Viscoelastic Properties of Concentrated Solutions of Poly(methyl methacrylate) in Diethyl Phthalate

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ABSTRACT: The viscoelastic properties of concentrated solutions of poly(methyl methacrylate) in diethyl phthalate were measured by means of a concentric cylinder type rheometer and capillary viscometer.

The Vogel parameters, α_f and T_0 were calculated from the temperature dependence of viscosity and the shift factor a_T obtained from the time—temperature superposition. Moreover, the viscoelastic parameters characteristic of polymer liquids such as the zero-shear viscosity η_0, steady-state compliance J_e^0, and entanglement compliance J_{eN}^0 were evaluated from the frequency dependence of the storage shear modulus G' and the loss modulus G''.

With decreasing concentration, the Vogel temperature T_0 decreases at higher concentrations, but increases at lower concentrations after passing through a minimum at about 20 wt%. The temperature coefficient of the fractional free volume, α_f, however, is almost constant at and above 20 wt%, and then rapidly increases with decreasing concentration. This particular concentration of 20 wt% is very near the critical concentration of entanglement coupling.

η_0 is proportional to $w_2^{4.0}$, where w_2 is the weight fraction of polymer, in the iso-free-volume state, and this exponent 4.0 is equal to that for molecular weight, which was obtained from the molecular weight dependence of η_0. Both J_e^0 and J_{eN}^0 are proportional to w_2^{-2}, and J_e^0 is six times higher than J_{eN}^0 over the entire range of concentration where J_{eN}^0 can be evaluated.

KEY WORDS Concentrated Solution / Entanglement Coupling / Poly(methyl methacrylate) / Steady-State Compliance / Viscoelasticity / The Vogel Parameters /

In our previous papers[1-5] the viscoelastic properties of the binary blends of polymer in molten state have been measured extensively, and significant conclusions has been obtained about the dependence of the rheological properties of amorphous polymers upon molecular weight distribution. The main conclusions are summarized as follows: The Vogel temperature T_0 plotted against the weight fraction of the high molecular weight component, w_2, has a minimum at about $w_2=0.2$, while the temperature coefficient of fractional free volume, α_f, is almost constant over the entire range of w_2. The steady-

state compliance J_e^0 of the blend is proportional to w_2^{-2} when w_2 is near unity, and it decreasing w_2 after passing through a maximum at around $w_2=0.2$. The blend of the narrow-distribution polystyrenes prepared by anionic polymerization shows the "two-step" rubbery plateau,[4] indicating the existence of the two or three sets of relaxation mechanisms for entanglement slippage in the polymer blends. On the basis of these conclusions, it was suggested that Ninomiya's linear blending law should be modified into a quadratic blending law.[4,6] And also, it was emphasized that the rheological studies on concentrated polymer solutions would be very important to clearify the nature of entanglement coupling between macromolecular chains.[5,6]

In the present paper, the viscoelastic proper-

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ties have been measured for poly(methyl metha-crylate) solutions to determine the concentration dependence of the parameters such as T_0 and α_f, zero-shear viscosity η_0, steady-state compliance $J_e{}^0$, and so on.

EXPERIMENTAL

Materials

Poly(methyl methacrylate)s (PMMA) used in our previous study[3] were also employed in this study. The sample were prepared by bulk polymerization and fractionated.

The weight-average molecular weight M_w, number-average molecular weight M_n and their ratio for the PMMA samples are shown in Table I. As is evident from this Table, the

Table I. Weight- and number-average molecular weight and their ratio for poly(methyl methacrylate) samples

Sample	M_w	M_n	M_w/M_n
715	1.91×10^5	1.51×10^5	1.26
714	2.29×10^5	1.75×10^5	1.31

two samples have similar molecular weights and distributions. For the measurements of viscoelastic properties of the concentrated solutions, the sample 715 has been employed. And the sample 714 has been used for the measurements of zero-shear viscosity in the lower concentration range to evaluate the Vogel parameters.

