** 335 (1968).

(21) H. Fujita, A. Kishimoto, and K. Matsumoto, *Trans. Faraday Soc.*, **56**, 424 (1960).

Here f is the fractional free volume, v_2 is the volume fraction of the polymer in the polymer–diluent system, a_c the ratio between the friction coefficients ζ_0 at concentrations v_2 and v_2^0, and β is the concentration coefficient of free volume, defined as

$$\beta = \frac{f(v_2) - f(v_2^0)}{v_2^0 - v_2} \qquad (4)$$

The results, which may be subject to some errors because only three independent measurements of log ζ_0 were at our disposal, are compared with the results obtained in our previous study[16] in Table IV. From Table IV it follows that the agreement between the free volume parameters calculated from the c_1 parameter (column c) and from the log a_c shifts of the creep curves in the rubberlike region (column b) is very good for both concentrations, $v_2 = 0.319$ and 0.606; the results from a_c in the transition zone (column a) agree reasonably considering that the slope for the $f(v_2^0)$ determination could be estimated only from two points. (The fact that the shape of the H spectrum is influenced partly by the secondary dispersion may make the time–concentration shifts less reliable when samples swollen to very different degrees are compared.)

TABLE IV
FREE VOLUME PARAMETERS CALCULATED FROM THE FUJITA PLOT AND FROM THE c^0_1 AND c^0_2 CONSTANTS OF THE WLF EQUATION

	$f(v_2) \times 10^2$				$\alpha_f \times 10^4$	$\beta \times 10^2$		
v_2	a	b	c	d	c	a	b	d
0.319	7.8	6.8	6.8	4.9	4.1	10.4	10.1	7.0
0.495	5.9	5.1		3.7				
0.606	4.8	3.9	3.6	2.9	4.0			

[a] Present study, from log ζ_0 corresponding to slope $-1/2$ in H spectrum. [b] Previous study,[16] from the time–concentration superposition of the creep curves in the rubberlike region. [c] $f(v_2) = 1/2.303c^0_1$, $\alpha_f = 1/2.303c^0_1c^0_2$, where c^0_2, c^0_1 are the parameters of the WLF equation (Table II). [d] As b, for the sample A1, cross-linked to a lower degree (cross-linking agent content $C = 0.0855 \times 10^{-4}$).

If the values in columns b and c are considered, it follows that the cross-linking degree has some influence on the $f(v_2)$ values; the latter are lower for sample A1 than for sample A2, as seen from the comparison with column d of Table IV. The α_f values, thermal expansion coefficients calculated from the well-known expression $\alpha_f = 1/2.303c_1c_2$, have their usual magnitude. If the free volume at the temperature T_g is taken as $f_g = 0.025$, T_g can be estimated from $f(v_2)$ and α_f values, using equation

$$f(25°) = f_g + \alpha_f(25 - T_g) \qquad (6)$$

The estimated T_g values were (using data of column b) -10.8 and $-80.5°$ for $v_2 = 0.606$ and 0.319, respectively, which agree quite well with our previous data estimated from the isochronal modulus–temperature measurements.[22]

The concentration of diethylene glycol corresponding to T_g at 25° can be estimated from eq 5. Using the values shown in colums a, b, and d of Table IV, the v_2 values were found to be 0.738, and 0.748 or 0.666, respectively. The agreement between the first values is very good, perhaps fortuitously. A lower value of v_2, found for the sample cross-linked to a lower degree, is in agreement with the lower values of free volume of this network found in ref 16.

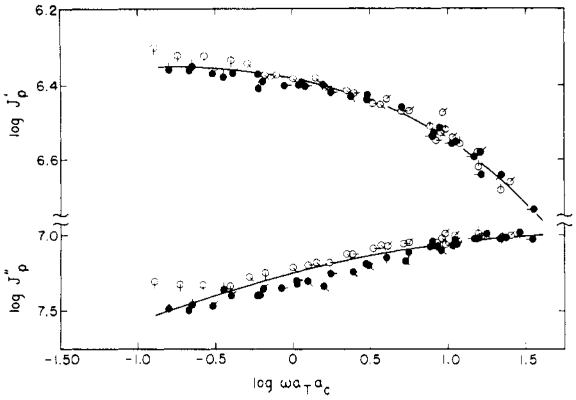

Figure 11. Log J_p' and log J_p'' plotted against log ωa_T: ●, time–temperature superposition of the data for sample A2, corresponding to $v_2 = 0.55$. Successive rotation of the pips clockwise denote seven successively lower temperatures. ○, time–concentration superposition of the data making use of the free volume parameters from Table III, column b. Successive rotations of the pips clockwise denote five successively lower concentrations.

