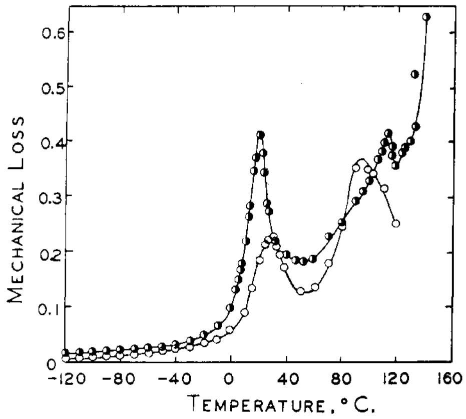

Figure 3. Mechanical loss-temperature spectrum for (O) poly(γ-benzyl-L-glutamate) and for (◑) poly(γ-benzyl-DL-glutamate).

parent in each of the curves above the glass transition temperature. In Figures 1 and 2 a shoulder and rather marked decrease in G'' occurs near this temperature. Such behavior is somewhat reminiscent of a melting point in polymers. However, the polypeptides gave no evidence of a melting point when examined by the usual methods (loss of birefringence or visual observation) near these transition temperatures. Above these temperatures the polymers appear to be quite leathery, but not very strong for they tear quite easily. It has been suggested[6] that films of PγB-L-G contain both paracrystalline and mesomorphic regions. It is possible that the relaxation observed near 90° for PγB-L-G is indicative of a change from a mesomorphic phase to a paracrystalline phase. Likewise, the relaxation at about 115° for PγB-DL-G may be related to such a phase change.

To determine whether these apparent transitions were accompanied by changes in infrared absorption, such data were obtained at three different temperatures with films of PγB-L-G which had been deposited from chloroform solution on salt plates. Selected portions of these curves are shown in Figure 4. The remainder of the ir curves were essentially independent of temperature. While there are some minor changes in these spectra with temperature, they do not suggest any significant conformational change over the temperature range of interest.

Conclusions

It would appear that the differences in T_g found in our work and the cited work[1] cannot be attributed to molecular weight differences since all polymers used should have been above the asymptotic value required for constancy of properties. We conclude the following on the basis of these studies.

(a) The method of sample preparation for these systems can be an important factor affecting mechanical loss results. The possibility that a small amount of solvent is tenaciously held by the polypeptide and therefore plasticizes the polymer and/or causes a structural change appears consistent with the results.

(b) A significant difference exists in mechanical loss measurements for the DL polymer compared with the L polypeptide. The DL polymer examined in these studies appeared significantly more brittle than the L form suggesting the absence of a low-temperature peak in the former material.

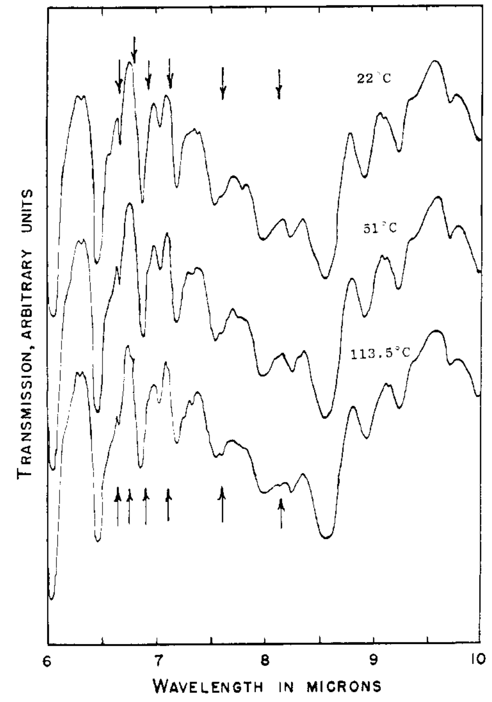

Figure 4. Portions of infrared spectra that show real differences for poly(γ-benzyl-L-glutamate).

(c) In both L and DL forms, a high-temperature secondary transition at 90–115° occurs.