Diethyl phthalate (DEP) has been used as the solvent. To prepare 40 wt% and more concentrated solutions, the mixture of PMMA and

Table II. Sample codes and weight fractions of poly(methyl methacrylate) solutions in diethyl phthalate(DEP) and bulk polymer

Sample	w_2	Sample	w_2
715	1.000	MC205	0.050
MC192	0.920	MC202	0.020
MC180	0.800	MC201	0.010
MC174	0.740	DEP	0.000
MC165	0.654		
MC150	0.500		
MC140	0.403		
MC130	0.300		
MC120	0.200		

DEP was first dissolved in benzene by stirring, and then benzene was removed by evaporation from the thin film of the solution. For preparation of solutions of lower concentration, PMMA was directly dissolved in DEP by stirring. The sample codes and the concentrations in weight fractions of polymer are tabulated in Table II. MC1 and MC2 denote the DEP solutions of 715 and 714, respectively. The last two figures of the sample code denote the weight per cent of polymer in solution.

Measurements

The measurements of viscoelastic properties of the MC1 series were carried out by means of the concentric cylinder type rheometer[7] at various temperatures. The Maron–Krieger–Sisko viscometer[8] was also used to measure the zero-shear viscosity of the MC2 series. These apparatuses are the same as those used in previous papers,[1-5] and the details of the apparatuses and measuring techniques are not described here.

The viscoelastic functions, the storage shear modulus G' and loss modulus G'' were calculated by the usual method. The frequency dependence curves of the viscoelastic functions at various temperatures have been superposed into respective master curves according to the time-temperature superposition principle.

RESULTS AND DISCUSSION

Effect of Temperature and the Vogel Parameters

The shift factor a_T for the MC1 series and the bulk polymer 715 is plotted against temperature in Figure 1. The reference temperature T_r was chosen arbitrarily for all the samples. The plot of $-(T-T_r)/\log a_T$ against $(T-T_r)$ for each sample can be represented by a straight line, and hence it is clear that the temperature dependence of the shift factor shown in this figure can be expressed by the following WLF type equation:[9]

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

The reference temperature T_r and two constants $c_1{}^r$ and $c_2{}^r$ in this equation are tabulated in Table III. It is well known[9,10] that the constants in the WLF type equation can be connected with the parameters in the free volume theory by the following relations:
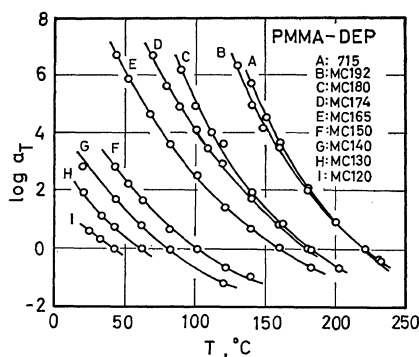
Figure 1. Temperature dependence of shift factor a_T for bulk PMMA (715) and its solutions (MC1 series).

$$c_1{}^r = B/2.303 f_r \qquad (2)$$

$$c_2{}^r = f_r/\alpha_f \qquad (3)$$

where B is the constant near unity, f_r is the fractional free volume at T_r, and α_f is the temperature coefficient of the fractional free volume. Equations 1—3 are valid when the fractional free volume f changes linearly with temperature difference from the constant temperature T_0, which is referred to as the Vogel temperature:[10]

$$f = \alpha_f (T - T_0), \qquad (T \geq T_g) \qquad (4)$$

The Vogel parameters α_f and T_0, and $T_r{}'$ calculated from eq 2, 3, and 4 are shown in Table III, where $T_r{}'$ is the temperature at which each solution has the same fractional free volume, 0.062, as that of bulk polymer 715 at 220°C. This condition is referred to as the iso-free-volume

