Steady Flow Properties of Monodisperse Polymer Solutions. Molecular Weight and Polymer Concentration Dependences of Steady Shear Compliance at Zero and Finite Shear Rates

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ABSTRACT: Shear-stress and primary normal-stress differences in solutions of monodisperse poly(α-methylstyrenes) are measured by a Weissenberg rheogoniometer. Steady shear viscosity and compliance are given in terms of molecular weight and polymer concentration at various shear rates. The steady shear compliance at zero shear rate J_e for different molecular weights and concentrations can be expressed by a universal line of log (J_e/M^2) *vs.* log (CM), which is composed of two straight lines with slopes of 1 and 2. The intersection of the two straight lines is at $CM = 1.35 \times 10^5$ (g/ml). A molecular interpretation of this relationship is given. In addition, the effect of shear rate on the molecular weight and concentration dependences of the apparent steady shear compliance is discussed by taking into account the change in entanglement density with shear rate.

Simultaneous determination of steady shear viscosity and compliance is useful to clarify the rheological properties of linear polymer in terms of polymer characteristics. The former is a measure of energy dissipation and the latter is a measure of energy storage.[1] A number of both experimental and theoretical studies on steady shear viscosity have been accumulated. The dependence of steady shear viscosity on temperature, molecular weight, concentration, and imposed deformation rates has been fairly well clarified.[2,3] Compared with the study on viscosity, however, studies of steady shear compliance are less extensive, probably because of difficulties in measurement. Several measurements have been tried by various investigators using different methods, and a review on those results was given by Ferry[4] and Osaki, Einaga, Kurata and Tamura.[5]

The Weissenberg rheogoniometer, which is used in the present work, is one of the most powerful apparatus for studying steady shear compliance, since it is possible to observe the primary normal stress difference $P_{11} - P_{22}$ at various shear rates in addition to shear stress P_{21}. Both the non-Newtonian viscosity and the apparent steady shear compliance J_s defined by

$$J_s = (P_{11} - P_{22})/2P_{21}^2 \qquad (1)$$

can be calculated from the measurements based on the theory of second-order fluids.[1] J_s is equal to the equilibrium compliance J_e at the limit of zero shear rate, which was shown to be a measure of energy storage in the solution.[1] Except at the limit of zero shear rate, the meaning of J_s is not very clear, but it may be reasonable to proceed by assuming that J_s is also a measure of energy storage at any rate of shear. It has been experimentally confirmed[6-8] that the values of J_e obtained from eq 1 agree well with the values determined from the storage component of the complex shear modulus at the limit of zero frequency. The Weissenberg rheogoniometer, however, cannot be used for materials with very long relaxation times. Therefore, for measurements in highly concentrated solutions of linear polymers, one should use solvents with low viscosity at relatively high temperatures.

At the limits of low and high concentrations of "linear" polymer solutions, two types of dependence of J_e on molecular weight M and concentration C have been reported. In a range of (low) concentration, J_e shows the so-called "Rouse-like behavior," while in the other J_e behaves "like that of cross-linked networks." The behavior of J_e in dilute solutions was extensively studied by Ferry and his coworkers,[9] Ashare,[10] and Endo, Fujimoto, and Nagasawa.[11] J_e for undiluted polymers and higher concentrated polymers was reported by Akovali,[12] Onogi,[13] Nemoto,[14] Einaga,[15] and Fujimoto, *et al.*[16] Some investigators showed that J_e of linear polymer solutions moves from one type of J_e to the other as a smooth function of concentration or molecular weight. Recently, however, Einaga, *et al.*,[15] showed an interesting behavior of J_e in which a maximum is observed in the double logarithmic plot of J_e *vs.* concentration: that is, J_e shows a transition at a concentration of polymer, and the transition point depends on molecular weight.

The main purpose of this paper is to present further data on the molecular weight, concentration, and also shear rate dependences of J_s and to present a molecular interpretation of J_s.