Polymer Entanglement Spacings Estimated from Integration of the Loss Compliance

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There are two common measures of the average molecular weight between entanglements in an amorphous polymer of high molecular weight:[1-3] M_C, the critical molecular weight for influence of entanglements on steady-flow viscosity, and M_e, the effective network strand molecular weight calculated from the magnitude of a viscoelastic modulus or compliance. They are not related in a simple manner. Although M_C can be obtained with reasonable precision from the dependence of viscosity on molecular weight and several alternative sources, there has been no reliable method for obtaining M_e. Its estimation from the plateau level of a relaxation modulus, storage modulus, creep compliance or storage compliance involves an arbitrary choice. Calculation from the maximum in the loss compliance[4] involves application of a theory which describes the

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(1) F. Bueche, "Physical Properties of Polymers," Interscience Publishers, New York, N. Y., 1962, p 79.

(2) G. C. Berry and T. G Fox, *Advan. Polym. Sci.*, **5**, 261 (1967).

(3) R. S. Porter and J. F. Johnson, *Rheol. Acta*, **7**, 332 (1968).

(4) J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1961, p 279.

TABLE I
ENTANGLEMENT COMPLIANCES AND ENTANGLEMENT SPACINGS

Polymer	Temp, °C	Log J_{eN}^0	$M_c \times 10^{-3}$	Log J''_{max}	$\frac{J''_{max}}{J_{eN}^0}$	Data ref
		Methacrylate Polymers				
2-Ethyl butyl	100	−6.16	21.4	−6.69	0.29	*g*
n-Hexyl	100	−5.94	33.9	−6.49	0.28	*h*
n-Octyl	100	−5.52	87	−6.14	0.24	*i*
		Rubbers				
Hevea[a]	25	−6.59	5.75			*j*
1,4-Polybutadience, *cis*[a,b]	25	−6.88	2.95	−7.37	0.32	*k*
1,2-Polybutadiene	25	−6.79	3.55	−7.33	0.29	7
Styrene–butadiene copolymer[c]	25	−6.89	3.00	−7.43	0.29	6
Ethylene–propylene copolymer[d]	25	−7.10	1.66	−7.72	0.29	9
Butyl rubber[a]	25	−6.46	8.50	−7.10	0.24	*k*
		General				
Polyisobutylene	25	−6.40	8.90	−6.94	0.25	*l*
Polydimethylsiloxane[a,e]	25	−6.47	8.10			*m*
Polystyrene[f]	160	−6.30	18.1			*n*

[a] Estimated from very lightly cross-linked sample. [b] *cis*:*trans*:vinyl = 96.5:1.9:1.6. [c] Random copolymer, 23.5% styrene by weight; calculated from both eq 1 and 2. [d] Ethylene 56 mol %. [e] Calculated from eq 2. [f] Calculated from integration over loss modulus. [g] T. P. Yin and J. D. Ferry, *J. Colloid Sci.*, **16,** 166 (1961). [h] W. C. Child, Jr., and J. D. Ferry, *ibid.*, **12,** 389 (1957). [i] W. Dannhauser, W. C. Child, Jr., and J. D. Ferry, *ibid.*, **13,** 103 (1958). [j] R. A. Dickie and J. D. Ferry, *J. Phys. Chem.*, **70,** 2594 (1966). [k] J. F. Sanders, Ph.D. Thesis, University of Wisconsin, 1968. [l] J. D. Ferry, L. D. Grandine, Jr., and E. R. Fitzgerald, *J. Appl. Phys.*, **24,** 911 (1953). [m] N. R. Langley and J. D. Ferry, *Macromolecules*, **1,** 353 (1968). [n] S. Onogi, T. Masuda, and K. Kitagawa, in preparation.

viscoelastic functions only semiquantitatively.[5] It has been judged[2] that published estimates of M_e may be in error by 40%.

The present Note gives some estimates of M_e obtained by an alternative, less arbitrary method of calculation. It has been pointed out recently[6–8] that the compliance associated with the entanglement network, J_{eN}^0, can be obtained by a modification of the Kronig–Kramers relations by integrating over the loss compliance J'' in the region of its primary maximum

$$J_{eN}^0 = (2/\pi)\int_a^b J''\, d\ln\omega \qquad (1)$$

where the limits a and b are chosen to encompass this maximum. Alternatively, the almost identical quantity J_{eN} for a very lightly cross-linked network can be obtained from the equilibrium compliance J_e and an integration over the secondary maximum in J'' at lower frequencies

$$J_{eN} = J_e - (2/\pi)\int_{-\infty}^{a} J''\, d\ln\omega \qquad (2)$$

The number-average molecule weight between entanglements can then be obtained by applying the theory of rubberlike elasticity in the form

$$M_e = J_{eN}^0 g_N \rho RT \qquad (3)$$

where ρ is the density and g_N is a front factor (not far from unity) appropriate for the entanglement network. The latter is unknown, but if it is taken as unity the resulting value of M_e is an effective spacing from which the magnitudes of other viscoelastic properties in the plateau zone can be estimated.