Table III. Reference temperature T_r, the WLF constans $c_1{}^r$ and $c_2{}^r$, the Vogel parameters α_f and T_0, and the temperature, corresponding to $f=0.062$ for bulk PMMA (715) and its solutions (MC1 series)

Sample	T_r, °C	$c_1{}^r$	$c_2{}^r$	$\alpha_f \times 10^4$	T_0, °C	$T_r{}'$, °C
715	220	7.00	173	3.59	47.2	220
MC192	221	6.94	183	3.43	38.4	219
MC180	182	6.99	181	3.43	1.0	182
MC174	180	6.71	196	3.29	−16.0	169
MC165	160	6.50	209	3.20	−48.7	145
MC150	102	7.06	205	3.01	−103	104
MC140	83	6.99	195	3.19	−112	82.7
MC130	63	6.67	202	3.22	−139	53.5
MC120	43	6.25	205	3.39	−162	21.0
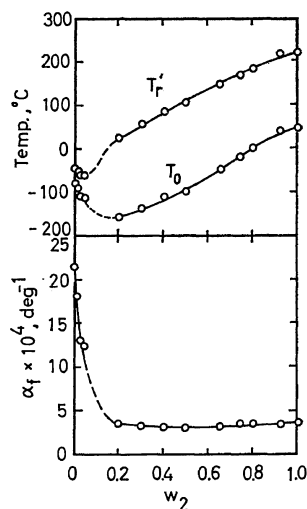
Figure 2. $T_r{}'$, T_0 and α_f plotted against weight fraction of polymer in solution for bulk PMMA (715), its solutions (MC1 and MC2 series) and the solvent DEP.

Table IV. Reference temperature T_r, the WLF constans $c_1{}^r$ and $c_2{}^r$ and the Vogel parameters α_f and T_0, for PMMA solutions (MC2 series) and the solvent DEP

Sample	T_r, °C	$c_1{}^r$	$c_2{}^r$	$\alpha_f \times 10^4$	T_0, °C
MC205	0	3.13	112	12.5	−112
MC202	0	2.98	111	13.1	−111
MC201	0	2.60	92.3	18.1	−92.3
DEP	0	2.42	84.1	21.4	−84.1

state, where each polymer in solution has the same monomeric friction factor ζ. Similar parameters evaluated from the temperature dependence of zero-shear viscosity are shown in Table IV for the MC2 series and the solvent, DEP. $T_r{}'$, T_0, and α_f are plotted against the weight fraction of polymer in solution, w_2, in Figure 2. With decreasing concentration, $T_r{}'$ and T_0 decrease at higher concentrations and after passing through a minimum they increase at lower concentrations. A similar behavior was observed also for T_0 of binary blends of PMMA.[5] The temperature coefficient of the fractional free volume, α_f, is almost constant at concentrations ranging from $w_2=1.0$ to 0.2, as is clearly seen in Figure 2. At lower concentrations, however, α_f increases rapidly with decreasing w_2. The critical concentration

of entanglement couplings is probably located at around $w_2=0.2$, as will be discussed later. From the results shown in Figure 2, it can be concluded that α_f of polymer solutions is almost constant in the entanglement region and changes in the lower concentration region where no continuous structure due to entanglements can be formed in the solution. This constancy of α_f is also reflected in the fact that the difference between T_r' and T_0, about 190°C, is constant, as seen from Figure 2. The fractional free volume of bulk PMMA at glass transition temperature T_g was calculated to be 0.021, assuming $T_g=105$°C. This value is close to the well-known value of 0.025 but different from the literature value of 0.013 for PMMA.[9]

