Viscoelastic Properties of Cross-Linked Solutions of Poly(β-hydroxyethyl methacrylate) in Diethylene Glycol. IV. Dynamic Measurements. Dependence on Cross-Link Density in the Rubbery Zone

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ABSTRACT: The storage and loss compliances of three solutions of poly(β-hydroxyethyl monomethacrylate) in diethylene glycol, cross-linked to different degrees by ethylene glycol dimethacrylate at concentrations (C) of 0.0855, 0.544, and 2.058×10^{-4} mol cm^{-3}, were measured by a torsion pendulum at frequencies from 0.2 to 2 cps in the temperature range from −5 to 52°. Data corresponding to lower frequencies were provided by converting creep measurements from a previous study. The samples with the lowest and highest cross-linking degrees were measured at two different concentrations of diluent, at $v_2 = 0.55$ and near the equilibrium swelling degree; the third, only at $v_2 = 0.55$. In addition, the sample with the highest cross-linking degree was measured in the glass–rubber transition, by the Fitzgerald double transducer at frequencies from 30 to 1600 cps and temperatures from −55 to 55°. The results were compared with those from our previous study, obtained on a similar solution cross-linked by ethylene glycol dimethacrylate to $C = 0.136 \times 10^{-4}$ mol cm^{-3} and swollen to several different polymer concentrations. The parameters of the WLF equation obtained previously from the time–temperature superposition in the transition zone could be successfully used also for the viscoelastic data in the rubberlike state. The torsion pendulum, double transducer, and creep measurements data matched together well and the resulting viscoelastic functions could be calculated for 8 to 16 logarithmic decades of time. Comparisons of losses in samples swollen and cross-linked to different degrees depend on whether the basis is the loss compliance J'', loss modulus G'', or loss tangent tan δ. With increasing swelling and cross-linking degree, the secondary losses expressed as J'' diminish for samples in the rubberlike state. If G'' is compared, increasing swelling degree results in lower losses, but increasing cross-linking degree results in higher losses. The shapes of the superimposed J''_p curves were more sensitive to dilution for samples swollen to low degrees, where an effect of entanglements is important, than for samples cross-linked to higher degrees. In the latter case dilution results only in a shift of the superimposed curves toward lower values of J'' and higher frequencies. The decrease in storage compliance J' with swelling was highly dependent on the cross-linking—in agreement with our previous results obtained for creep. For lightly cross-linked networks, J' decreased with increasing swelling degree from $v_2 = 0.55$ to 0.34; for the sample cross-linked to the highest degree, J' actually increased slightly. The shapes of the retardation (L) and the relaxation (H) spectra in the glass–rubber transition found for the two solutions swollen to $v_2 = 0.34$ whose cross-linking degrees differed by a factor of 15 were quite different. A symmetrical L spectrum was exhibited by the solution cross-linked to the higher degree; the decay of the L values observed on the long time part of the spectrum indicated that the secondary relaxation is nearly entirely missing. The spectrum of this polymer was, however, less steep in the short-time region, suggesting a greater contribution from the high-frequency secondary dispersion.

For rubberlike polymers cross-linked to a low degree, some relatively high mechanical losses have been found at very low frequencies.[2–4] These losses, which sometimes lead to maxima in the loss tangent or the loss compliance, have been ascribed to secondary relaxation mechanisms involving entanglements.

In our previous studies of creep[5,6] we measured the equilibrium and viscoelastic behavior of poly(β-hydroxyethyl monomethacrylate) [poly(ethylene glycol monomethacrylate)] cross-linked to various degrees and swollen by diethylene glycol. Next,[7] we investigated the influence of the swelling degree for this polymer cross-linked by ethylene glycol dimethacrylate (at a concentration of 0.136×10^{-4} mol cm^{-3}) on the main transition region and on the secondary losses. Our primary purpose in the present continuation of this study was to investigate the influence of cross-linking and swelling on secondary losses by measuring three samples having various concentrations of cross-linking agent. Consideration was also given to the influence of the cross-linking degree on the shapes of the retardation (L) and relaxation (H) spectra.

Experimental Section

Polymers. The three copolymer samples used were polymerized from β-hydroxyethyl monomethacrylate together with small amounts of the cross-linking agent, ethylene glycol dimethacrylate,[5] at the following concentrations (C) in moles per cubic centimeter: A1, 0.0855×10^{-4}; A6, 0.544×10^{-4}; A8, 2.058×10^{-4}. The preparation of the samples is described in ref 5.

Torsion Pendulum Measurements. Samples A1, A6, and A8 were swollen to v_2 (volume fraction of the polymer in the polymer–diluent system) in the neighborhood of 0.55. Two other samples, A1 and A8, were swollen to the neighborhood of their equilibrium swelling degrees. All the five solutions

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(2) (a) R. A. Stratton and J. D. Ferry, *J. Phys. Chem.*, **67**, 2781 (1963); (b) E. Maekawa, R. G. Mancke, and J. D. Ferry, *ibid.*, **69**, 2811 (1965).

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(4) R. A. Dickie and J. D. Ferry, *J. Phys. Chem.*, **70**, 2594 (1966).

(5) J. Janáček and J. D. Ferry, *Rheol. Acta*, in press.