Experimental Section

Materials. The (nearly) monodisperse poly(α-methylstyrene) samples used in this work were prepared by an anionic polymerization method.[17] Low and high molecular weight tails were removed

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TABLE I
THE SAMPLES

Sample no.	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$
PαS-001		6.02
PαS-3	14.2	14.5
PαS-6	43.8	44.4
PαS-9	118	119
PαS-12		182
PαS-13		330

by two fractional precipitations from benzene or toluene solution with addition of methanol. These samples are the same as used in previous papers,[11,18–23] and the details of their molecular characteristics were reported previously.[11,17,18,21] The samples were freeze-dried, followed by drying *in vacuo* at 50°. The molecular weights of six samples used are listed in Table I. These values were determined by light scattering and osmometry in a previous work.[18] Because of the independent purification of the samples, the molecular weights may be slightly changed, but the difference is believed to be negligible since the molecular weight distributions of the unfractionated samples are very sharp. The purification of sample PαS-6 was done by Dr. Endo previously.[11] Moreover, the tacticity of PαS-001 may be a little different from that of the other samples because of its low molecular weight.[18]

The solvent, α-chloronaphthalene, was obtained from Wako Pure Chemical Industrials, Ltd., and was purified by distillation at a reduced pressure (3.5×10^{-4} mm, 80°). The density and viscosity of the solvent were 1.1844 g/ml and 2.82×10^{-2} P, respectively, at 30°. Densities and viscosities at this and other temperatures as needed were determined by pycnometers and capillary viscometers.

Solutions were made up by weight and converted to C (g/ml) by assuming additivity of the specific volumes of polymer and solvent. An original solution of a high concentration was first prepared and sequentially diluted to lower concentrations by weight. The original solutions were prepared by heating the mixtures of weighted amount of polymer and solvent at 50° for about 3 weeks with protection from sunlight. Also, gentle stirring a few times a day at 80° by a magnetic stirring chip operated manually was employed in making the solution, to prevent degradation of the samples. Moreover, methylene chloride was added to accelerate the dissolution and later removed by evaporation under high vacuum. The concentration ranges of the solutions were between 0.03 and 0.55 g/ml.

Measurement. The Weissenberg Model R-17 rheogoniometer with a gap servo system, manufactured by Sangamo Controls Ltd., was used. It is a cone-and-plate viscometer with a facility for normal force measurement. Experiments were generally carried out according to the instruction manual supplied by the manufacturer,[24] as reported in previous papers.[7,11] The temperature was held at 50.0 ± 0.1° for solutions of high viscosity and at 30.0 ± 0.1° for those of low viscosity. In the present work, platens of 5-cm diameter and with 4° and 2° angles were used with a torsion bar of 2-mm diameter.

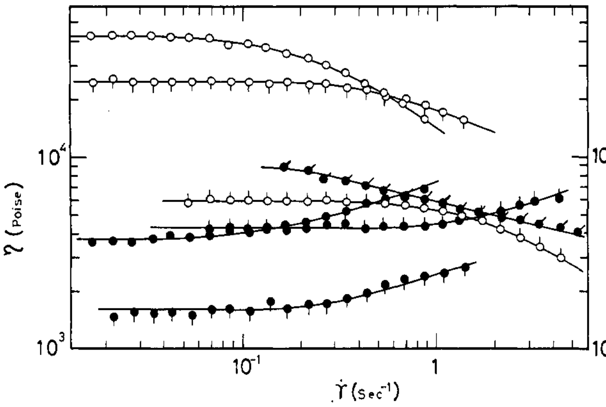

Figure 1. Examples of shear rate dependence of steady shear viscosity η and apparent steady shear compliance J_s. Open circles denote η, while filled circles denote J_s. (○) PαS-13, 0.188 g/ml, 50°; $(\overset{|}{\circ})$ PαS-12, 0.192 g/ml, 50°, $(\underset{|}{\circ})$ PαS-9 0.268 g/ml, 50°, $(\overset{/}{\circ})$ commercial polydisperse polystyrene, 0.1989 g/ml, 30°. The solvents used are α-chloronaphthalene for the former three and a chlorinated diphenyl for the last experiment.