Dependence of Viscoelastic Functions on Frequency

When we compare the frequency dependence curves of viscoelastic functions of polymer solutions at various concentrations, it is important to compare them in the iso-free-value state, where the monomeric friction factor is kept constant. In Figure 3 are shown the master
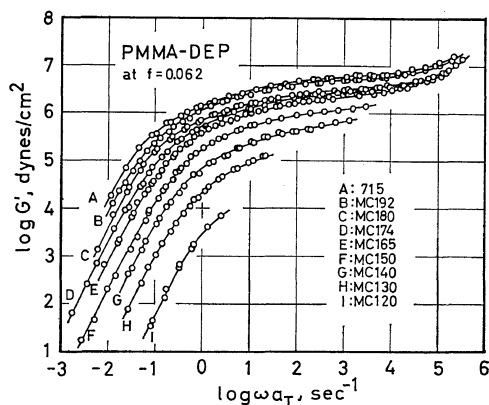

Figure 3. Master curves of G' for bulk PMMA (715) and its solutions (MC1 series) at $f=0.062$.

curves of G' for the polymer 715 and its solutions at different concentrations in the iso-free-volume state. The abscissa of the figure is the reduced angular frequency ωa_T, and the reference temperatures are tabulated in Table III as T_r'. As is evident from Figure 3, master curves for highly concentrated solutions show the rubbery plateau and terminal zone clearly. The height of the rubbery plateau becomes lower and lower,

and the terminal zone shift to the higher frequency side as the concentration decreases. It is not clear whether the G' curves for solutions of low concentrations, such as MC130 and 120, have the rubbery plateau or not. However, when we consider that the zero-shear viscosity η_0 is proportional to $w_2^{4.0}$ at w_2 between 0.2 and 1.0 in the iso-free-volume state as described below, such curves must have the rubbery plateau.
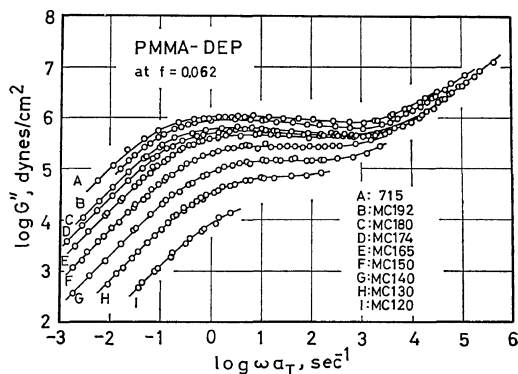

Figure 4. Master curve of G'' for bulk PMMA (715) and its solutions (MC1 series) at $f=0.062$.

This suggests that the critical concentration for entanglement couplings is located at about $w_2=0.2$. The master curves for the loss modulus G'' at $f=0.062$ are shown in Figure 4. The frequency dependence curves of G'' for samples having higher concentrations show maxima in the intermediate region between the terminal and rubbery zones. Such maxima enable us to evaluate the pseudo-equilibrium modulus by the integration method proposed by Sanders, *et al.*[11] The results will be discussed later.

Viscoelastic Properties in the Terminal Zone

The concentration dependence of the zero-shear viscosity η_0 for PMMA solutions is shown in Figure 5, where η_0 is defined by
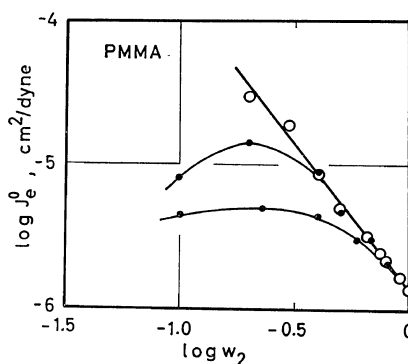
$$\eta_0=\lim_{\omega\to0} G''/\omega \qquad (5)$$

