Macromolecules

Volume 3, Number 2 March–April 1970

Rheological Properties of Anionic Polystyrenes. I. Dynamic Viscoelasticity of Narrow-Distribution Polystyrenes

Shigeharu Onogi, Toshiro Masuda, and Keishi Kitagawa

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

Received November 13, 1969

ABSTRACT: The viscoelastic properties of narrow-distribution polystyrenes have been measured in the molten state by means of a concentric cylinder type rheometer over wide ranges of frequency and temperature. From the frequency dependence of the storage shear modulus G' and the loss modulus G'', the characteristic parameters in the so-called terminal zone, such as zero-shear viscosity η_0, elasticity coefficient A_G, and steady-state compliance J_e^0 have been evaluated, and the dependence of these parameters on the molecular weight M has been discussed. η_0, A_G, and J_e^0 for samples having molecular weight higher than the critical molecular weight M_C are proportional to $M^{3.7}$, $M^{7.5}$, and M^0, respectively. For samples having molecular weights lower than M_C, J_e^0 is proportional to M, as is predicted by the modified Rouse theory. The quasi-equilibrium modulus G_{eN}^0 evaluated from G' in the rubbery region shows a constant value of 2.0×10^6, independent of M. This value agrees very well with that obtained by integration of the G'' *vs.* log ω curve. The average molecular weight between entanglement coupling loci, M_e, and the average chain length, Z_e, have been calculated from G_{eN}^0 to be 18,000 and 346, respectively. The current molecular theories for entanglement coupling have been discussed on the basis of these experimental results. The temperature and molecular weight dependences of the shift factor a_T were also discussed, and a few parameters on the free volume, such as the Vogel temperature T_0 and the temperature coefficient of the fractional free volume α_f have been determined for narrow-distribution polystyrenes.

The viscoelastic behavior of concentrated systems of high polymers, such as concentrated solutions and melts, has been studied for a long time by many authors. Theoretical and experimental investigations hitherto published have revealed that the entanglement couplings[1] between molecular chains constitute one of the most significant factors which determine the rheological properties of these concentrated systems. However, there still remain some unsolved problems on the true nature of the entanglement couplings and their effect on the rheological properties. A difficulty met in the theoretical treatments of the entanglement couplings in concentrated systems is that we can not describe satisfactorily very strong interactions between molecular chains or segments.

In our recent papers,[2–6] rheological properties of various high polymers, such as polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), and poly(vinyl acetate) in the molten state were measured in wide ranges of temperature and frequency, and the effects of various factors such as temperature, molecular weight, molecular weight distribution, and branching were studied. The general purpose of these studies was to generalize the effect of entanglement couplings. However, it was impossible to clarify fully the true nature of the entanglements, mainly because the samples employed in these studies still had rather broad distributions of molecular weight even when they were fractionated.

As was shown by several recent investigations[1] and will be mentioned in the next paper[7] of this series, the rheological properties of concentrated polymer systems are affected strongly by the molecular weight and its distribution, especially in the terminal and rubbery zones. However, polymer samples having broad distributions of molecular weight cannot afford exact information on the effects of molecular weight and its distribution on the rheological properties.

In the present paper, viscoelastic properties have been measured for many polystyrene samples which were obtained by anionic polymerization and have very narrow distributions of molecular weight. On the basis of the experimental results, the molecular weight dependences of zero-shear viscosity, steady-state compliance, and the shear modulus characteristic of entanglement networks are discussed.

---

(1) J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1961; also 2nd ed, Chapter 13, in press.

(2) M. Horio, T. Fujii, and S. Onogi, *J. Phys. Chem.*, **68**, 778 (1964).

(3) S. Onogi, T. Fujii, H. Kato, and S. Ogihara, *ibid.*, **68**, 1598 (1964).

(4) S. Onogi, *Nippon Kagaku Zasshi*, **87**, 1245 (1966).

(5) S. Onogi, H. Kato, S. Ueki, and T. Ibaragi, *J. Polym. Sci., Part C*, **15**, 481 (1966).

(6) S. Onogi, T. Masuda, and T. Ibaragi, *Kolloid-Z. Z. Polym.*, **222**, 110 (1968).

(7) T. Masuda, K. Kitagawa, T. Inoue, and S. Onogi, *Macromolecules*, 3, 116 (1970).

Table I
The Weight- and Number-Average Molecular Weights and Their Ratio for the Narrow-Distribution Polystyrene Samples

	Mol wt			Mol wt (gpc)		
Sample	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
L18	581,000	550,000	1.06	616,000	563,000	1.09
L19	513,000	471,000	1.09	547,000	498,000	1.10
L5	351,000	330,000	1.06	409,000	363,000	1.13
L22	275,000	257,000	1.07	318,000	288,000	1.10
L15	215,000	215,000	1.00	229,000	203,000	1.13
L27	167,000	199,000	0.84	185,000	164,000	1.13
L37	113,000	113,000	1.00	131,000	108,000	1.21
L16	58,700	62,200	0.94	59,000	52,300	1.13
L34	46,900	49,500	0.95	43,100	38,400	1.12
L14	28,900	28,300	1.02	29,100	24,300	1.20
L3	24,500	22,600	1.08	27,400	19,700	1.39
L10	19,300	18,200	1.06	22,700	16,100	1.41
L12	14,800	12,900	1.15	20,800	15,100	1.38
L9	8,900	8,800	1.01	11,900	9,100	1.31

Table II
The Weight- and Number-Average Molecular Weights and Their Ratio for the Standard Polystyrenes Obtained from Pressure Chemical Co.