(6) J. Janáček and J. D. Ferry, *J. Polym. Sci.*, in press.

(7) J. Janáček and J. D. Ferry, *Macromolecules*, **2**, 370 (1969).

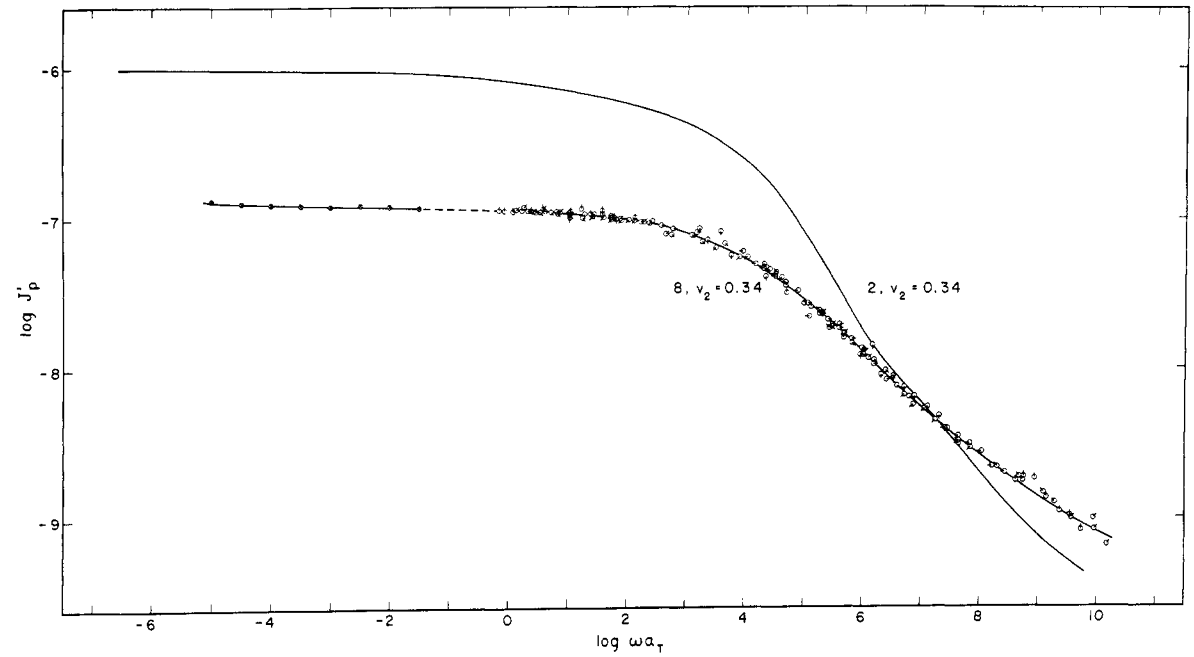

Figure 1. Log J_p' plotted against log ωa_T for cross-linked poly(β-hydroxyethyl monomethacrylate) solution A8 ($C = 2.058 \times 10^{-4}$ mol cm^{-3}) in diethylene glycol, at various temperatures reduced to 25°. Double transducer data from 55.3 to −54.5° in 18 steps, torsion pendulum data from 32.8 to 0.28° in 6 steps. In each series pip up denotes highest temperature and successively 45° rotation clockwise denote successively lower temperatures listed in text. Solid curve is for sample A2 from ref 7 ($C = 0.136 \times 10^{-4}$ mol cm^{-3}) shifted to $v_2 = 0.34$.

were measured at four to six frequencies and usually at six temperatures by the Plazek torsion pendulum[8] as described elsewhere.[4] Values of tan δ, log J', and log J'' were calculated with a program written by Mr. C. P. Wong for a Varian Data Machines 620i computer. For time–temperature superposition of the data for the three samples swollen to $v_2 = 0.55$, the constants $c_1 = 12.2$ and $c_2 = 159.4$ for the WLF equation[9] with 25° as reference were used. These constants were calculated previously from the double transducer data for the sample A2 with $C = 0.136 \times 10^{-4}$ mol cm^{-3} swollen to $v_2 = 0.606$. For superposition of the data obtained from sample A1 swollen near equilibrium, the constants $c_1 = 6.345$ and $c_2 = 166.8$ were used. These were calculated from the double transducer data[7] of sample A2 swollen to 0.319. For superposition of the data of the sample A8, swollen to near equilibrium, c_1 and c_2 were used as calculated from the present double transducer data (see below).

In some cases the samples changed weight slightly during measurements in the torsion pendulum cell, especially if they were left in the cell for some time before measurements; this was attributed to absorption of traces of water vapor. The polymer concentration was calculated on the basis of the final sample weight and the measured values were corrected using the log a_c shift factors as described previously;[7] the corrections were usually small.