An example of the integration of eq 1 is shown in Figure 1 for an ethylene–propylene copolymer with 56 mol % ethylene.[9] The minimum in J'' has been arbitrarily decomposed at the left to obtain a convergent integral. Although this causes some uncertainty, 85% of the area is defined by the measured curve and the total integral should be reliable within about 5%. If the lower limit a were taken as the minimum in the curve, the integral would be smaller by 5% than that shown.

In Table I, values of log J_{eN}^0 obtained from eq 1 for a number of polymers (and two from eq 2) are listed, together with M_e calculated from eq 3 with the assump-

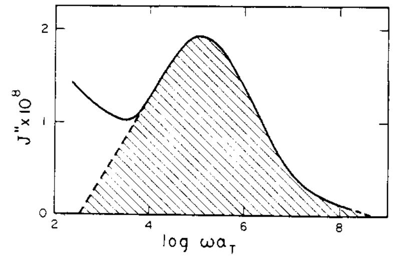

Figure 1. Integration over primary maximum in J'', plotted against log ω, for ethylene–propylene copolymer with 56 mol % ethylene. (The area is multiplied by 2.303 to correspond to the integral in eq 1.)

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(5) R. S. Marvin and H. Oser, *J. Res. Nat. Bur. Stand.*, **66B,** 171 (1962); H. Oser and R. S. Marvin, *ibid.*, **67B,** 87 (1963).

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

(7) J. F. Sanders, J. D. Ferry, and R. H. Valentine, *J. Polym. Sci., Part A-2*, **6,** 967 (1968).

(8) We have adopted the symbols J_e^0 and J_{eN}^0 for steady-state compliance and entanglement network compliance in uncross-linked systems to distinguish them from the corresponding quantities J_e (equilibrium compliance) and J_{eN} (a plateau involving both entanglements and cross-links) in cross-linked systems.

(9) J. R. Richards, R. G. Mancke, and J. D. Ferry, *J. Polym. Sci., Part B*, **2,** 197 (1964).

tion that $g_N = 1$. It is believed that these are more reliable, at least on a relative basis, than most previously reported values; the higher the molecular weight, the less uncertainty.

Values of the maximum in log J'' are also listed, together with the ratio $J_{\max}''/J_{eN}^0$, which has been observed to be 0.29 for several polymers.[7] According to the theory of Marvin and Oser[5] it should be 0.42, but if this is modified for a most probable distribution of strand lengths the expectation[7] is 0.29. The values of the ratio range from 0.24 to 0.32.

Comparison of M_e values in Table I, and some others calculated simply from $J_{\max}''$ on the assumption that $J_{\max}''/J_{eN}^0 = 0.29$, with M_C for those polymers with reported values of the latter[2] gives M_C/M_e ratios in the neighborhood of 2, as recently shown in other compilations.[2,3] However, it can be argued that g_N in eq 3 should be one-half instead of unity.[10,11] In this case, M_C/M_e would be near 4. It is doubtful whether much significance can be attached to this ratio at the present time. For interpreting the magnitudes of viscoelastic properties in the plateau zone, either the entanglement compliance J_{eN}^0 may be used directly or else the spacing M_e recognizing that its absolute value depends on eq 3 with an arbitrary choice of g_N.

Acknowledgment. This work was supported in part by a grant from the National Science Foundation.

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(10) J. A. Duiser and A. J. Staverman, "Physics of non-Crystalline Solids," J. A. Prins, Ed., North Holland Publishing Co., Amsterdam, 1965, p 376.

(11) K. Dušek and W. Prins, *Advan. Polym. Sci.*, **6**, 1 (1969).