	Mol wt			Mol wt (gpc)		
Sample	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
S1	867,000	773,000	1.12	839,000	736,600	1.14
S2	411,000	392,000	1.05	483,000	428,400	1.13
S3	173,000	164,000	1.05	178,000	159,000	1.12
S4	98,200	96,200	1.02	100,400	91,200	1.10
S5	51,000	49,000	1.04	51,500	47,000	1.10
S6	19,850	19,650	1.01	19,700	18,000	1.09
S7	10,300	9,700	1.06	10,800	9,800	1.10
S8	5,000	4,600	1.09	5,700	5,200	1.10

Experimental Section

Preparation of Anionic Polystyrene Samples. The narrow-distribution polystyrenes used in this study were prepared by anionic polymerization[8] at a low temperature (−78°) under pressure below 10^{-6} mm, using tetrahydrofuran as the solvent and *n*-butyllithium as the initiator. The polymerization procedure was similar to that reported by Morton, *et al.*,[9] with certain improvements introduced by the authors. The concentration of the initiator was 0.232 *N* in *n*-hexane. The weight of polymer obtained in each batch was about 60 g. The polymer was precipitated and purified with methanol. Some of the polymers were fractionated by precipitation in benzene–methanol systems to remove higher and lower molecular weight fractions present in small amounts. The samples thus prepared were dried in a vacuum oven at 60°.

Characterization of the Samples. The weight-average molecular weights M_w of the narrow-distribution polystyrenes were obtained from the intrinsic viscosity $[\eta]$ of dilute solutions in cyclohexane at 34.5°, using the following equation proposed by Altares, *et al.*,[10] for narrow-distribution polystyrene. The number-average molecular weight M_n,

$$[\eta] = 8.5 \times 10^{-4}(M_w^{0.5}) \qquad (1)$$

on the other hand, was determined by the osmotic pressure technique using the high speed membrane osmometer, Model 502, of Mecrolab Inc.

The molecular weight distribution of all the samples was measured by means of the gel permeation chromatograph, Model 200, manufactured by Waters Associates Inc. The measurements were carried out with tetrahydrofuran as the solvent at room temperature. The flow rate was 1 ml/min. The weight- and number-average molecular weights were also evaluated from the gel permeation chromatograms.

The weight- and number-average molecular weights and their ratios thus determined are tabulated in Table I for the 14 samples employed in this study. M_w and M_n values determined by the gpc method coincide fairly well with those obtained by the viscosity and osmotic pressure methods, but the ratios of M_w/M_n from the gpc have somewhat larger values than those from the other methods. For a comparison, similar measurements were carried out for the standard polystyrene polymers prepared by Pressure Chemical Co., and the result is shown in Table II. The values of M_w and M_n in the second and third columns of the table are taken from the data sheets issued by Pressure Chemical Co., and were obtained by the light scattering and osmotic pressure methods, respectively.

Comparing Table I with Table II, it is clear that the samples prepared by us have molecular weight distributions as narrow as the standard polystyrenes from Pressure Chemical.

Measurements. The measurements of viscoelastic properties were carried out with the concentric cylinder type rheometer described in the previous papers.[2,11] The strain was applied to the sample by the oscillation of the outer cylinder or cup, and the oscillation of the inner cylinder or bob which was suspended by a torsion wire was changed into electrical potential by means of a differential transformer, and after being amplified was recorded on a X–Y recorder. The frequency of the oscillations ranged from 4×10^{-3} to 0.5 cps. The measuring temperature ranged from 120 to 280°. Nitrogen gas was flowed over the surface of the sample in order to minimize chemical degradation at high temperatures.

The viscoelastic functions such as the storage shear modulus G' and loss modulus G'' were calculated by the use of the general equation given by Markovitz.[12]

Results

In Figure 1, the storage modulus G' at various temperatures is logarithmically plotted against the

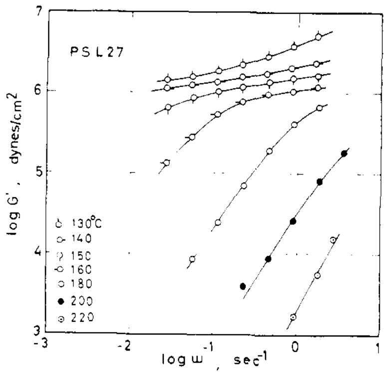

Figure 1. Frequency dependence of G' for narrow-distribution polystyrene L27, molecular weight 167,000, at various temperatures.

---

[8] L. Reich and A. Schindler, "Polymerization by Organometallic Compounds," Interscience Publishers, New York, N. Y., 1966, Chapter VII.

[9] (a) M. Morton, P. Milkovich, D. B. McIntyre, and L. J. Bradley, *J. Polym. Sci., Part A*, 1, 443 (1963); (b) M. Morton, A. A. Rembaum, and J. L. Hall, *ibid., Part A*, 1, 461 (1963).

[10] T. Altares, Jr., D. P. Wyman, and V. R. Allen, *ibid., Part A*, 2, 4533 (1964).

[11] M. Horio, S. Onogi, and S. Ogihara, *J. Jap. Soc. Testing Mater.*, 10, 350 (1961).

[12] (a) H. Markovitz, *J. Appl. Phys.*, 23, 1070 (1952); (b) H. Markovitz, P. M. Yavorsky, R. C. Harper, Jr., L. J. Zapas, and T. W. DeWitt, *Rev. Sci. Instr.*, 23, 430 (1952).