Sample A1 ($v_2 = 0.569$) was measured at temperatures (in sequence) of 23.3, 50.3, 43.5, 35.9, 27.9, and 23.9°; its weight was 0.2864 g; height varied between 0.240 and 0.243 cm. Sample A6 ($v_2 = 0.545$) was measured at 23.2, 51.9, 44.8, 36.3, 29.9, and 23.7°; its weight was 0.2847 g; height varied between 0.238 and 0.243 cm. Sample A8 ($v_2 = 0.562$) was measured at 25.1, 30.1, 38.6, 44.8, and 50.9°; its weight was 0.2784 g; height varied between 0.241 and 0.244 cm. Sample A1 ($v_2 = 0.133$) was measured at 25.3, −5.7, −0.9, 6.8, and 14.1°; its weight was 1.1305; height varied between 0.387 and 0.392 cm. Sample A8 ($v_2 = 0.34$) was measured at temperatures 0.3, 10.1, 20.8, 24.8, 28.3, and 32.8°; weight was 0.4335 g; height varied between 0.266 and 0.268 cm. The compression of all samples was between 3 and 5%, except for sample A1 swollen to $v_2 = 0.133$ whose compression was 10–15%.

Since the concentrations of the first three samples were not quite identical, the results for these were shifted slightly along the frequency scale to a concentration of $v_2 = 0.55$ using the free volume parameters calculated from the creep measurements obtained in our previous study.[6] The calculated shift factors, log a_c, were A1, 0.43; A6, −0.11; and A8, 0.25.

Double Transducer Measurements. Two samples of A8 swollen to $v_2 = 0.34$ were measured also in the main transition region by using the double transducer. Their micrometer heights were 0.103 and 0.107 in., thickness *in situ* 0.1022 and 0.0996, compression *ca.* 4%. The mass, $\bar{m}$, was 0.9126 g with a sample coefficient $\rho C = 14.195$. The two samples were measured at 18 temperatures in the frequency range 45–1600 cps: T = 55.3, 45.4, 33.6, 23.4, 14.7, 3.5, −0.7, −5.9, −12.1, −11.6, −15.5, −20.2, −25.7, −31.2, −36.6, −42.3, −47.5, and −54.5°.

Results and Discussion

Influence of Difference in the Cross-Linking Degree of the Same Solutions on the Main Transition and on the Rubberlike State. To save space, the original J' and J'' values of sample A8 at various frequencies and temperatures are not given. From the double transducer measurements, log J' and log J'' were reduced to 25° with shifts (log a_T) obtained empirically for various temperatures. The constants c_1 and c_2 were calculated from the WLF equation in the form

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

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[8] D. J. Plazek, M. N. Vrancken, and J. W. Berge, *Trans. Soc. Rheol.*, **2**, 39 (1958).

[9] J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1961.

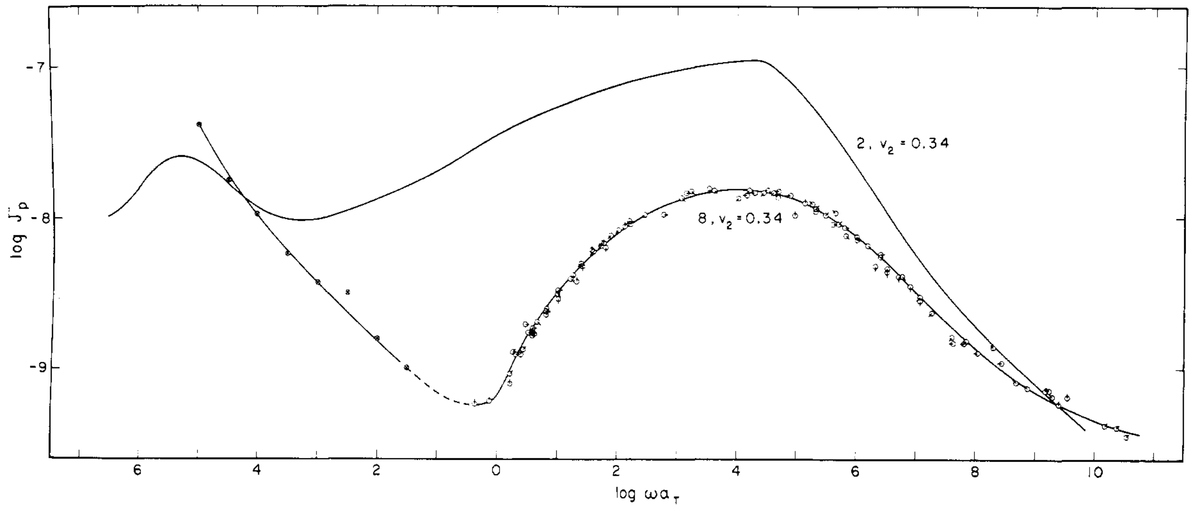

Figure 2. Log J_p'' plotted against log ωa_T as in Figure 1.

where $T_0 = 25°$, $c_1 = 9.5$, and $c_2 = 187.7$. These values were also used for the superposition of the data obtained by the torsion pendulum. The agreement was very good as can be seen in Figures 1 and 2. Both log J'_p and log J''_p obtained from the double transducer were higher by 0.12 than the data obtained from the torsion pendulum. It was believed that the torsion pendulum data, which were in full agreement with the creep data, were correct. The difference of the double transducer data is probably caused by errors in height determination of the samples in the transducer; therefore, the transducer data were arbitrarily adjusted to match the torsion pendulum data by a shift on the vertical axis.

