Viscoelastic Properties of Poly(Methyl Methacrylates) Prepared by Anionic Polymerization

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ABSTRACT: The viscoelastic properties of poly(methyl methacrylates) obtained by anionic polymerization were 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 modulus G' and the loss modulus G'' , the characteristic parameters in the terminal zone, such as zero-shear viscosity η_0 and steady-state compliance J_e^0 were evaluated, and the dependence of these parameters on the molecular weight M was discussed. η_0 and J_e^0 for samples having molecular weights higher than the critical molecular weight M_C were respectively proportional to $M^{4.4}$ and M . The quasi-equilibrium modulus G_{eN}^0 and the average molecular weight between entanglement coupling loci, M_e , were also evaluated. M_e was found to increase gradually from 6760 to 13100 with increasing molecular weight. The ratio M_C/M_e was not constant but varied from 6 to 2, being larger than the value of 2 obtained by previous authors, both theoretically and experimentally. The parameters for this material are discussed in connection with molecular structure, together with those for anionic polystyrene published in the previous paper.

KEY WORDS Viscoelasticity / Poly(Methyl Methacrylate) / Anionic Polymerization / Entanglement Coupling / Steady-State Compliance / Molecular Weight / Modified Rouse Theory / Polarity /

The viscoelastic behavior of polymer liquids, such as concentrated polymer solutions and melts, is largely determined by the mechanisms known as entanglement coupling^{1,2} or intermolecular interaction between polymer chains. As is well known, the effects of entanglement coupling and accordingly those of molecular weight and molecular weight distribution on the viscoelastic properties are found particularly in the terminal and rubbery zones.

In the terminal or flow zone, the rheological behavior of polymer liquids can be characterized by the zero-shear viscosity η_0 and the steady-state compliance J_e^0 , which are defined as follows;

$$\eta_0 = \lim_{\omega \rightarrow 0} \frac{G''}{\omega} \quad (1)$$

$$J_e^0 = \lim_{\omega \rightarrow 0} \frac{G'}{\omega^2 \eta_0^2} \quad (2)$$

where G' and G'' are respectively the storage

and loss moduli, and ω is the angular frequency.

In recent years, many investigators have concluded for several polymers that η_0 is proportional to $M_w^{3.4}$, where M_w is the weight-average molecular weight. This result holds regardless of molecular weight distribution, provided that M_w is higher than the critical molecular weight M_C . The molecular weight dependence of J_e^0 appears rather complicated. Ninomiya, *et al.*, reported that J_e^0 for poly(vinyl acetates)⁴ was proportional to molecular weight, supporting the prediction of the modified Rouse theory presented by Ferry, *et al.*,⁵

$$J_e^0 = \frac{2}{5} \cdot \frac{M}{\rho RT} \quad (3)$$

where ρ , R , and T are respectively the density of polymer, gas constant and absolute temperature. However, some recent studies for a few polymers such as polystyrene,⁶⁻⁸ poly(α -methylstyrene)^{9,10} and polyisoprene¹¹ show that J_e^0 is quite independent of, or at least much less dependent on, molecular weight than this equation

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would predict.

One of the most important parameters in the rubbery zone is the quasi-equilibrium modulus G_{eN}^0 which is closely related to the average molecular weight M_e or chain length $Z_e = jM_e/M_0$ between the entanglement coupling loci, where j is the number of chain atoms per monomer unit, and M_0 the molecular weight of a monomer unit. From an analogy to the kinetic theory of rubber elasticity, the relation between G_{eN}^0 and M_e can be given² by

$$G_{eN}^0 = 1/J_{eN}^0 = g_N \rho RT / M_e \quad (4)$$

where g_N is a front factor near unity and J_{eN}^0 is referred to as the entanglement compliance. Although it has been shown in several cases—including polystyrene of very narrow distribution of molecular weight⁸—that M_e does not depend on molecular weight, if $M \geq M_C$, this has not been fully confirmed for various polymers in general.

In our earlier study,¹² the viscoelastic properties of poly(methyl methacrylate) prepared by radical polymerization were measured, and the effect of molecular weight was mainly discussed. However, the samples employed had rather broad molecular weight distributions, and therefore some rheological parameters such as J_e^0 , G_{eN}^0 , J_{eN}^0 and M_e could not be determined accurately.