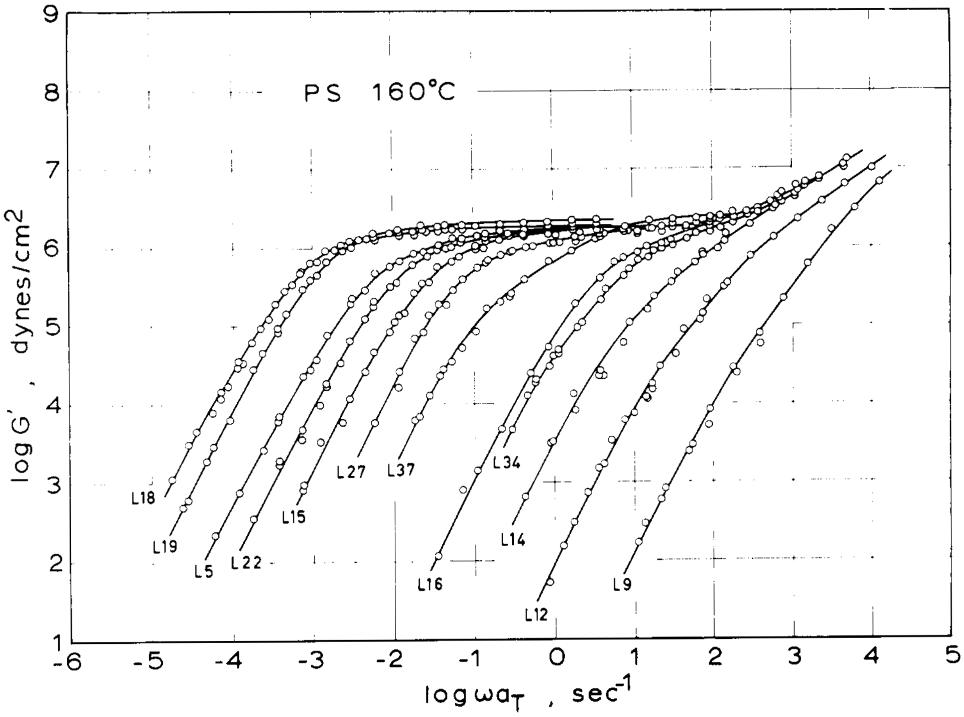

Figure 2. Master curves of G' for narrow-distribution polystyrenes having different molecular weights. The reference temperature is 160°.

angular frequency for one of the narrow-distribution polystyrenes, L27, having molecular weight of 167,000 as an example. Such log G' *vs.* log ω curves as well as the similar curves for the loss modulus G'' and dynamic viscosity η' at various temperatures can always be superposed into respective master curves by use of the time–temperature superposition principle. In Figure 2 are shown the master curves of G' for narrow-distribution polystyrenes having different molecular weights. The abscissa of the figure is the reduced angular frequency ωa_T, and the reference temperature is 160°. The molecular weights of the samples range from 581,000 (L18) to 8900 (L9). As may be seen from Figure 2, the master curve includes not only the flow or terminal zone but also rubbery and glass transition zones. The terminal zone shifts progressively to the low frequency side and the rubbery plateau becomes longer and longer as the molecular weight increases. The samples having very low molecular weights, such as L14, L12, and L9, do not manifest the rubbery plateau. The height of the rubbery plateau for the samples of higher molecular weights seems to be independent of molecular weight, and has a value of about 2.0×10^6 dyn/cm^2. The G' curves for high molecular weight samples unite in the transition zone, while those for low molecular weight samples do not unite but shift to the high frequency side because of the excess free volume, as will be discussed later. Each G' curve shows a very sharp transition from the rubbery to the terminal zone, where the curve has the slope of 2.0. The extremely flat rubbery plateau and the very sharp rubbery-flow transition are characteristic features most remarkable in the narrow-distribution polymers.

Figure 3 shows master curves of G'' for the same samples as in Figure 2. The reference temperature is 160° here again. The shift factors a_T determined in the course of the time–temperature superposition of the G'' curves are the same as those for G'. As is evident from Figure 3, the effect of molecular weight on G'' is also very marked. For the samples having molecular weights higher than the 167,000 of L27, the G'' curve shows a peak at the low-frequency end of the rubbery zone. This indicates that narrow-distribution polystyrenes having very high molecular weight have two sets of relaxation times corresponding to two relaxation mechanisms separated in the time scale. The two sets of relaxation times, of course, correspond to the glass transition in the high-frequency region, which is not fully observed in this study, and the entanglement slippage in the low-frequency region, which appears as a peak of the G'' curve in Figure 3. For polymers such as L37, L16, and L34 having molecular weights low but higher than the critical molecular weight M_C, the above two sets of relaxation times approach and overlap each other, and hence the peak in G'' disappears and only a plateau can be observed.

The shift factor a_T for the same samples is plotted against temperature in Figure 4. The large open circles in the figure represent the values obtained for samples having molecular weights of 28,900 (L14) and higher, the closed and small open circles those for L12 (M = 14,800) and L9 (M = 8900), respectively. It is clear from this figure that the shift factor is independent of molecular weight so far as the molecular weight exceeds a certain limiting value of about 30,000, which is close to the critical molecular weight M_C. For the polymers of low molecular weights, the shift factor decreases with decreasing molecular weight. Log a_T for high molecular weight polystyrenes can be expressed by the following WLF-type equation[1,13]

---

(13) M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, 77, 3701 (1955).