In Figure 1 the superimposed J' curves of sample A8 are compared with that of sample A2 from ref 7, having the cross-linking agent content 0.136×10^{-4} mol cm^{-3}. The A2 curve corresponding to $v_2 = 0.319$ was shifted to 0.34, by use of the free volume data calculated earlier;[6] the shift was log $a_c = -0.20$. The differences in the storage compliances at low frequencies are consistent with the cross-linking degrees, which differ by a factor of 15. Furthermore, it can be seen that when samples having great differences in the cross-linking degrees are compared, the slopes of the log J'_p curves in the main transition are dissimilar. Increasing cross-linking degree should increase the relaxation times, as shown previously,[10] so J' should move toward lower frequencies. This statement seems to be valid for the curves of Figure 1 only when the storage compliance is higher than log $J'_p = -8.4$; for lower compliances the log J'_p curve of sample A8 is shifted to higher frequencies in comparison to the same curve of sample A2. The explanation can be connected with a different contribution of the low-temperature secondary dispersion as discussed previously,[7] to the low-temperature regions of both samples.

The log J''_p values are compared in Figure 2. The loss compliance of sample A2 (solid line) exhibits an asymmetry in the direction of low frequencies. On the other hand, that of sample A8 is nearly symmetrical with no evidence of a substantial contribution with very long retardation times. The differences may be explained as follows. The network cross-linked to a high degree has few entanglements capable of relaxing by long-range configurational adjustments; most of the entanglements are trapped, and contribute to the elastic modulus at equilibrium. On the other hand, the system cross-linked to a low degree possesses many entanglements which are able to disentangle after a long period of time; their contributions produce the asymmetry found for sample A2. The losses at very low frequencies in both curves are calculated from creep data; those for sample A8 from the creep curve shown in Figure 8 of ref 5, and those for sample A2 from Figure 1 of ref 6. The values of log J''_p corresponding to log $\omega a_T < 0$ are influenced by an additional creep effect, as found previously from our creep measurements[5] and connected with a slight heterogeneity of the network. In agreement with ref 5, the retardation times of this effect are longer for the network cross-linked to higher degrees; therefore, a loss maximum of sample A8, corresponding to that of sample A2, is perhaps shifted to still lower frequencies.

The differences in response of the two networks, when the low frequency region is taken into account, is clearly seen in the tan δ results of Figure 3. On the left side of the maximum, the curves of log tan δ *vs.* log ωa_T are

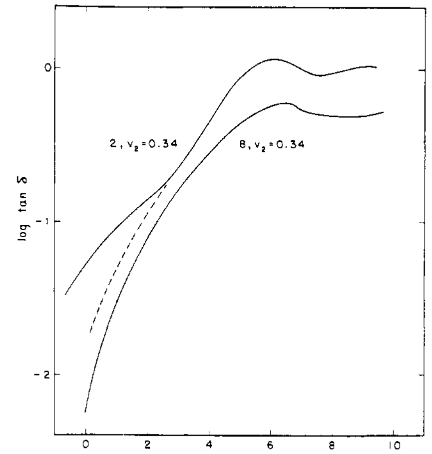

Figure 3. Log tan δ plotted against log ωa_T for samples A8 and A2 where $v_2 = 0.34$.

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(10) M. Ilavský, J. Hasa, and J. Janáček, *Collect. Czech. Chem. Commun.*, 33, 764 (1968).

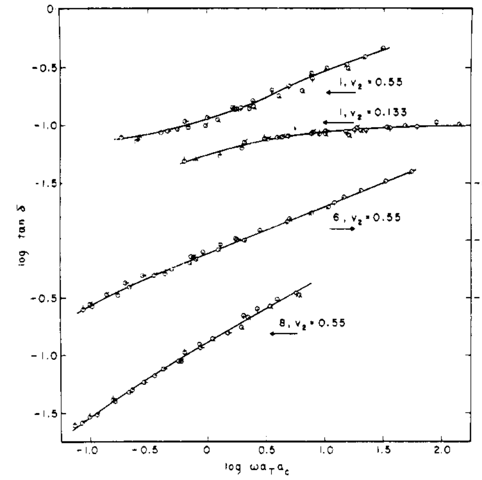

Figure 4. Log tan δ plotted against log $\omega a_T a_c$ for the samples A1, A6, and A8, measured at various temperatures, reduced to 25° and $v_2 = 0.55$; and for another sample A1 reduced to 25° and $v_2 = 0.133$. In each series pip up denotes highest temperature and successively 45° rotations clockwise denote successively lower temperatures listed in text.

nearly parallel for both samples compared; at log $\omega a_T \leqq 2.3$, log tan δ values of sample A2 are higher than expected from the previous trend and from the comparison with the sample A8, because of the effect of entanglements. In the high-frequency range, an indication of a second loss peak is related to the low-temperature relaxation mechanism ($\beta_{(\text{sw})}$) as discussed previously.[7,11] This secondary relaxation in the glassy state is ascribed to the molecular motions of the parts of the side chains in the diluted state[11] and it should not be therefore influenced by the degree of cross-linking. However, lower values of log tan δ of sample A8 in comparison to A2 were found in the whole range of the frequencies used (Δ log tan δ = 0.3 for the maximum of tan δ). This would mean that the low losses of the denser networks persist also in the very high-frequency region with very small relaxation times.