The present paper is principally aimed at a more accurate evaluation of various rheological parameters for poly(methyl methacrylates) having narrower distributions and detailed discussion of the effect of molecular weight on these parameters. The characteristic parameters studied were the rheological parameters η_0 , J_e^0 , G_{eN}^0 , J_{eN}^0 , M_e , as well as the shift factor a_T .

EXPERIMENTAL

Preparation of Samples

Polymethyl methacrylate (PMMA) samples of different molecular weight were prepared by anionic polymerization at low temperature (-78°C) under pressures below 10^{-6} mmHg, using tetrahydrofuran as the solvent and sodium naphthalene as the initiator. Each polymer thus prepared had a rather broad distribution of molecular weight and therefore was fractionated

in acetone-*n*-hexane mixtures. The fractions were purified in methanol and then dried in a vacuum oven.

Characterization of the PMMA Samples

The weight-average molecular weight M_w of each fraction was determined from the intrinsic viscosity in acetone at 25°C by the following equation¹³

$$[\eta] = 7.5 \times 10^{-5} M_w^{0.70} \quad (5)$$

The number-average molecular weight M_n was determined by osmotic pressure measurements using the High Speed Membrane Osmometer,

Table I. The weight- and number-average molecular weights and the ratio of these values for anionic PMMA

Sample	M_w	M_n	M_w/M_n
MF 2	342000	224000	1.53
MF 3	270000	188000	1.44
MF 5	197000	146000	1.35
MF 6	158000	139000	1.14
MF 7	116000	98000	1.18
MF 8	96300	71800	1.34
MF 9	63900	52800	1.21
MF10	45200	37100	1.22
MF11	35100	25300	1.39
MF12	28400	18000	1.58
MF13	11400	9120	1.25

Figure 1. An Example of the NMR spectrum for anionic PMMA (MF2), compared with that for radical PMMA (702).

Table II. The tacticity parameters for anionic and radical PMMA

Samples	M_w	I	H	S	i	s	B
MF 2	342000	0.141	0.519	0.340	0.401	0.599	1.080
MF 7	116000	0.141	0.512	0.347	0.397	0.603	1.063
702	174000	0.065	0.370	0.565	0.250	0.750	0.987
910	52000	0.063	0.406	0.531	0.266	0.734	1.040

Model 502, of Mecrolab Inc. Values for M_w , M_n and the ratio M_w/M_n for the eleven samples used in this study are tabulated in Table I.

The tacticity of the samples prepared by anionic polymerization was examined by nuclear magnetic resonance (NMR) spectroscopy and compared with that of PMMA obtained by the radical polymerization. An example of the NMR spectrum for anionic PMMA is shown in Figure 1 together with that for radical PMMA. The tacticity parameters proposed by several authors,¹⁴⁻¹⁶ triad (I , H and S), diad (i and s) and heterogeneity parameter B were evaluated from these spectra, and the results are shown in Table II. In this table, the samples MF 2 and MF 7 are the anionic PMMA used in this study, while 702 and 910 are the radical PMMA used in the previous study.¹²

The NMR spectra shown in Figure 1 and the tacticity parameters in Table II show that the samples of anionic PMMA are a little more isotactic than the radical PMMA. Furthermore, the amorphous character of the samples, as determined by the X-ray diffraction method, was found to be about the same in the anionic material as in the radical material.

Measurements of Viscoelasticity

The measurements of viscoelastic properties were carried out with the concentric cylinder type of rheometer, previously described.¹⁷ This rheometer enables us to measure the storage shear modulus G' and the loss modulus G'' as functions of the angular frequency ω at different temperatures. The measuring frequency ranged from 4×10^{-3} to 0.5, and the temperature from 120 to 280°C.

The frequency dependence curves of the viscoelastic functions at various temperatures were superposed into their respective master curves by the use of the time-temperature superposition principle.

RESULTS AND DISCUSSION

Frequency Dependence of Viscoelastic Functions

In Figures 2 and 3 are shown, respectively, the master curves of the storage shear modulus G' and loss modulus G'' for the PMMA samples having different molecular weights. The abscissa in the figure is the reduced angular frequency ωa_T , where a_T is the shift factor determined from the time-temperature superposition, and the reference temperature is 220°C. The mole-

Figure 2. Master curves of G' for anionic PMMA having different molecular weights. The reference temperature is 220°C.