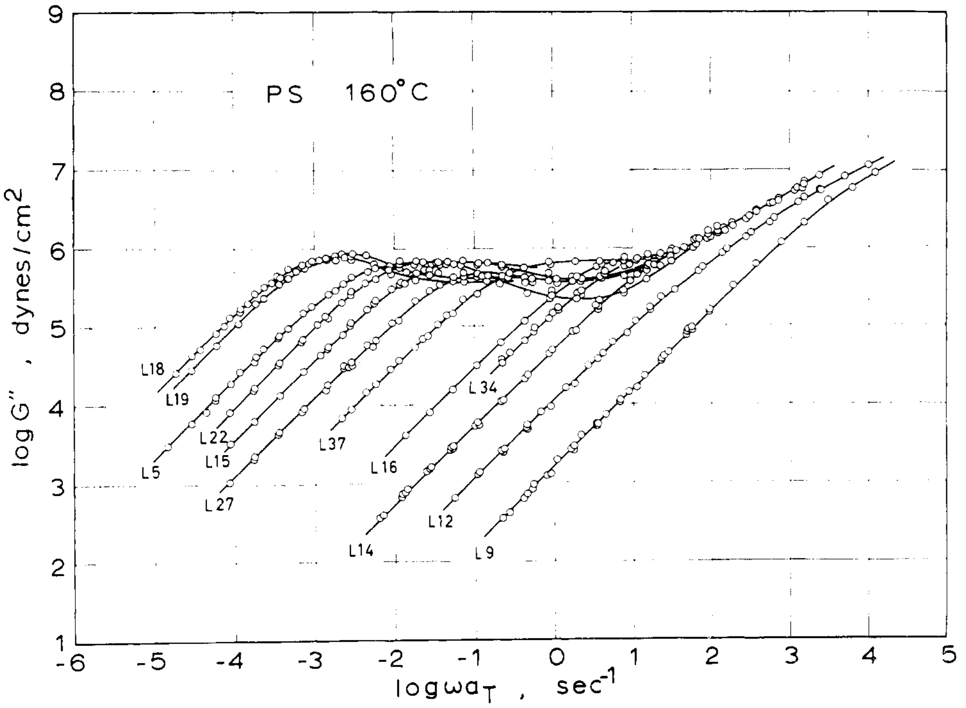

Figure 3. Master curves of G'' for narrow-distribution polystyrenes having different molecular weights. The reference temperature is 160°.

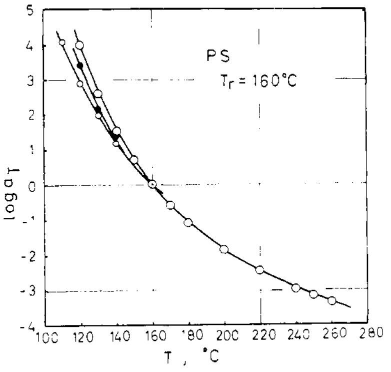

Figure 4. The logarithm of the shift factor a_T plotted against temperature for narrow-distribution polystyrenes. Large open circles indicate the results for $M \geq M_C$, closed circles for $M = 14{,}800$ (L12), and small open circles for $M = 8900$ (L9).

$$\log a_T = \frac{-7.14(T - 160)}{112.1 + (T - 160)} \qquad (2)$$

Discussion

Effect of Temperature and Free Volume. According to Doolittle[14] as well as Cohen and Turnbull,[15] the viscosity of liquids can be given by

$$\ln \eta = \ln A + B \frac{v}{v - v_0} \qquad (3)$$

where A and B are constants for the liquid, v the specific volume, and v_0 the occupied volume at temperature T. The fractional free volume f is defined by

$$f = (v - v_0)/v \qquad (4)$$

which is also a function of temperature. Above the glass transition temperature T_g, f can be written approximately as[13, 16]

$$f = f_g + \alpha_f(T - T_g) = \alpha_f(T - T_0) \qquad T \geq T_g \qquad (5)$$

where α_f is the temperature coefficient of the fractional free volume, f_g is the fractional free volume at T_g, and T_0 is an imaginary temperature well known as the Vogel temperature, at which the free volume would vanish. Using eq 4 and 5, eq 3 may be rewritten as

$$\ln \eta = \ln A + \frac{B/\alpha_f}{(T - T_0)} \qquad (6)$$

This equation is usually referred to as the Vogel equation[16] or the modified Arrhenius equation.[17] The WLF equation can be derived from eq 6 in the following forms

$$\log a_T = \frac{-c_1^g(T - T_g)}{c_2^g + (T - T_g)} \qquad (7)$$

with $c_1^g = B/2.303f_g$ and $c_2^g = f_g/\alpha_f$, or

$$\log a_T = \frac{-c_1^r(T - T_r)}{c_2^r + (T - T_r)} \qquad (8)$$

with $c_1^r = B/2.303f_r$, $c_2^r = f_r/\alpha_f$, the reference temperature T_r, and f_r, the fractional free volume at T_r. Equations 5 and 8 show that the plot of $-(T - T_r)/\log a_T$ against $(T - T_r)$ should give a straight line, and that from its slope and intercept, c_1^r, c_2^r, f_r, α_r, and T_0 can be evaluated, assuming $B = 1$.[13, 16] The plot for the

---

(14) (a) A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951); (b) A. K. Doolittle and D. B. Doolittle, *ibid.*, **28**, 901 (1957).

(15) (a) M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959); (b) D. Turnbull and M. H. Cohen, *ibid.*, **34**, 120 (1961).

(16) G. C. Berry and T. G Fox, *Advan. Polym. Sci.*, **5**, 261 (1968).

(17) A. A. Miller, *J. Polym. Sci., Part A*, **1**, 1857 (1963); *Part A*, **1**, 1865 (1963); *Part A*, **2**, 1095 (1964).