The various problems coherent with the Weissenberg rheogoniometer of Sangamo Controls Ltd. have been discussed in previous papers.[7,25] Although there are several published criticisms on the instrument, it is our opinion that the reliability has been confirmed by (1) the agreement of the values of J_e calculated from eq 1 with those from the storage component of complex shear modulus[7] and (2) the satisfactory agreement between the values obtained with platens of 4° and 2° angle. The development of flow instability at high shear rates, which causes exudation of the solution from the gap, limited our experimental range. The shear rates for all solutions lay within the range 1×10^{-2} through 2×10^{2} sec⁻¹. Degradation of the polymer samples due to high shear stress during the measurements was found negligible by measuring intrinsic viscosity $[\eta]$ of the highest molecular weight polymer (PαS-13) before and after the rheological measurements. The agreement of those intrinsic viscosities was within experimental error.

Results

Steady shear viscosity η and compliance J_s were calculated from shear stress and normal stress differences observed, using conventional equations such as eq 1. Examples of η and J_s are shown as functions of shear rate $\dot{\gamma}$ in Figure 1. J_s for monodisperse poly(α-methylstyrene) samples increases with increasing shear rate, whereas that of a commercial polydisperse polystyrene decreases with shear rate, in agreement with previous results.[11,26] Moreover, it is to be pointed out that the limiting value of J_s at low $\dot{\gamma}$ can be determined without difficulty if we use the polymers with narrow molecular weight distribution but cannot easily be determined with polydisperse polymers.[8,11]

The quantities η^0 and J_e for all samples at zero shear rate are listed in Table II. The values of η^0 for various molecular weight samples are plotted logarithmically against polymer concentration C (g/ml) in Figure 2. The data of η^0 at 30° were converted to the values at 50° by using a multiplying factor determined from comparisons of η^0 for the same samples at 30° and 50°. Therefore, the converted values may include an uncertainty, but it would be negligible for the present purposes. Superposition of the data in Figure 2 was tried by shifting them along both polymer concentration and viscosity axes. The superposition is not successful, however, over the entire range of experiments. Only in each range of high and low concentrations can the superposition be successfully carried out by shifting the curves along log η^0 axis at