Figure 3. Master curves of G'' for anionic PMMA having different molecular weights. The reference temperature is 220°C.

cular weight of the samples ranges from 342000 to 11400. As seen from these figures, the master curves include not only the terminal and rubbery zones but also the long time end of the glass transition zone. In the terminal zone the G' and G'' curves have, respectively, the slopes of 2.0 and 1.0, and shift to the lower frequency side and the rubbery plateau becomes longer and longer as the molecular weight increases.

All G' and G'' curves unite in the glass transition zone, excepting these for the sample MF13 having very low molecular weight. The G' curves for the samples having higher molecular weights manifest the rubbery plateau, whose intensity is about $3-6 \times 10^6$ dynes/cm².

Shift Factor a_T —Effect of Temperature

The shift factor a_T for the PMMA samples used in this study is plotted against temperature T in Figure 4. The large open circles in this

Figure 4. The logarithm of the shift factor a_T plotted against temperature for anionic PMMA. Large open circles represent the results for $M \geq M_C$ and other circles for the samples indicated.

figure represent results for the samples having molecular weights of 45200 and higher, while the other circles are those for the samples indicated. The shift factor is independent of molecular weight provided that the molecular weight exceeds a certain limiting value. This limiting value, about 40000, can be referred to as the critical molecular weight M_C and will be discussed in more detail later. For the polymers of lower molecular weight, the shift factor decreases with decreasing molecular weight, as has been reported for some other polymers.³

By the use of several parameters in the free volume theory,³ the WLF equation^{2,18} can be expressed as follows

$$\log a_T = \frac{-c_1^g(T - T_g)}{c_2^g + (T - T_g)} \quad (6)$$

$$\log a_T = \frac{-c_1^r(T - T_r)}{c_2^r + (T - T_r)} \quad (7)$$

In these equations, $c_1^g = 1/2.303f_g$, $c_2^g = f_g/\alpha_f$, $c_1^r = 1/2.303f_r$, $c_2^r = f_r/\alpha_f$, glass transition temperature T_g and the reference temperature T_r , where f_g and f_r are respectively the fractional free volume at T_g and T_r , α_f the temperature coefficient of the fractional free volume $f(T)$ defined by the following approximate equation above T_g

$$f(T) = f_g + \alpha_f(T - T_g) = \alpha_f(T - T_0) \quad (8)$$

T_r was chosen as 220°C in this study and T_0 is well known as the Vogel temperature. Eq 7 shows that the plot of $-(T - T_r)/\log a_T$ against $(T - T_r)$ should give a straight line and that the parameters can be evaluated from the slope and the intercept. The plots for anionic PMMA are given in Figure 5. The free volume parameters calculated from this figure are tabulated in Table III, and c_1^r and c_2^r are, respectively, 6.69 and 189.8 for the samples of high molecular weight. When T_g is assumed to be 105°C for PMMA,¹⁹ c_1^g and c_2^g can be calculated to be 16.98 and 74.76, respectively, for the same samples.

As seen from Table III, α_f increases with decreasing molecular weight below M_C , while

Figure 5. Linear plots of $-(T - T_r)/\log a_T$ vs. $(T - T_r)$ for anionic PMMA. The circles are used as in Figure 4.

Table III. Free volume parameters from the temperature dependence of the shift factor

Sample	M_w	α_f , deg $^{-1}$	T_0 , °C	f_{220}	T_r' , °C	f_g
MF2-10	≥ 45200	3.42×10^{-4}	30.2	0.065	220.0	0.026
MF11	35100	3.96×10^{-4}	37.1	0.073	200.8	(T_g , 105°C)
MF12	28400	4.20×10^{-4}	34.4	0.078	189.1	
MF13	11400	4.48×10^{-4}	34.4	0.083	178.9	

T_0 seems to be unchanged. This is in marked contrast to the case of the anionic polystyrenes of narrow molecular weight distribution used in the previous study,⁸ where α_f was constant while T_0 decreased. The value of f_g for the PMMA samples having molecular weights above M_C is 0.026, assuming $T_g = 105^\circ\text{C}$. This value compares well with the famous value of 0.025.