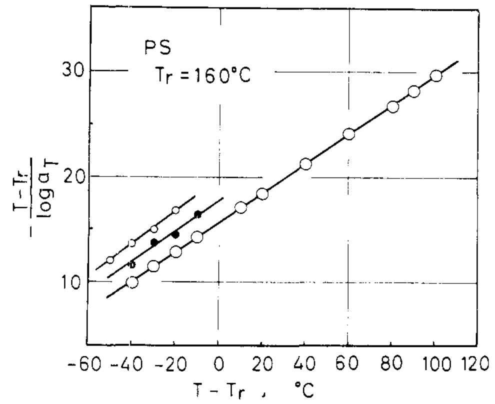

Figure 5. Linear plots of $-(T - T_r)/\log a_T$ *vs.* $T - T_r$ for narrow-distribution polystyrenes. The reference temperature is 160°. The circles are used as in Figure 4.

TABLE III
FREE VOLUME PARAMETERS FROM THE TEMPERATURE DEPENDENCE OF THE SHIFT FACTOR

Sample	Mol wt	α_f, deg^{-1}	T_0, °C	f_{160}	f_g
	$\geq M_C$	5.42×10^{-4}	47.9	0.0608	0.0283
L12	14,800	5.20×10^{-4}	38.1	0.0634	($T_g = 100°$)
L 9	8,900	5.28×10^{-4}	31.8	0.0677	

narrow-distribution polystyrenes is given in Figure 5, where the same circles as in Figure 4 are employed to distinguish the three samples. The calculated values of the free volume parameters are tabulated in Table III.

It is evident from Table III that the T_0 decreases with decreasing molecular weight below M_C, while α_f appears almost constant. The fractional free volume at the glass temperature, f_g, is 0.028 when we assume T_g = 100°. Polystyrenes having molecular weights below M_C possess excess free volume as compared with those having molecular weights above M_C at the same temperature; for example, at 160°, f_g = 0.068 for M = 8900 < M_C, while f_g = 0.061 for $M \geq M_C$. This excess free volume causes the shifts of the storage modulus and loss modulus curves for low molecular weight polymers to the high-frequency side in the transition zone, as seen in Figures 2 and 3.

The temperatures at which polymers having molecular weights below M_C have the same fractional free volume as that of higher molecular weight polymers were calculated from eq 5 to be 155 and 147° for L12 and L9, respectively, instead of 160°. Therefore, G' and G'' for L12 and L9, respectively, at 155 and 147° should correspond to the values for the higher molecular weight polymers at 160° or in the iso-free-volume state, in which f = 0.0608. The G' and G'' curves for the seven polymers, including L12 and L9, in the iso-free-volume state are compared in Figures 6 and 7, respectively. The curves drawn with the broken line in these figures are those for L12 and L9 at 160°. It is evident in these figures that the curves for low molecular weight polymers corrected for the free volume unite with the others in the transition zone.

Rheological Behavior in the Terminal Zone. The rheological behavior of a polymer liquid in the long-time region or terminal zone can be characterized by such parameters as the zero-shear viscosity η_0, elasticity coefficient A_G, normal stress coefficient θ, and steady-state compliance $J_e{}^0$, which are defined respectively as

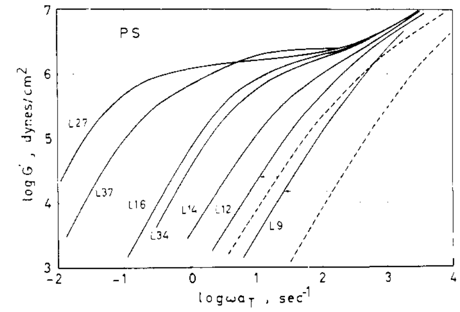

Figure 6. Frequency dependence of G' for narrow-distribution polystyrenes reduced to the iso-free-volume state, f = 0.0608.

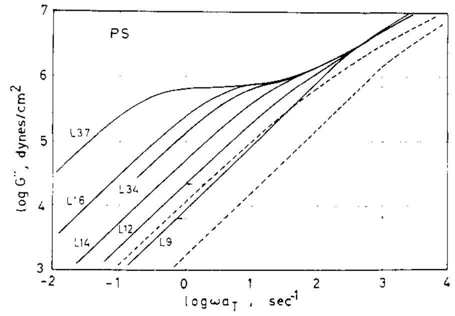

Figure 7. Frequency dependence of G'' for narrow-distribution polystyrenes reduced to the iso-free-volume state, f = 0.0608.

$$\eta_0 = \lim_{\omega \to 0} (G''/\omega) = \lim_{\kappa \to 0} (\sigma_{12}/\kappa) \tag{9}$$

$$A_G = \lim_{\omega \to 0} (G'/\omega^2) \tag{10}$$

$$\theta = \lim_{\kappa \to 0} (\sigma_{11} - \sigma_{22})/\kappa^2 \tag{11}$$

$$J_e{}^0 = \lim_{\omega \to 0} J' = A_G/\eta_0{}^2 \tag{12}$$

where σ_{12} and $\sigma_{11} - \sigma_{22}$ are, respectively, the shearing stress and principal normal stress difference in steady shear flow with the rate of shear κ. According to the second-order fluid theory,[18] A_G is equal to $\theta/2$. This has also been confirmed by experimental results obtained by several authors.[19]

The molecular weight dependence of zero-shear viscosity η_0 for the narrow-distribution polystyrenes is shown in Figure 8. It is clear from this figure that, above M = 40,000, the dependence can be represented by a straight line having the slope of 3.7; η_0 is proportional to $M^{3.7}$. The value of this exponent of M reported recently by different authors[20-23] ranges from

---

(18) B. D. Coleman and H. Markovitz, *J. Appl. Phys.*, **35**, 1 (1964).

(19) (a) W. Philippoff, *ibid.*, **36**, 3033 (1965); (b) K. Osaki, M. Tamura, T. Kotaka, and M. Kurata, *J. Phys. Chem.*, **69**, 3642 (1965); (c) T. Kotaka and K. Osaki, *J. Polym. Sci., Part C*, **15**, 453 (1966).