In this figure, the closed and open circles represent, respectively, the zero-shear viscosities for the solutions at a constant temperature, $T=220$°C, and in the iso-free-volume state, where $f=0.062$. As the abscissa, the weight fraction of polymer, w_2, is employed instead of $\rho_s w_2$ or volume fraction of polymer, ϕ_2, where
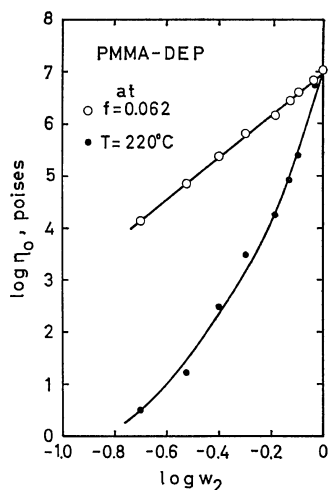
Figure 5. Concentration dependence of zero-shear viscosity η_0 for PMMA solutions in DEP at 220°C (closed circles) and $f=0.062$ (open circles).

Figure 6. Concentration and composition dependence of steady-state compliance $J_e{}^0$ for PMMA solutions in DEP (open circles) and binary blends of PMMA (closed circles).

ρ_s is the density of the solution. The densities of the solvent DEP and the solute polymer PMMA are respectively 1.12 and 1.17 at room temperature. Thermal expansion coefficient of these solutionscan be estimated to be around 5×10^{-4} from the α_f values shown in Table III and Figure 2. Therefore the density of each solution at 220°C is close to unity, and w_2, $\rho_s w_2$ and ϕ_2 give almost the same value when we assume the additivity of volume in mixing. Hence the use of these different expressons for concentration as the abscissa bears no serious difference in the concentration dependence curves of the visco-elastic parameters which will be discussed hereafter.

As shown in Figure 5, the concentration dependence of η_0 at 220°C (closed circles) gives a smooth curve, and its slope varies from 4 at lower concentrations to 17 at higher concentrations. The plots of $\log\eta_0$ against $\log w_2$ in the iso-free-volume state at $f=0.062$, however, can be represented by a straight line having the slope of 4.0 over the entire range of concentration. This value of the exponent of w_2 coincides well with that of the molecular weight (M) dependence, $\eta_0\propto M^{4.0}$, found previously.[3] This behovior of η_0 seems to support the suggestion by Fox, et al.[10] that η_0 can be expressed by power dependence of $(M\phi_2)$: η_0 should be proportional to $(M\phi_2)^{4.0}$ in this case.

In Figure 6 is shown the concentration dependence of the steady-state compliance $J_e{}^0$ defined by

$$J_e{}^0=\lim_{\omega\to0} G'/(\omega^2\eta_0{}^2) \qquad (6)$$

for the solutions (open circles) and the two binary blend series of PMMA (closed circles) reported in a previous paper.[5] In the case of blends, w_2 denotes the weight fraction of the high molecular weight component having similar molecular weight and distribution to the sample 715 employed in this study. It is clear from Figure 6, that the dependence of $J_e{}^0$ on w_2 for the solutions can be represented by a straight line having the slope of -2, which is the asymptote of the curves for the blends. This behavior of $J_e{}^0$ strongly supports our view[4,5]

Table V. Numerical values of zero-shear viscosity η_0 at $f=0.062$, steady-state compliance $J_e{}^0$ and iso-thermal viscosity $\eta_0{}^{220}$ for bulk PMMA (715) and its solutions (MC1 series)

Sample	η_0, poise	$J_e{}^0$, cm²/dyn	$\eta_0{}^{220}$, poise
715	1.06×10^7	1.33×10^{-6}	1.06×10^7
MC192	6.92×10^6	1.67×10^{-6}	6.34×10^6
MC180	4.05×10^6	2.13×10^{-6}	2.57×10^5
MC174	2.85×10^6	2.46×10^{-6}	8.40×10^4
MC165	1.50×10^6	3.11×10^{-6}	1.77×10^4
MC150	6.40×10^5	4.88×10^{-6}	3.01×10^3
MC140	2.30×10^5	8.32×10^{-6}	3.00×10^2
MC130	7.00×10^4	1.84×10^{-5}	1.45×10
MC120	1.40×10^4	2.93×10^{-5}	3.19×10

that polymer blends and solutions should manifest similar viscoelastic behavior at long time scales. The numerical values of η_0 at $f=0.062$, $J_e{}^0$, and iso-thermal viscosity $\eta_0{}^{220}$, at $220°C$ are tabulated in Table V for the bulk polymer 715 and its solutions.