The reference temperature T_r' in Table III is the temperature at which the polymer having very low molecular weight has the same fractional free volume, namely, 0.065 as polymers having molecular weights above M_C at 220°C . At this temperature, each system has the same fractional free volume, and this state is often referred to as the iso-free-volume state.^{2,18}

Rheological Behavior in the Terminal Zone

The molecular weight dependence of the zero-shear viscosity η_0 for anionic PMMA at 220°C is shown by the open circles in Figure 6. The

dependence can be represented by a straight line having the slope of 4.4 in the higher molecular weight range. This slope is not only higher than the famous values of 3.4 but also higher than the value of 4.0 for the radical PMMA in the previous paper.¹²

The critical molecular weight M_C for the anionic PMMA cannot accurately be determined from Figure 6, but it is likely to be located between 30000 and 40000 which is not too different from the reliable values of 27500 and 31500, obtained by Fox, *et al.*³ The closed circles in Figure 6 represent the zero-shear viscosity at the temperature T_r' , or in the iso-free-volume state where $f = 0.065$. It is evident from Figure 6 that the molecular weight dependent of η_0 in the iso-free-volume state for the lower molecular weight PMMA can be represented by a straight line. It is also found that the molecular weight at the intersection of the two straight lines drawn in this figure is around 80000, being much higher than the M_C values so far published. This is in marked contrast to the case of the anionic polystyrenes⁸ studied previously, where M at the intersection was very close to M_C . This discrepancy is associated with the fact that the dependence of shift factor on molecular weight is very great for PMMA as shown in Figures 4 or 5. The reason why such a peculiar result is obtained for PMMA is not clear, but it appears probable that the critical molecular weight above which the free volume does not vary with molecular weight it not always the same as M_C . The molecular weight at which the shift factor decreases may not be directly related to M_C but rather only to the chemical structure of the polymer chains, because this high value of M_C (80000) is not believed to be correct based upon the curve at 220°C shown in Figure 6 and certain other reliable values.³

In Figure 7 is shown the molecular weight

Figure 6. Molecular weight dependence of zero-shear viscosity η_0 for anionic PMMA at 220°C (open circles) and at $f = 0.065$ (closed circles).

Figure 7. Molecular weight dependence of steady-state compliance J_e^0 and entanglement compliance J_{eN}^0 for anionic PMMA (open circles) at 220°C. Closed circles indicate the results for radical PMMA.

dependence of the steady-state compliance J_e^0 , calculated by eq 2, for the anionic PMMA, together with that for the radical PMMA studied in the previous paper.¹² It is clear from Figure 7 that J_e^0 of both the radical and anionic PMMA is roughly proportional to the molecular weight. The broken line drawn in the figure shows the prediction of the modified Rouse theory⁵ given eq 3. The proportionality between J_e^0 and M has also been found for polyvinyl acetate (PVAc) by Ninomiya, *et al.*,⁴ but not for several non-polar polymers, such as polystyrene and poly(α -methylstyrene), as has been revealed by recent investigations.⁶⁻¹¹ This discrepancy might be attributed to the polar groups in the polymer chains of PMMA and PVAc, though the effect of the branching in these materials should not be completely disregarded.

Rheological Behavior in the Rubbery Zone

As seen from Figure 2, all the G' curves do not show the flat rubbery plateau, and hence it difficult to determine the quasi-equilibrium modulus G_{eN}^0 accurately. According to Sanders, *et al.*,^{20,21} therefore, G_{eN}^0 was evaluated by the integration of G'' over values of $\ln \omega$ encompassing the maximum of G''

$$G_{eN}^0 = 1/J_{eN}^0 = \frac{2}{\pi} \int_{-\infty}^{a'} G'' d \ln \omega \quad (9)$$

In practice, the G'' vs. $\ln \omega$ curve was numerically integrated from $\ln \omega = -\infty$ to the maximum of G'' and the result was doubled. This

Table IV. Entanglement modulus and compliance, and entanglement spacings obtained by integration of the loss modulus