(20) J. F. Rudd, *ibid.*, **44**, 459 (1960).

(21) R. A. Stratton, *J. Colloid Interfac. Sci.*, **22**, 517 (1966).

(22) G. Akovali, *J. Polym. Sci., Part A-2*, **5**, 875 (1967).

(23) A. V. Tobolsky, J. J. Aklonis, and G. Akovali, *J. Chem. Phys.*, **42**, 723 (1965).

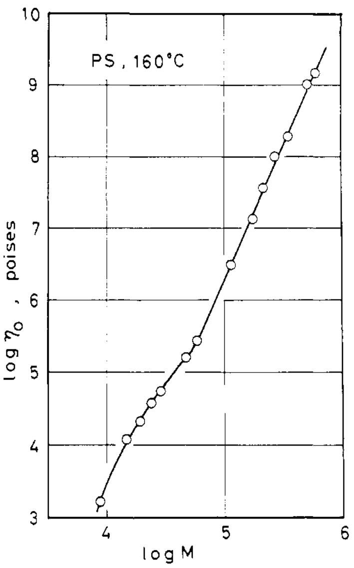

Figure 8. Molecular weight dependence of zero-shear viscosity η_0 for narrow-distribution polystyrenes at 160°.

3.14 to 4.0. The small deviations of these values from the well-known value[16,24] of 3.4 seem not to be essential, when one allows for the differences in the measuring methods employed by the different authors.

The critical molecular weight of entangelment M_C for the narrow-distribution polystyrenes cannot be accurately determined from Figure 8 itself, but it must have a value between 30,000 and 40,000, which is consistent with the reliable values of 31,200 and 38,000 published in recent papers.[1,16,21]

The relationship between log η_0 and log M below M_C cannot be approximated by a straight line, but in the iso-free-volume state it can be represented by a straight line having the slope of unity.[16]

The values of A_G calculated by eq 10 are plotted logarithmically against molecular weight in Figure 9. Above M_C, the plot can be approximated by a straight line having the slope of 7.5, but below M_C it is very similar in shape to the log η_0 *vs.* log M curve of Figure 8. This portion also becomes a straight line having a slope of about 3 in the iso-free-volume state.

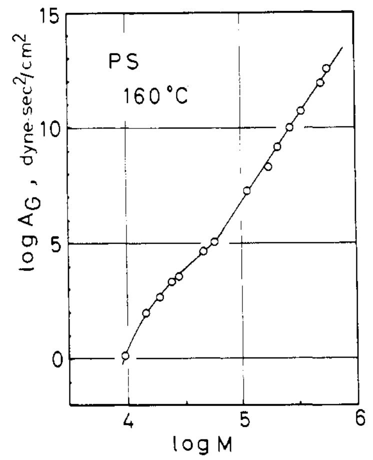

Figure 9. Molecular weight dependence of elastic coefficient A_G for narrow-distribution polystyrenes at 160°.

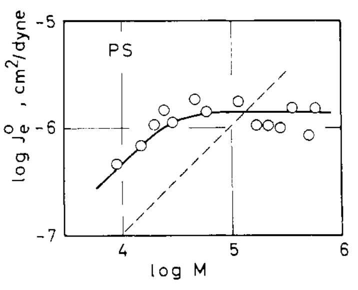

Figure 10. Molecular weight dependence of steady-state compliance J_e^0 for narrow-distribution polystyrenes at 160°.

The molecular weight dependence of the steady-state compliance J_e^0 is shown in Figure 10. As is evident in this figure, J_e^0 does not depend on molecular weight in the high molecular weight region, but it is approximately proportional to M in the low molecular weight region. The break point of the curve is located near M_C.

The modified Rouse theory[1,25] predicts that J_e^0 should be proportional to M as follows

$$J_e^0 = 2M/5\rho RT \tag{13}$$

where ρ is the density of the polymer. The straight line predicted by this equation is shown by the broken line in Figure 10. The experimental points diverge from this line over the entire range of molecular weight covered in this study. The independence of J_e^0 from molecular weight has also been reported by several authors for narrow-distribution polystyrene[22,23] and poly-α-methylstyrene.[26]

Rheological Behavior in the Rubbery Zone. The rheological behavior of polymer liquids in the rubbery zone is fundamentally affected by the entanglement couplings between molecular chains. Almost all the theories of entangelments have been based upon the treatments[27] of Rouse and Zimm for the dynamics of an isolated macromolecular chain. These theories can be classified roughly into two categories. The modified Rouse theory,[1,25] Marvin–Oser theory,[28] and Chompff–Duiser theory[29] belong to the first category, which predicts that the relaxation spectrum will have a maximum characteristic of the entanglement slipping mechanism. These theories are based on the idea that the friction coefficients of submolecules increase owing to the presence of entanglement couplings. The other type theory, presented by Hayashi,[30] is based on the assumption that not only the friction coefficient but also the elastic coefficient of the submolecules changes due to the entanglement couplings, and it predicts a box-

---

(24) T. G Fox, S. Gratch, and S. Loshaek, "Rheology," Vol. I, F. R. Eirich, Ed., Academic Press, New York, N. Y., 1956, Chapter 12.

(25) J. D. Ferry, R. F. Landel, and M. L. Williams, *J. Appl. Phys.*, **26,** 359 (1955).

(26) H. Odani, S. Kitamura, N. Nemoto, and M. Kurata, *Rep. Progr. Polym. Phys. Jap.*, **10,** 321 (1967).

(27) B. H. Zimm, "Rheology," Vol. III, F. R. Eirich, Ed., Academic Press, New York, N. Y., 1960, Chapter 1.