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TABLE II
STEADY FLOW VISCOSITY AND COMPLIANCE AT ZERO RATE OF SHEAR

Sample	$C \times 10^2$, g/ml	Temp, °C	η^0, P	J_e, cm²/dyn
PαS-001	56.62	50.00 ± 0.05	2.84×10^4	4.64×10^{-6}
	51.37	50.0 ± 0.01	3.42×10^3	1.60×10^{-6}
	46.69	50.0 ± 0.1	7.61×10^2	2.45×10^{-6}
	42.16	50.0 ± 0.1	1.69×10^2	2.50×10^{-6}
	35.33	30.0 ± 0.1	1.12×10^2	3.12×10^{-6}
	28.76	30.0 ± 0.1	1.79×10	
	13.44	30.0 ± 0.1	7.20×10^{-1}	
	7.22	30.0 ± 0.1	1.55×10^{-1}	
PαS-3	50.35	50.0 ± 0.1	1.81×10^4	5.72×10^{-6}
	46.93	50.00 ± 0.05	5.13×10^3	5.30×10^{-6}
	42.71	50.0 ± 0.1	1.39×10^3	3.92×10^{-6}
	38.72	50.0 ± 0.1	4.09×10^2	4.40×10^{-6}
	34.55	50.0 ± 0.1	1.24×10^2	4.53×10^{-6}
	28.90	30.0 ± 0.1	9.21×10	6.42×10^{-6}
	23.76	30.0 ± 0.1	2.24×10	7.70×10^{-6}
	11.98	30.0 ± 0.1	1.20	
	5.94	30.0 ± 0.1	2.32×10^{-1}	
PαS-6	36.23	50.0 ± 0.1	7.06 ± 10^3	8.93×10^{-6}
	33.58	50.00 ± 0.05	3.30×10^3	8.82×10^{-6}
	30.62	50.00 ± 0.07	1.29×10^3	1.20×10^{-5}
	27.67	50.00 ± 0.05	5.60×10^2	1.45×10^{-5}
	24.56	50.0 ± 0.1	2.12×10^2	1.54×10^{-5}
	20.73	50.0 ± 0.1	7.40×10	2.0×10^{-5}
	17.18	50.00 ± 0.03	2.37×10	2.45×10^{-5}
	17.18	30.0 ± 0.1	4.80×10	2.00×10^{-5}
	8.70	30.0 ± 0.1	2.64	
	4.37	30.0 ± 0.1	4.53×10^{-1}	
PαS-9	29.00	50.00 ± 0.05	4.51×10^4	1.78×10^{-5}
	26.81	50.00 ± 0.05	2.45×10^4	1.89×10^{-5}
	24.40	50.0 ± 0.1	1.10×10^4	2.68×10^{-5}
	22.19	50.0 ± 0.1	5.59×10^3	2.77×10^{-5}
	19.84	50.0 ± 0.1	2.45×10^3	4.10×10^{-5}
	16.62	50.0 ± 0.1	8.35×10^2	5.35×10^{-5}
	13.86	50.0 ± 0.1	2.88×10^2	8.00×10^{-5}
	11.32	50.00 ± 0.05	9.81×10	1.18×10^{-4}
	9.22	50.0 ± 0.1	3.73×10	1.38×10^{-4}
	7.56	50.0 ± 0.1	1.55×10	1.71×10^{-4}
	6.73	30.00 ± 0.05	1.64×10	2.10×10^{-4}
	6.02	30.0 ± 0.2	1.06×10	2.50×10^{-4}
PαS-12	23.10	50.00 ± 0.07	2.09×10^4	2.90×10^{-5}
	21.04	50.0 ± 0.1	1.34×10^4	3.82×10^{-5}
	19.18	50.00 ± 0.1	5.82×10^3	4.22×10^{-5}
	17.37	50.0 ± 0.1	3.28×10^3	4.85×10^{-5}
	14.73	50.0 ± 0.1	1.18×10^3	7.53×10^{-5}
	12.34	50.0 ± 0.1	4.47×10^2	1.03×10^{-4}
	10.05	50.0 ± 0.1	1.56×10^2	1.52×10^{-4}
	8.21	50.0 ± 0.1	5.91×10	2.28×10^{-4}
	6.76	50.0 ± 0.1	2.47×10	2.70×10^{-4}
	5.03	50.0 ± 0.1	7.42	3.60×10^{-4}
	4.50	30.0 ± 0.1	8.15	5.10×10^{-4}
	4.04	30.0 ± 0.1	5.8	5.30×10^{-4}
PαS-13	20.05	50.00 ± 0.07	7.24×10^4	3.50×10^{-5}
	18.76	50.0 ± 0.1	4.26×10^4	3.80×10^{-5}
	17.06	50.0 ± 0.1	2.43×10^4	6.25×10^5
	15.52	50.0 ± 0.1	1.40×10^4	6.72×10^{-5}
	13.16	50.0 ± 0.1	5.33×10^3	9.05×10^{-5}
	11.03	50.0 ± 0.1	2.07×10^3	1.43×10^{-4}
	8.95	50.0 ± 0.1	7.13×10^2	2.14×10^{-4}
	7.33	50.0 ± 0.1	2.61×10^2	3.02×10^{-4}
	5.88	50.0 ± 0.1	8.97×10	4.80×10^{-4}
	4.02	50.0 ± 0.1	1.66×10	9.18×10^{-4}
	3.58	30.0 ± 0.1	1.75×10	1.10×10^{-3}
	3.21	30.0 ± 0.1	1.15×10	1.18×10^{-3}
	2.85	30.0 ± 0.2	7.57	1.40×10^{-3}