Sample	M_w	G_{eN}^0 , dyn/cm ²	J_{eN}^0 , cm ² /dyn	M_e
MF 2	342000	3.94×10^6	2.54×10^{-7}	10400
MF 3	270000	3.89×10^6	2.57×10^{-7}	10500
MF 5	197000	3.12×10^6	3.20×10^{-7}	13100
MF 6	158000	4.33×10^6	2.31×10^{-7}	9480
MF 8	96300	5.41×10^6	1.85×10^{-7}	7580
MF10	45200	6.07×10^6	1.65×10^{-7}	6760

convenient procedure produces no serious error.^{8,22} The calculated values of G_{eN}^0 and J_{eN}^0 , and also the value of M_e evaluated from eq 4 are tabulated in Table IV. It is clear from this table that G_{eN}^0 increases gradually, while M_e decreases with decreasing molecular weight. J_{eN}^0 , the reciprocal of G_{eN}^0 , is logarithmically plotted against molecular weight in Figure 7. The plot can be approximated by a straight line having the slope of 0.3, as seen in the figure. This molecular weight dependence of J_{eN}^0 and M_e in the entanglement region does not agree with the generally accepted viewpoint that $\partial \log J_{eN}^0 / \partial \log M = 0$ nor with the result obtained by us for the anionic polystyrene. As seen from Table IV, M_e ranges from 13100 to 6760, while M_C is estimated to be 30000–40000. Therefore, the ratio M_C/M_e is as high as 2–6, though it is about 2 for the usual non-polar polymers.⁸ The anomaly found in the molecular weight dependence of M_e and in the ratio M_C/M_e for PMMA may be attributed to the fact that the polarity affects the internal structure, due to the entanglement couplings between molecular chains in the liquid.

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REFERENCES

1. J. D. Ferry, Proc. 5th Intern. Congress on Rheology, Vol. 1, S. Onogi, Ed., University of Tokyo Press, Tokyo, 1969, p 3.
2. J. D. Ferry, "Viscoelastic Properties of Polymers", 2nd ed, John Wiley and Sons, Inc., New York, N.Y., 1970.
3. G. C. Berry and T. G. Fox, *Adv. Polym. Sci.*,

- 5, 261 (1968).
4. K. Ninomiya and J. D. Ferry, *J. Phys. Chem.*, **67**, 2292 (1963).
5. J. D. Ferry, R. F. Landel, and M. L. Williams, *J. Appl. Phys.*, **26**, 359 (1955).
6. A. V. Tobolsky, J. J. Aklonis, and G. Akovali, *J. Chem. Phys.*, **42**, 723 (1965).
7. G. Akovali, *J. Polym. Sci., Part A-2*, **5**, 875 (1967).
8. S. Onogi, T. Masuda, and K. Kitagawa, *Macromolecules*, **3**, 109 (1970).
9. H. Odani, S. Kitamura, N. Nemoto, and M. Kurata, *Rep. Prog. Polym. Phys. Japan*, **10**, 321 (1967).
10. T. Fujimoto, N. Ozaki, and M. Nagasawa, *J. Polym. Sci., Part A-2*, **6**, 129 (1968).
11. N. Nemoto, private communication.
12. S. Onogi, T. Masuda, and T. Ibaragi, *Kolloid-Z. Z. Polym.*, **222**, 110 (1968).
13. G. V. Schulz, H.-J. Cantow, and G. Meyerhoff, *J. Polym. Sci.*, **10**, 79 (1953); F. W. Billmeyer, Jr. and C. B. den Than, *J. Amer. Chem. Soc.*, **77**, 4763 (1955).
14. F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci.*, **44**, 173 (1960).
15. G. Natta, *J. Polym. Sci.*, **16**, 143 (1955).
16. R. L. Miller and L. E. Nielsen, *J. Polym. Sci.*, **46**, 303 (1960).
17. M. Horio, S. Onogi, and S. Ogihara, *J. Japan. Soc. Testing Mater.*, **10**, 350 (1961).
18. M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Amer. Chem. Soc.*, **77**, 3701 (1955).
19. W. A. Lee and G. J. Knight, "Polymer Handbook", J. Brandrup and E. H. Immergut, Ed., Interscience Publishers, New York, N.Y., 1966, p III-68.
20. J. F. Sanders, J. D. Ferry, and R. H. Valentine, *J. Polym. Sci., Part A-2*, **6**, 967 (1969).
21. J. F. Sanders and J. D. Ferry, *Macromolecules*, **2**, 440 (1969).
22. T. Masuda, K. Kitagawa, T. Inoue, and S. Onogi, *Macromolecules*, **3**, 116 (1970).