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

(29) (a) A. J. Chompff and J. A. Duiser, *J. Chem. Phys.*, **45,** 1505 (1966); (b) A. J. Chompff and W. Prins, *ibid.*, **48,** 235 (1968).

(30) S. Hayashi, *J. Phys. Soc. Jap.*, **18,** 131, 249 (1963); **19,** 101, 2306 (1964).

shaped relaxation spectrum without any maximum in the rubbery zone.

The two types of theory predict distinctive behavior of various viscoelastic parameters. According to the first type, the frequency dependence curve of G'' should have a maximum, and that of G' should show a very flat plateau. Furthermore, J_e^0 should be proportional to M. The Hayashi theory, on the other hand, predicts that G'' will never show any maximum, and that J_e^0 will be independent of molecular weight. Therefore, the experimental finding that J_e^0 for high molecular weight polystyrenes is independent of M seems to support the Hayashi theory. The G'' curves given in Figure 3 for these polystyrenes, however, undoubtedly show maxima, and the G' curves shown in Figure 2 have very flat and long plateaus. This suggests that the narrow-distribution polystyrenes of very high molecular weights have two sets of relaxation times, which are separated from each other due to the narrow distribution of molecular weights. As the molecular weight approaches M_C, the peak associated with the entanglement slippage becomes more and more ambiguous, because of the overlapping of the two sets of relaxation times. Such features are very similar to the frequency dependence of G' and G'' predicted by the Marvin–Oser theory.

In our previous studies of the viscoelastic properties of various high polymers, a clear peak in the G'' curves has never been observed. The reason is that the samples employed in those studies had fairly broad distributions of molecular weights, though some of them were fractionated. The broadening of the distribution of relaxation times associated with entanglement slippage due to the broadening of molecular weight distribution will be discussed in more detail in the succeeding paper[7] of this series.

In the conceptual scheme of entanglement coupling,[1] the most important parameter is the average molecular weight between coupling loci, M_e, or the corresponding average chain length $Z_e = jM_e/M_0$, where j is the number of chain atoms per monomer unit, and M_0 the molecular weight of a monomer.

As is evident in Figure 2, G' for high molecular weight polymers in the rubbery zone is constant, independent of frequency. The entanglement modulus G_{eN}^0 denotes this constant value of G' and is often referred to as the pseudoequilibrium modulus of the entanglement network. The relation between G_{eN}^0 and M_e can be given by

$$G_{eN}^0 = 1/J_{eN}^0 = g_N\rho RT/M_e \qquad (14)$$

where g_N is a front factor near unity, ρ the density of polymer, and J_{eN}^0 the entanglement compliance, which is the storage compliance on the rubbery plateau. This equation is analogous to the relation between the modulus and the average molecular weight between cross-link points in the kinetic theory of rubber elasticity. The value of G_{eN}^0 evaluated from Figure 2 is 2.0×10^6 dyn/cm², and those of M_e and Z_e calculated by eq 14 are, respectively, 18,000 and 346.

When the log G' *vs.* log ω curve does not show a flat plateau, as in the case of broad-distribution polymers, G_{eN}^0 or J_{eN}^0 can be evaluated[31] by the integration of the G'' *vs.* ln ω or J'' (loss compliance) *vs.* ln ω curves according to

$$G_{eN}^0 = \int_a^{\infty} H(\tau)\,\mathrm{d}\ln\tau = \frac{2}{\pi}\int_{-\infty}^{a'} G''\,\mathrm{d}\ln\omega \qquad (15)$$

$$J_{eN}^0 = \int_c^{b} L(\tau)\,\mathrm{d}\ln\tau = \frac{2}{\pi}\int_{b'}^{c'} J''\,\mathrm{d}\ln\omega \qquad (16)$$

where $H(\tau)$ and $L(\tau)$ denote the relaxation and retardation spectra, respectively, and τ the relaxation time. The integral limits a', b', and c' should be taken to encompass the maximum of G'' or J''. In Figure 11 are shown two examples of G'' *vs.* log ω curves for the narrow-distribution polystyrenes, L18 and L15. The solid and broken lines show the experimental and estimated values of G''. It has been confirmed that no serious error is introduced when the value of ω at which the loss tangent tan δ takes its maximum is taken as one of the integration limits or when the whole curve is assumed to be symmetric.

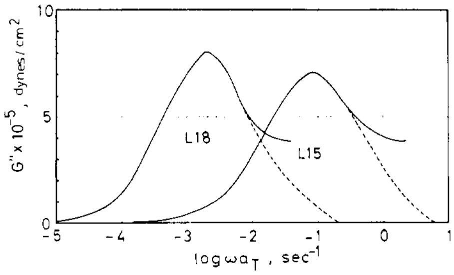

Figure 11. Two examples of G'' *vs.* log ω curves for obtaining G_{eN}^0 by integration.

TABLE IV
ENTANGLEMENT MODULUS AND ENTANGLEMENT SPACINGS OBTAINED BY INTEGRATION OF THE LOSS MODULUS

Sample	Mol wt	G_{eN}^0, dyn/cm²	M_e	Z_e
L18	581,000	2.05×10^6	17,500	337
L19	513,000	2.22×10^6	16,200	311
L22	275,000	1.80×10^6	20,100	386
L15	215,000	1.90×10^6	18,900	364
	Av	1.99×10^6	18,100	347
From G' plateau		2.0×10^6	18,000	346

The values of G_{eN}^0 thus evaluated for several high molecular weight polymers are tabulated in Table IV, together with those of M_e and Z_e determined from G_{eN}^0. In this table are also listed the values calculated from G' of the rubbery plateau in Figure 2. It is clear from this table that the molecular weight or chain length between entanglement coupling loci is almost constant independent of molecular weight, and that the result of the integration of the curves coincides very well with that obtained directly from G' of the plateau. When we assume the critical molecular weight M_C to be between 31,200 and 38,000, we obtain M_C/M_e = 1.7–2.1, which compares well with the 1.9 predicted by Bueche.[32]

According to the Marvin–Oser theory, the maximum

---

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

(32) F. Bueche, "Physical Properties of Polymers," Interscience Publishers, New York, N. Y., 1962, p 80.