Influence of Cross-Linking Degree and Dilution on the Rubberlike Region. 1. Tan δ Data. To obtain further information about the influence of the cross-linking degree, some other samples were measured in the rubberlike region only. The time–temperature superposition, used as shown in the experimental part, was quite successful. The influence of the concentration of diethylene glycol on the frequency dependence of tan δ of sample A1 cross-linked by ethylene glycol dimethacrylate ($C = 0.0855 \times 10^{-4}$ mol cm^{-3}) is shown in Figure 4. At $v_2 = 0.55$, tan δ increases substantially with log $\omega a_T a_c$; but for v_2 corresponding to equilibrium swelling, tan δ is very low and nearly independent of frequency. For samples swollen to $v_2 = 0.55$, the slope d log tan δ/d log $\omega a_T a_c$ increases with increasing cross-linking degree. An indication of additional secondary losses, seen for sample A1 at low values of log $\omega a_T a_c$, disappears if the concentration of a diluent is increased from v_2 = 0.55 to 0.133.

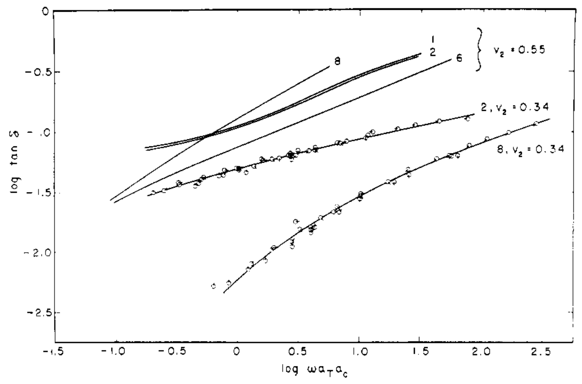

Figure 5. Log tan δ plotted against log $\omega a_T a_c$ for samples A1, A2, A6, and A8 ($v_2 = 0.55$) and A2 and A8 ($v_2 = 0.34$). Values for A2 taken from ref 7.

In Figure 5, all the tan δ curves measured are plotted on the same scale and can be, therefore, better compared with each other. At $v_2 = 0.55$, log tan δ of A2 was only slightly lower than that of A1. The log tan δ curve of sample A6 ($C = 0.544 \times 10^{-4}$ mol cm^{-3}) was, however, lower and at lower frequencies steeper in slope. It seems that some of the mechanisms with longer relaxation times in the networks cross-linked to very low degrees are no longer present in sample A6. The sample cross-linked to the highest degree, A8 (C = 2.058) had a still steeper slope of the curve of log tan δ *vs.* log $\omega a_T a_c$ in the whole frequency range. This means that some of the relatively shorter relaxation times due to entanglements, still present in the sample A6, are missing or diminished in sample A8. The higher tan δ for A8 is associated with a comparatively low value of J'.

Similar conclusions concerning the steepness of the log tan δ curves are valid also for samples swollen to a higher degree ($v_2 = 0.34$). In Figure 5, increasing swelling degree diminishes tan δ; the change is greater for sample A8 than for sample A2. A fundamental difference is noted when comparing the effect of the swelling degree on both samples. The shape of the log tan δ curve corresponding to sample A8 was not changed by dilution; it only shifted to higher frequencies and lower magnitudes. Also the log tan δ curve of the sample A2 was shifted to lower magnitudes with dilution of the sample. However, an indication of a second relaxation mechanism in the low-frequency range disappeared and the shape of the tan δ curve resembles that of sample A8, although not so steep. In comparing Figures 4 and 5, the same changes are evident when samples A1 and A2 were swollen to higher degrees. The explanation can be given as follows: samples cross-linked to low degrees contain entanglements with long retardation times; hence, the magnitude of the tan δ remains high even at low frequencies. If the samples are cross-linked at higher degrees, a part of the long-time retardation spectrum does not exist any more because there are no more chains of such a length and the entanglements are now trapped. Also if the sample cross-linked to a low degree is highly swollen, the chains are now stretched; this diminishes the longest relaxation times.

2. Storage Compliance Data. In Figure 6, log J'_p is plotted against log ωa_T; it decreases with increasing cross-linking degree. The low-frequency parts of the curves shown were calculated from creep data measured previously;[5] they match quite well with the direct mea-

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(11) J. Janáček and J. Kolařík, *J. Polym. Sci., Part C*, **16**, 279 (1967).