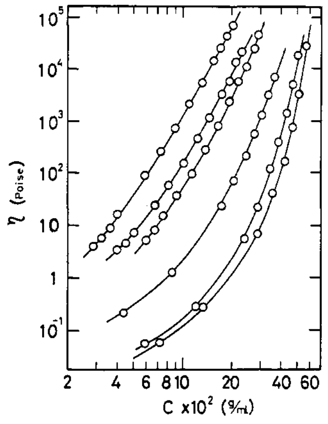

Figure 2. Polymer concentration dependence of η^0 at the limit of zero shear rate for samples with different molecular weights. The samples are PαS-13, -12, -9, -6, -3, and -1, from top to bottom. Temperature 50°.

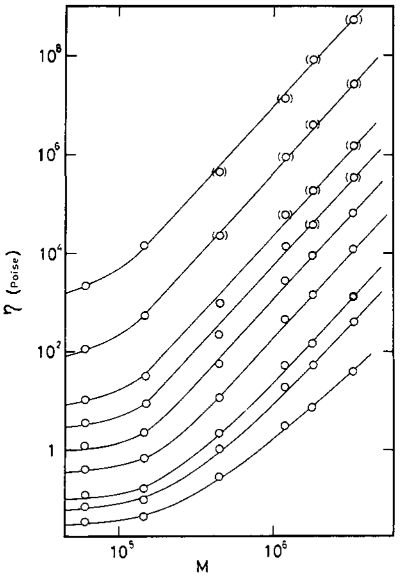

Figure 3. Molecular weight dependence of η^0 at various polymer concentrations. Concentrations are 0.500, 0.400, 0.300, 0.250, 0.200, 0.150, 0.100, 0.080, and 0.050 g/ml, from top to bottom. Temperature 50°. Parentheses denotes the values estimated from the superposition curve.

constant concentrations. Then the shift factor is found to be exactly proportional to $M^{3.4}$ in the range of high concentrations and approximately to M in the range of low concentrations. The molecular weight dependence of η^0 at various selected concentrations is illustrated in Figure 3, in which the values of η^0 for the samples with high molecular weights at high concentrations were estimated from the superposition curve. The lines in the high molecular weight range, except at three low concentrations, were drawn with the slope 3.4.

J_e is plotted against C for six molecular weights in a double logarithmic scale in Figure 4, in which the data published previously for the same samples are also shown. The data at C = 0.0259 and 0.0896 (g/ml) were obtained for Kanechlor (a chlorinated diphenyl) solutions by using the same rheogoniometer.[11] The datum for an undiluted amorphous polymer was previously determined by stress relaxation experiments at 186°.[16] This coincidence between the values determined by different experimental techniques may confirm the reliability of the values obtained here. All data of J_e

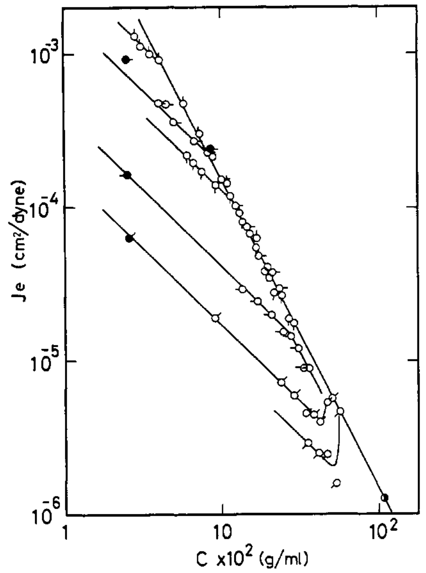

Figure 4. Polymer concentration dependence of J_e at the limit of zero shear rate. Samples are (O) PαS-13, (O-) PαS-12, (O) PαS-9, (—O) PαS-6, (O) PαS-3, (O) PαS-001. Temperature 50°. Filled circles denote the values of J_e in Kanechlor reported previously.[11] The half-filled circle denotes the value for undiluted samples with high molecular weights reported previously.[16]