Communications to the Editor

Donor-Acceptor Complexes in Copolymerization. I. Preparation of Styrene-Acrylonitrile Alternating Copolymers in the Presence of Zinc Chloride

The free radical initiated copolymerization of allylic and olefinic compounds with polar monomers, such as acrylonitrile and methyl methacrylate, in the presence of zinc chloride yields copolymers containing concentrations of olefinic monomer higher than normally encountered in the absence of the metal halide.[1,2] The uncatalyzed spontaneous copolymerization of α olefins with these polar monomers in the presence of an ethyl aluminum halide at −78° yields high molecular weight 1:1 alternating copolymers.[3-5]

It has been proposed[6,7] that analogous mechanisms are operative in both cases, *i.e.*, the alternating copolymer results from the spontaneous homopolymerization of an equimolar (olefin–polar monomer $\cdots$ $(C_2H_5)_xAlCl_{3-x}$) complex while the nonequimolar copolymer results from the free radical initiated copolymerization of (olefin–polar monomer $\cdots$ $ZnCl_2$) and (polar monomer–polar monomer $\cdots$ $ZnCl_2$) complexes.

Confirmation of the postulated analogy between the spontaneous formation of equimolar copolymer and the radical-initiated formation of nonequimolar copolymer was demonstrated[7] by the formation of high molecular weight 1:1 copolymer from styrene and methyl methacrylate in the presence as well as in the absence of a free radical initiator. The equimolar copolymer was produced at 25–30° in the presence of $Et_{1.5}AlCl_{1.5}$ alone or together with 2-methylpentanoyl peroxide, irrespective of monomer charge. The presence of the radical catalyst increased the rate of copolymerization and decreased the copolymer molecular weight to a very slight extent, without influencing the 1:1 structure of the copolymer.

Further confirmation of the identity of the spontaneous and catalyzed complex polymerizations has now been obtained in the uncatalyzed as well as radical initiated copolymerization of styrene and acrylonitrile at 60° in the presence of zinc chloride. This system forms a high molecular weight 1:1 alternating copolymer, irrespective of monomer charge.

As shown in Table I, the presence of zinc chloride alone or zinc chloride plus benzoyl peroxide at 60° yields high molecular weight 1:1 copolymers at styrene: acrylonitrile molar ratios of 3:1, 1:1, and 1:3. In the absence of zinc chloride the radical catalyst yields a lower molecular weight copolymer whose composition is dependent on monomer charge. This observation is consistent with conventional radical polymerization.

The formaion of 1:1 copolymer from the styrene–acrylonitrile system but nonequimolar copolymer from other olefin–acrylonitrile systems in the presence of zinc chloride is indicative of the strong electron-donating character of styrene as compared to the other olefins. The S–AN $\cdots$ $ZnCl_2$ complex is either formed preferentially, to the exclusion of the AN–AN $\cdots$ $ZnCl_2$ complex, or the rate of homopolymerization of the former complex is greater than the rate of copolymerization of the two complexes. A similar result has been noted in the attempted spontaneous terpolymerization of cyclopentene, styrene, and sulfur dioxide.[8] Although the cyclopentene–sulfur dioxide and the styrene–sulfur dioxide systems readily copolymerize separately, the termonomer composition gives a copolymer containing only styrene and sulfur dioxide.

The 1:1 copolymer is obtained from a 3:1 styrene: acrylonitrile comonomer charge at 60° even when the

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(2) G. E. Serniuk and R. M. Thomas (to Esso Research and Engineering Co.), U. S. Patent 3,183,217 (May 11, 1965); U. S. Patent 3,278,503 (Oct 11, 1966).

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(4) M. Hirooka, H. Yabuuchi, S. Morita, S. Kawasumi, and K. Nakaguchi, *J. Polym. Sci., Part B*, **5**, 47 (1967).

(5) M. Hirooka, H. Yabuuchi, J. Isaki, and Y. Nakai, *ibid., Part A-1*, **6**, 1381 (1968).

(6) N. G. Gaylord and A. Takahashi, *ibid., Part B*, **6**, 743 (1968).

(7) N. G. Gaylord and A. Takahashi, *ibid., Part B*, **6**, 749 (1968).

(8) S. Iwatsuki, T. Okada, and Y. Yamashita, *ibid., Part A-1*, **6**, 2451 (1968).