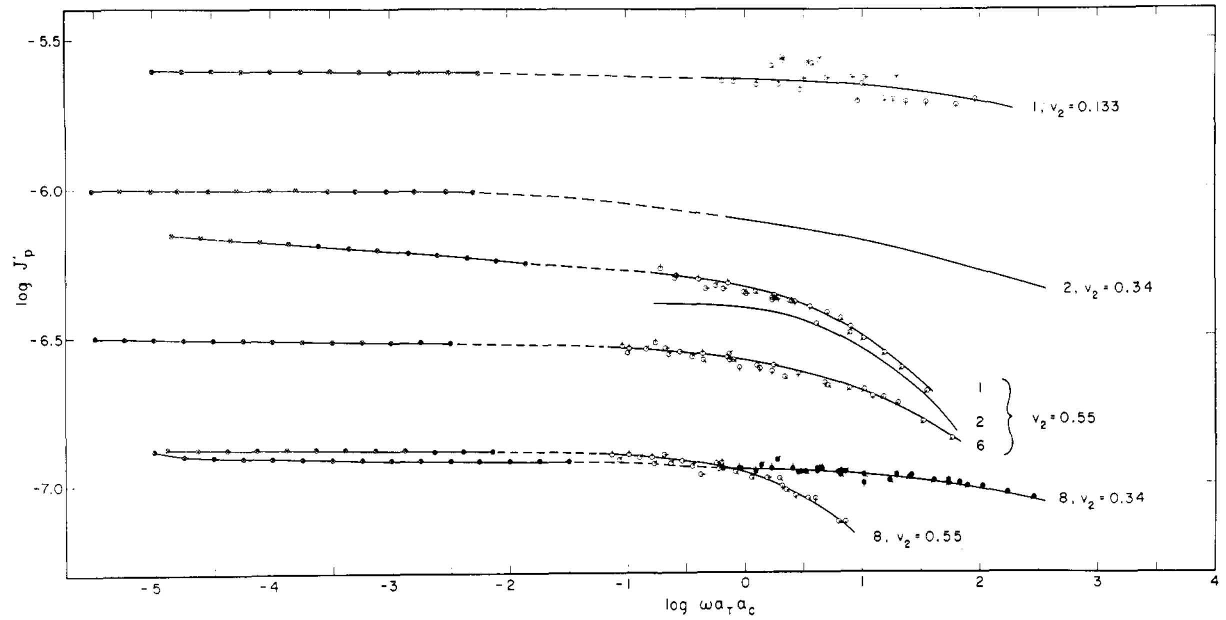

Figure 6. Log J_p' plotted against log $\omega a_T a_c$ for samples identified by number and swollen to different values of v_2 as indicated. The J_p' values for lower frequencies recalculated from the creep data of Figure 1, ref 5 (for v_2 = 0.55); Figure 4 of ref 6 (v_2 = 0.144).

surements by the torsion pendulum. In the ranges of cross-linking and swelling degrees used, log J'_p varied from 5.6 to 7.2; its change with frequency was from 0.1 to 0.7 decades. Changing the swelling degree of sample A1 from v_2 = 0.55 to 0.133 increased log J'_p by about 0.7 decade. Change of v_2 from 0.55 to 0.34 also increased log J'_p, but less. But increase of the diluent content from v_2 = 0.55 to 0.34 for sample A8 cross-linked to a high degree had an opposite result, a slight decrease of log J'_p. This is in full agreement with the creep data.[16]

3. Loss Compliance Data. Similar conclusions can be made from log J''_p as from log tan δ (Figure 7). The losses decreased with increasing cross-linking for the whole range studied; the effect of the swelling degree is smaller for sample A2 than sample A8. Large values of the loss compliance were found for sample A1 swollen to v_2 = 0.133, compared with those of other samples; this behavior is unlike that of tan δ. Also the secondary losses found in the low-frequency region were separated better from the main maximum in loss compliance than with sample A1 swollen to a lower degree. Both J'_p and J''_p of sample A1 swollen to v_2 = 0.133 exhibited great scatter because of the difficulties in keeping the sample height constant. The loss maxima at low frequencies, mentioned above, were calculated from the creep curves. They do not correspond to secondary relaxations of the entanglements, but to inflections in the slopes of the creep curves discussed earlier.[5]

4. Loss Modulus Data. It may be of interest to examine the conclusions which can be obtained from the comparison of the J'' and G'' data. To do this, log G'' was plotted against log $\omega a_T a_c$ in Figure 8. Samples A1, A2, and A6 differed only slightly, showing that G'' is less sensitive to the cross-linking degree. Increasing swelling degree lowers G'', to much the same extent for samples A2 and A8. For sample A2, the effect of increasing the content of the diluent from v_2 =

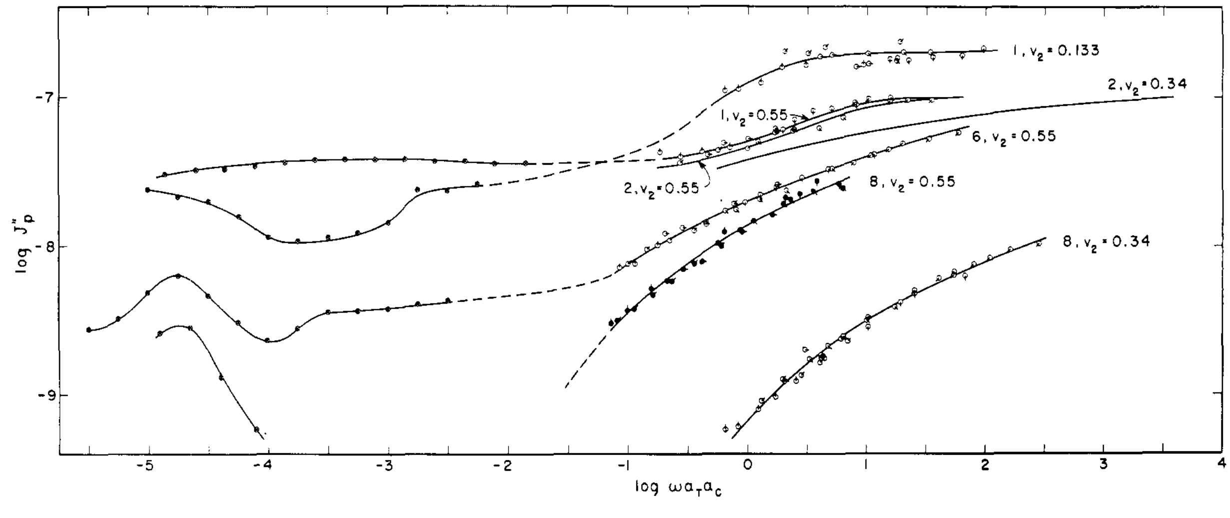

Figure 7. Log J_p'' plotted against log $\omega a_T a_c$ for samples shown in Figure 6.