Time–Concentration Superposition. The values of J' and J'' obtained at room temperature for $v_2 = 0.605$–0.495 were superimposed by utilizing the log a_c factor calculated from the free volume parameters of the creep curves[16] (Figure 11). The agreement is quite good for J' but not exact for J'' (nor tan δ, not shown). It is felt that the 2 days period allowed to equilibrate the samples after each swelling was not sufficient. The results suggest, however, that if the concentration differences are not great, the time–concentration superposition can be used successfully.

Anomalies in Application of Reduced Variables. An example of the time–temperature superposition of log G' and log G'' for two solutions, with polymer concentrations $v_2 = 0.55$ and 0.34, is shown in Figure 12. The superposition was performed by c_1 and c_2 constants calculated from the double transducer data (for $v_2 = 0.606$ and 0.319); it is quite successful. Some small correction of log a_c had to be made, however, because of small changes of the concentration in the measuring cell. The shapes of the log G''_p curves are quite different for the two solutions, so the time–concentration superposition is not valid. Also the log a_c shift would be quite different for the G' and G'' data for qualitative matching, and this is inadmissible. Different shapes of the log G''_p curves can be explained in a similar way as the differences in the left branches of the log J''_p curves in Figure 2. Similar observations are valid also for G'_p (Figure 12).

From the above results it follows that both the low- and the high-frequency regions of the superimposed curves and therefore also the long and short time regions of the calculated spectra exhibit some deviations when reduced variables are used. Long-range motions of entanglements influence the compliance values in the low-

(22) J. Kolařík and J. Janáček, in preparation.

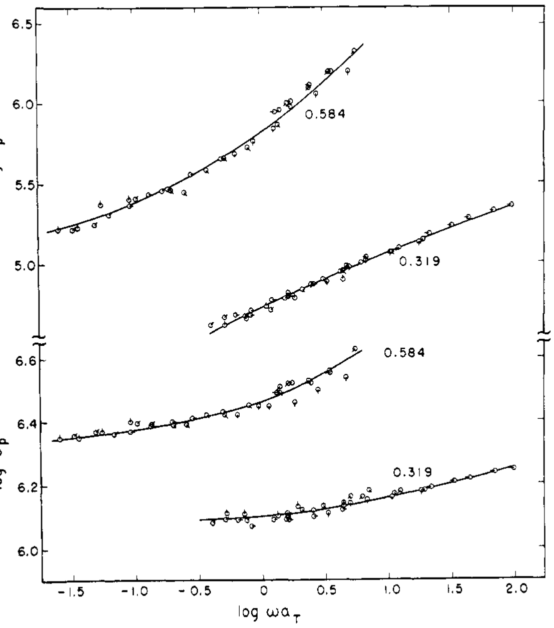

Figure 12. Log G_p' and log G_p'' from torsion pendulum data plotted against log ωa_T for two concentrations in diethylene glycol.

frequency range, especially J''. A distribution of longer retardation times corresponding to untrapped entanglements is sometimes not directly connected with the distribution of times corresponding to the main peak of J''. In spite of this fact, however, the same parameters c_1 and c_2, calculated from the main transition, are often used for the superposition of the data in the whole range. The agreement is quite good, as can be seen for example from Figure 2. For this polymer, an indication of still longer retardation times was found previously,[13] connected with another long-range mechanism, arising perhaps from a slight heterogeneity of a network structure (*cf.* Figure 2, $v_2 = 0.319$); however, also in this case the same c_1 and c_2 constants from the main transition could be used. As the slopes of the log J''_p − log ωa_T and especially of log J'_p − log ωa_T curves are very small, small differences in the c_1 and c_2 values have less importance than in the main transition.

The high-frequency secondary mechanism of the side chains in the diluted state can be discussed from a similar point of view. Although this mechanism is already present for the solutions $v_2 = 0.606$ and 0.319 (as seen from Figure 3) the superposition of the high-frequency range is fairly successful. However, composite plots with reduced variables can be only approximate when multiple mechanisms with different temperature and concentration dependences are involved.

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