at different temperatures were reduced to the values at 50° by multiplying $T\rho/(273 + 50)\rho_0$, where ρ and ρ_0 are the densities at the (absolute) temperature of measurement T and 50°, respectively.[9] The data in Kanechlor extend the data in α-chloronaphthalene to lower concentrations, reinforcing the conclusion that J_e does not depend on the choice of solvent so long as good solvents are used. This conclusion is the same as that of Kusamizu, Holmes, Moore, and Ferry.[9] In the high concentration range, J_e becomes independent of molecular weight and is proportional to the inverse square of polymer concentration C^{-2}. In the low concentration range, J_e is an increasing function of molecular weight and is proportional to inverse concentration of polymer; that is, a critical point is found for J_e. Near the critical point, J_e for samples PαS-001 and PαS 3 shows an abnormal, jump, as reported by Einaga, *et al.*,[15] but no abnormality was found for the other samples.

The appearance of the solutions in the range of the abnormal jump of J_e was entirely different from the other solutions and was like a jelly. When the solution is settled in a viscometer of U type[27] at room temperature (15°) and about 30-mm pressure difference (Δh) is applied between two menisci on both sides of the U tube, the menisci of the solution do not move at all over a day, whereas the other ordinary solutions flow without any abnormality. Although reasons for the abrupt change in the solution behavior are not clear and also we are not sure whether the abnormal peak in Figure 4 has the same origin as the peak found by Einaga, *et al.*,[15] it is certain that our Weissenberg rheogoniometer is incapable of measuring the viscoelastic properties of the solutions with such long relaxation times. We decided to neglect the abnormal peak in this paper. In practice, it is found that the solution structure is destroyed even at very low shear rates. Moreover, if the temperature of the solution in the viscometer of the U type is raised at a rate of 18°/hr, the meniscus *vs.* temperature plot shows a breaking point, as shown in Figure 5. Therefore, it may be speculated that the abnormal peak in the data for sample PαS-001 at C = 0.6067 g/ml would disappear if the experiments were carried out above 64°.

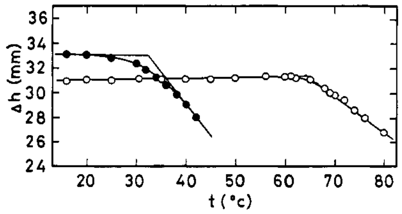

Figure 5. Flow test for two solutions of sample PαS-001. Polymer concentration: (○) 0.6067 g/ml, (●) 0.4970 g/ml. Rate of temperature increase 18°/hr.

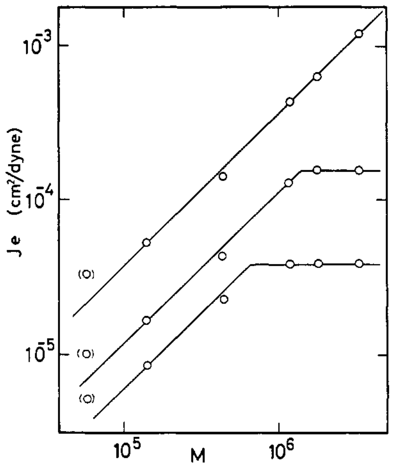

Figure 6. Molecular weight dependence of J_e at various polymer concentrations estimated from Figure 4. Polymer concentrations are 0.030, 0.100, and 0.200 g/ml from top to bottom. Temperature 50°. Parentheses denotes the value for PαS-001, which has a little different tacticity.

J_e at some selected concentrations is determined by interpolation of the data in Figure 4 and is plotted against M in a double logarithmic scale in Figure 6. In the lower polymer concentration range, J_e is proportional to M, in agreement with previous results.[4,9–11] If the concentration is high and/or if the molecular weight is high enough, J_e is independent of M. This is also in agreement with previous results.[12–15]

Moreover, it is important to show that all data of J_e in Figure 4 can be superposed on a single line if replotting them as log (J_e/M^2) *vs.* log CM, as shown in Figure 7. The universal line is made of two straight lines which show two features explained above, respectively. The transition from one region to the other occurs at a breaking point. The data for Pα S-6 make the transition less clear in Figure 7, but those data deviate from the other ones in Figure 4, too, because of unknown reasons.