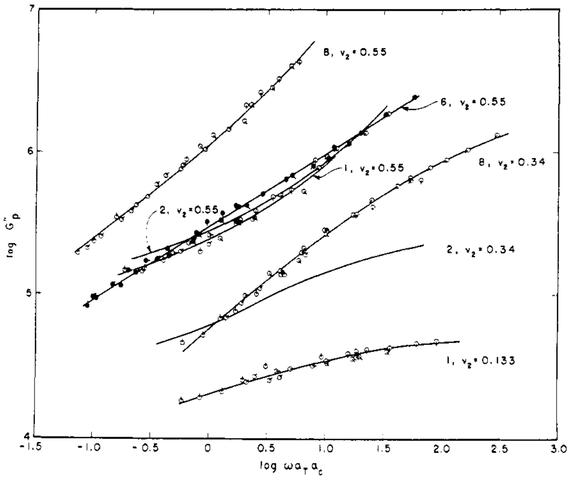

Figure 8. Log G_p'' plotted against log $\omega a_T a_c$ for samples A1, A2, A6, and A8 (v_2 = 0.55), A2 and A8 (v_2 = 0.34), and A1 (v_2 = 0.133). The values for sample A2 were taken from ref 7.

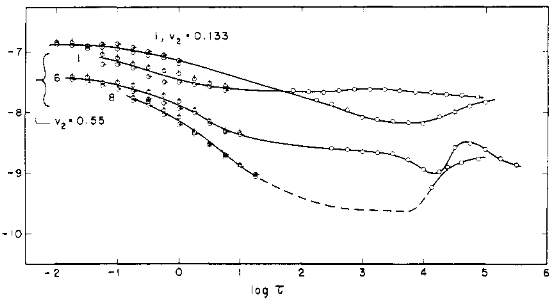

Figure 9. Comparison for the retardation spectra of samples A1, A6, and A8 (v_2 = 0.55) and A1 (v_2 = 0.133).

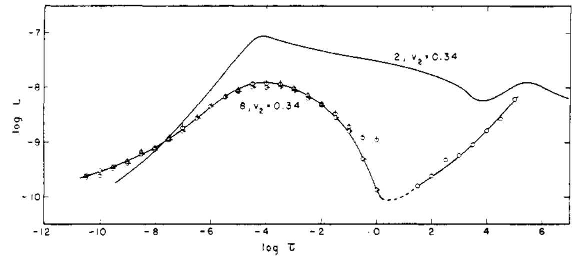

Figure 10. Comparison of the retardation spectra of samples A8 and A2 for v_2 = 0.34.

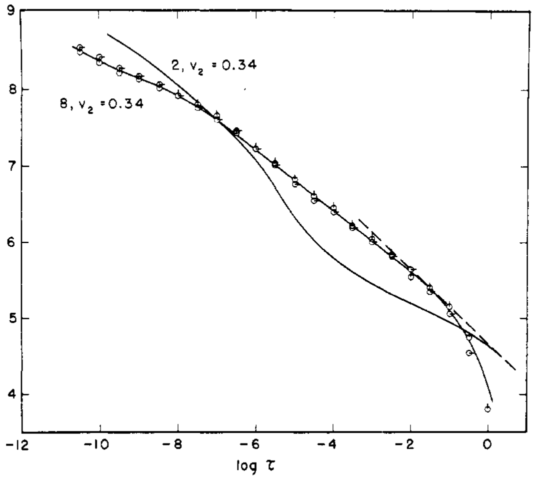

Figure 11. Comparison of the relaxation spectra of samples A8 and A2 (v_2 = 0.34).

0.55 to 0.34 is therefore larger than if the log J'' values are compared.

Lowest values of G'' were found for A1 swollen near its equilibrium value; this is in agreement with the highest values of the loss compliance J''. On the other hand, increasing swelling degree decreased the values of log J'' for both samples A2 and A8; whereas, the values of the loss moduli, log G'', also decreased. Thus, qualitative conclusions concerning the effects of swelling and cross-linking degree depend on whether J'' or G'' is chosen as a measure of losses.

Retardation and Relaxation Spectra. For an absolute comparison of the data, retardation (L) and relaxation (H) spectra were calculated using well-known approximation procedures.[9] The L spectra of samples A1, A6, A8 (v_2 = 0.55), and A1 (v_2 = 0.133) are given in Figure 9. A comparison of the L spectra of samples A8 and A2 over 17 logarithmic decades is shown in Figure 10. The parts of the spectra calculated from the dynamic measurements and from the creep match very well; however, L values calculated from the log J' and log J'' data exhibit some scatter as shown in Figure 9. Both Figures 9 and 10 show that the contribution from long relaxation times increases with decreasing degree of cross-linking. Increasing degree of swelling has the same effect as an increasing degree of cross-linking; it lowers secondary losses and the slope of the L (τ) − log τ plot is steeper and resembles sample A8 cross-linked to a high degree. The slope is perhaps more sensitive to the possible conformations of the effective strands (the number of which decreases if the strands are in a deformed state or if they are very short). The absolute values of L (τ) depend probably more on the cross-linking itself.