Viscoelastic Properties in the Rubbery Zone

The preudo-equilibrium modulus of the entanglement network, G_{eN}^0, denotes the height of the rubbery plateau in the frequency dependence curve of G'. The value of G_{eN}^0 can be related to the average molecular weight between entanglement coupling loci, M_e, by

$$G_{eN}^0 = g_N \rho RT/M_e = 1/J_{eN}^0 \qquad (7)$$

where g_N is a numerical factor not far from unity and ρ is the density of polymer for which $\rho_s w_2$ should be used for polymer solutions, where ρ_s is the density of the solution. J_{eN}^0, of reciprocal of G_{eN}^0, is often referred to as the entanglement compliance.[9]

As seen from Figure 3, all the G' curves do not show flat rubbery plateaus, and hence it is difficult to determine the value of G_{eN}^0 from the plateau accurately. In this study therefore the value of G_{eN}^0 was evaluated by the following integration method proposed by Sanders, et al.[11]

$$G_{eN}^0 = \frac{2}{\pi} \int_{-\infty}^{a'} G'' \, d\ln \omega \qquad (8)$$

The integration of G'' is carried out over values of $\ln \omega$ encompassing the maximum of G''.[4] The calculated values of G_{eN}^0 and J_{eN}^0 and also of M_e are shown in Table VI. The value of J_{eN}^0 for the bulk PMMA 715, $2.15 \times 10^{-7} \, cm^2/dyne$, is consistent with the result reported in our previous paper,[5] which showed that the J_{eN}^0 was slightly dependent upon the molecular weight. In Figure 7, the concentration dependence of J_{eN}^0 for PMMA solutions is compared with that of the steady-state compliance $J_e{}^0$. Each parameter can be represented by a straight line having the slope of -2. This means that both $J_e{}^0$ and J_{eN}^0 are proportional to $w_2{}^{-2}$ and that the average molecular weight between entanglement coupling loci, M_e, increases in proportion to the reciprocal of w_2. $J_e{}^0$ is six times higher than J_{eN}^0 for the PMMA solutions at and

Table VI. Pseudo-equilibrium modulus G_{eN}^0, entanglement compliance J_{eN}^0 and average molecular weight between entanglement coupling loci, M_e, for the bulk PMMA (715) and its solutions (MC1 series)

Sample	G_{eN}^0, dyn/cm²	J_{eN}^0, cm²/dyn	M_e
715	4.66×10^6	2.15×10^{-7}	8.79×10^3
MC192	4.18×10^6	2.39×10^{-7}	9.03×10^3
MC180	2.88×10^6	3.47×10^{-7}	1.14×10^4
MC174	2.43×10^6	4.11×10^{-7}	1.25×10^4
MC165	2.02×10^6	4.95×10^{-7}	1.32×10^4
MC150	1.12×10^6	8.89×10^{-7}	1.82×10^4
MC140	6.93×10^5	1.56×10^{-6}	2.56×10^4
MC130	3.29×10^5	3.04×10^{-6}	3.74×10^4
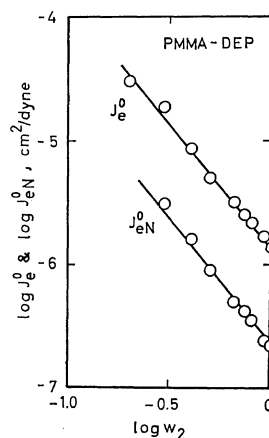
Figure 7. Concentration dependence of steady-state compliance $J_e{}^0$ and entanglement compliance for PMMA solutions in DEP.

above $w_2 = 0.3$.

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