In Figure 8, the apparent steady shear compliance J_s for sample PαS-13 at finite shear rates is plotted against C in a double logarithmic scale. If the shear rate is high enough, J_s appears to be proportional to C^{-1} over the whole range of polymer concentration. That is, at high shear rates, J_s for concentrated polymer solutions appears to behave like that for dilute solutions. If the shear rate is not high enough, however, J_s shows very interesting behavior, as seen in Figure 8; it again deviates from the line of $J_e \propto 1/C^2$ as the shear rate is

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[27] A. Takahashi, T. Nakamura, and I. Kagawa, *Polym. J.*, 3, 207 (1972).

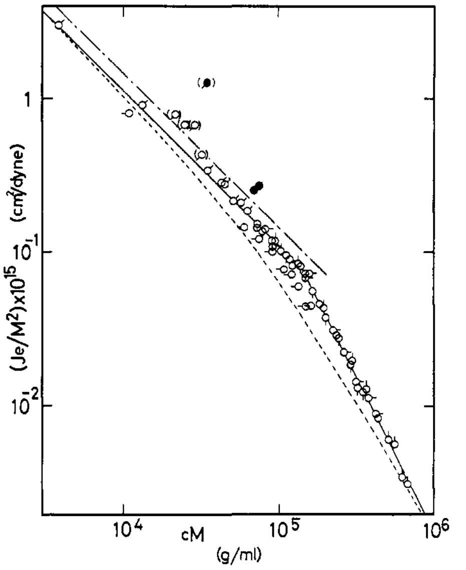

Figure 7. Plot of log (J_e/M^2) *vs.* log (CM) at 50°. Symbols are the same as in Figure 4. Filled circles denote the values obtained for the samples having a gel-like structure. The data of PαS-001, which has a little different tacticity, are emphasized by parentheses. The chain line denotes the values calculated from the Rouse theory and the broken line denotes the values calculated from eq 4 with $\alpha_1 = 7.45 \times 10^{-1}$ and $\alpha_2 = 7.12 \times 10^{-6}$.

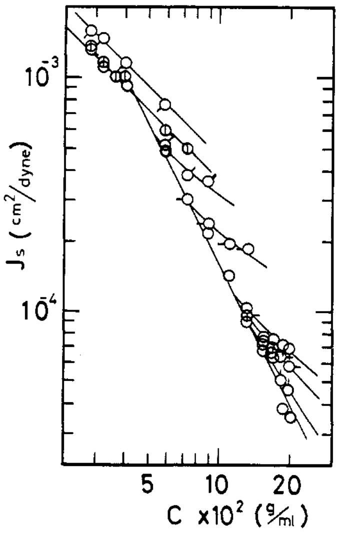

Figure 8. Polymer concentration dependence of the apparent steady shear compliance J_s at finite shear rates. Sample, PαS-13. Shear rates are 100, 50.0, 20.0, 5.00, 1.00, 0.700, and 0.300 sec^{-1} from top to bottom. Temperature 50°.

increased. The deviation depends on the shear rate applied. This effect of shear rate on log J_s *vs.* log C plot is similar to the shear rate dependence of log η *vs.* log M plot reported previously.[2,28-32]

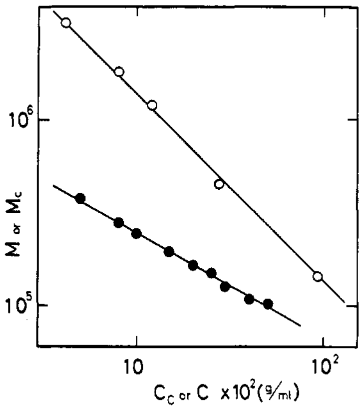

Figure 9. Molecular weight dependence of critical concentration C_c and polymer concentration dependence of critical molecular weight M_c. Open and filled circles denote the values determined from J_e and η^0, respectively.