TABLE V
ENTANGLEMENT MODULUS AND ENTANGLEMENT SPACINGS FROM THE MARVIN–OSER THEORY

Sample	Mol wt	G_{eN}^0, dyn/cm^2	M_e	Z_e
L18	581,000	3.86×10^6	9,300	179
L19	513,000	4.35×10^6	8,300	159
L22	275,000	3.48×10^6	10,300	199
L15	215,000	3.48×10^6	10,300	199
	Av	3.79×10^6	9,600	184

values of G'' and J'' are related to G_{eN}^0 and J_{eN}^0 by

$$G''_{\max} = 0.207 G_{eN}^0 \qquad (17)$$

and

$$J''_{\max} = 0.417 J_{eN}^0 \qquad (18)$$

Therefore, from $G''_{\max}$ we can determine G_{eN}^0 using eq 17, and hence M_e and Z_e using eq 14. The values thus determined for some of the narrow-distribution polystyrenes shown in Figure 2 are listed in Table V. The values in this table differ from those in Table IV by a factor of 1.9. Recently, it has been reported[33] that M_e calculated by the use of the Hayashi theory[30] for several polymer systems is two or three times larger than that obtained by the Marvin–Oser theory.[28]

Acknowledgments. This study was supported by a grant for scientific research (Kagaku Kenkyūhi) from the Ministry of Education. The authors wish to thank Professor John D. Ferry, University of Wisconsin, for his helpful discussions during his stay at our department in 1968. The gpc measurements by Mrs. K. Koga are also gratefully acknowledged.

---

(33) K. Osaki, Ph.D. Thesis, Kyoto University, 1968.

Rheological Properties of Anionic Polystyrenes. II. Dynamic Viscoelasticity of Blends of Narrow-Distribution Polystyrenes

Toshiro Masuda, Keishi Kitagawa, Toshio Inoue, and Shigeharu Onogi

Department of Polymer Chemistry, Kyoto University, Kyoto, Japan.

Received November 13, 1969

ABSTRACT: The dynamic viscoelastic properties of broad-distribution polystyrene and blends of narrow-distribution polystyrenes have been measured in the molten state. A comparison of the frequency dependences of the storage shear modulus G', loss modulus G'', and relaxation spectrum $H(\tau)$ of the blends and the broad-distribution polymer with those of the narrow-distribution polymers reveals that the effect of molecular weight distribution is very marked in the terminal and rubbery zones. The log G' *vs.* log ω curve for a binary blend composed of two components having very different molecular weights manifests the "two-step" rubbery plateau, suggesting that the blend has two sets of relaxation times associated with different kinds of entanglement couplings. The zero-shear viscosity η_0 of the blends is almost equal to that of a narrow-distribution polymer having the same weight-average molecular weight M_w, but the elasticity coefficient A_G for the blends is proportional to $M_w^{4.3}$, as against $M^{7.5}$ for the narrow-distribution polystyrene. The steady-state compliance J_e^0 of the blends is proportional to w_2^{-2} when w_2, the weight fraction of the high molecular weight component, is close to unity. The entanglement compliance J_{eN}^0 is also approximately proportional to w_2^{-2}, and J_{eN}^0 is lower than J_e^0 by a factor of about 3. The existence of three kinds of entanglement couplings has been pointed out, in which molecular chains of high–high, high–low, and low–low molecular weight components are involved.

Many investigations of the effect of molecular weight distribution on the rheological properties of amorphous polymers have revealed that the rheological properties in the terminal and rubbery zones are strongly affected by the molecular weight distribution. In the preceding paper of this series,[1] the viscoelastic properties of anionic polystyrenes having narrow distributions were reported, and it was found that the change from the rubbery to the flow region is very sharp, and that the distribution of relaxation times corresponding to entanglement slippage is very narrow.

In general,[2] the effect of molecular weight distribution on the rheological properties of polymers can be studied either employing polymer samples having a well-defined continuous distribution of molecular weights or using binary blends composed of the same species of polymers having different molecular weights. With broad-distribution polymer, however, no concrete result can be expected, because parameters to describe the shape or breadth of the distribution can hardly be found at present. In studies with blend samples, on the other hand, some parameters such as the molecular weights of the components and the blending ratio are known. However, most studies[2–7] of the rheological

---

(1) S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **3**, 109 (1970).

(2) J. D. Ferry, "Viscoelastic Properties of Polymers," John Wiley & Sons, Inc., New York, N. Y., 1961; also 2nd ed, Chapter 13, in press.

(3) K. Ninomiya, J. D. Ferry, and Y. Oyanagi, *J. Phys. Chem.*, **67**, 2297 (1963).

(4) M. Horio, T. Fujii, and S. Onogi, *ibid.*, **68**, 778 (1964).

(5) S. Onogi, *Nippon Kagaku Zasshi*, **87**, 1245 (1966).

(6) S. Onogi, H. Kato, S. Ueki, and T. Ibaragi, *J. Polym. Sci., Part C*, **15**, 481 (1966).

(7) S. Onogi, T. Masuda, and T. Ibaragi, *Kolloid-Z. Z. Polym.*, **222**, 110 (1968).