In the neighborhood of log τ = 4–5, samples A1, A6, and A8 of Figure 9 and samples A2 and A8 of Figure 10 exhibit an indication of a new maximum observed already for J'' in Figure 7. This maximum, due to the additional creep effect,[5] is shifting toward longer times with increasing network density and swelling degree, as observed previously.

A comparison of the relaxation spectra of samples A2 and A8 is given in Figure 11. From the theoretical slope $-{}^1/_2$ the friction coefficient ζ_0 was calculated for sample A8 making use of an estimated value[7] of the characteristic length $a = 7 \times 10^{-8}$ cm; log ζ_0 was −3.26, which is nearly two decades higher than that found for sample A2 swollen to approximately the same degree (log ζ_0 = −5.20 for sample A2 swollen to v_2 = 0.319).[7] Otherwise the spectrum for the sample A8 is very straight, with a slope of 0.4 which is quite different from that of sample A2. In the region of shorter times the deviations can be ascribed to the low-temperature relaxation of the side chains,[12] mentioned above.

From our results it follows that the shapes of the relaxation and retardation spectra are extremely sensitive to the swelling and cross-linking degrees of the poly-(β-hydroxyethyl monomethacrylate)–diethylene glycol system. The reason is that the long time parts of the spectra are influenced by all secondary effects due to relaxation of entanglements or perhaps by still greater long-range motions. Great differences in the cross-linking degrees can influence also the shape of the glass–rubber transition; the steepness of the retardation (*L*) and relaxation (*H*) spectra in this range is lower for highly cross-linked samples.

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Deformation and Structure of Cylindrical “Spherulites” in Transcrystalline Polyethylene. Detection and Characterization of the Pseudomonoclinic Crystalline Component

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ABSTRACT: The crystalline structure and the deformation of cylindrical spherulites were studied in transcrystalline polyethylene. The experimental results indicate that the cylindrical “spherulites” are comprised of symmetrically packed, specifically oriented lamellae which have their longest axis aligned predominantly with the long axis of the cylindrical spherulites, the long axis being normal to the plane of the polymer film. From the crystallographic data it is concluded that the banded structure observed is the result of lamellar cooperative twisting similar to that found in symmetric spherulites. The distribution of orientations observed in the X-ray diagrams supports evidence in the photomicrographs which suggests that the cylindrical “spherulites” start to grow as spheres in an umbrella-like fashion until they impinge on neighboring spherulites. From then on their growth is restricted to one direction. Under the force of lateral stretching (draw direction normal to the long axis of the spherulites) the lamellar ribbons within the spherulites are first found to spread apart to a certain degree with the retention of over-all cooperative twisting. Subsequently they tilt, aligning their longest axis with the direction of stretching, pull out from the spherulitic aggregates, and untwist. Soon thereafter, reorientation into a new fiberlike structure occurs in which the unit cell *c* axis is preferentially oriented in the draw direction, as evidenced by the X-ray diffraction results. A pseudo-monoclinic crystalline component was detected in this transcrystalline polyethylene and the unit cell parameters were established. This pseudomonoclinic component was also observed in all forms of crystalline polyethylene which we investigated and is considered likely to be a feature common to all polyethylenes. One possible manner of formation of this component is given in terms of a slightly different packing of the folded polymer chains in a somewhat strained lattice array. The proposed pseudomonoclinic unit cell accounts for all “extra” reflections observed in X-ray diagrams of polyethylenes we have investigated.

From the voluminous work done on crystalline morphology in polyethylene it is known that the polymer chains fold upon themselves to form lamellar crystallites[1] which have ribbonlike geometric structure. Crystallization in bulk is commonly found to occur in the form of spherulites composed of lamellar fibrils.[2–4] The unit cell *b* axis (for structure, see Bunn)[5] in polyethylene spherulites is predominantly oriented along the longest lamellar axis (which is also the growth axis) of the lamellar fibrils, and the fibrils lie predominantly along the spherulite radii.[1–4]

Among the several somewhat different habits of crystallization in high polymers is a so-called “transcrystalline,” or “rowlike,” morphology[6–9] which was observed some time ago. This morphology is characterized by the presence of cylindrical crystalline aggregates (cylindrical “spherulites”)[9] each of which (on the average) has its long axis predominantly perpendicular to the flat, large surfaces of the polymer sheet. The cylindrical “spherulites” have been found to form by growth from the molding surfaces into the polymer melt from both sides,[6] by nucleation within the molten polymer mass,[9] or by growth in one direction only, as shown in Figures 1, 2a, and 2b. (The figures are discussed in more detail later.)

X-Ray diffraction and birefringence studies[9,10] have revealed that the orthorhombic unit cell *b* axis and the longest lamellar axis are preferentially oriented parallel

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