Discussion

A. At the Limit of Zero Shear Rate. It was well established that linear polymer chains entangle each other when the molecular weight of the polymer is higher than a critical value and, hence, a breaking point is observed in the viscosity–molecular weight relationship. Similar critical points are also observed in the steady shear compliance–molecular weight or concentration relationship (Figures 6 and 7). This is understandable because the solution should show an elasticity similar to that of cross-linked networks if enough entanglements are made among polymers. That is, the η *vs.* M relationship may give the critical point for entanglement formation, whereas the J_e *vs.* M or J_e *vs.* C relationship may give the critical point for entanglement network formation. Therefore, the critical molecular weight in the η–M relationship should not generally agree with that in the J_e–M relationship.

In solution, moreover, the critical molecular weight M_c must be a function of polymer concentration. If the concentration is high enough so that entanglement junctions are distributed uniformly over the solution, the average number of entanglement points per molecule E may be proportional to the product CM, as was pointed out by Graessley and Segal.[2,26] The approximate values of the critical molecular weight determined from the viscosity data in Figure 3, M_c^{η}, are plotted against C in the double logarithmic scale in Figure 9. The corresponding critical molecular weight, M_c^J, can be determined from the J_e *vs.* M plots in Figure 6. More directly, however, the corresponding critical concentration C_c^J, which has the same physical meaning as the critical molecular weight M_c^J $(CM_c^J = C_c^JM)$, can be determined from J_e data in Figure 4. The values of C_c^J are also plotted against M in Figure 9. The values of C_c^J for samples PαS-001 and PαS-3 were estimated from the intersection of two straight lines, neglecting the abnormal ranges.

In Figure 9 we can easily see that: (1) the number of entanglement points per molecule calculated from M_c^{η} is much less than that calculated from M_c^J or C_c^J; (2) it is important to note that the slope in log M *vs.* log C_c^J plot or in log C *vs.* log M_c^J is 1.00 and, hence, $C_c^JM = CM_c^J$ = constant $(=1.35 \times 10^5$ g/ml) (this means that *the transition of* J_e *from the* $J_e \propto C^{-1}$ *region to the* $J_e \propto C^{-2}$ *region occurs at a constant number of entanglement point per molecule;* this transition point corresponds to the appearance of the breaking point in Figure 7); (3) the critical molecular weight M_c^J for undiluted sample at 50° is 1.3×10^5 since $CM_c^J = 1.35 \times 10^5$ at $C = \rho_0 = 1.06$ g/ml. In addition, Figure 6 shows that J_e is independent of M if $M \geqslant M_c^J$. Therefore, J_e for undiluted polymers at 50° must be independent of M if $M \geqslant 1.3 \times 10^5$. This conclusion agrees with the experimental results of M_c^J

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by Fujimoto, Ozaki, and Nagasawa,[16] who determined J_e from stress relaxation data.

The facts that J_e is proportional to M/C in dilute solutions and to $1/C^2$ (independent of M) in concentrated solutions and also that $C_c^J M = CM_c^J = 1.35 \times 10^5$ in all solutions lead to the conclusion that J_e/M^2 is a universal function of CM and the graph has a sharp transition point at $CM = 1.35 \times 10^5$. That is

$$J_e/M^2 = 1.11 \times 10^{-11}(CM)^{-1} \text{ for } CM < 1.35 \times 10^5 \quad (2)$$

$$J_e/M^2 = 1.56 \times 10^{-6}(CM)^{-2} \text{ for } CM \geqslant 1.35 \times 10^5 \quad (3)$$

This relationship is graphically shown in Figure 7, in which two straight solid lines are drawn with slopes 1 and 2, respectively.

A similar transition in the log J_e *vs.* log CM relation was pointed out by Graessley and Segal.[26,33] The molecular interpretation of eq 2 and 3, as described above, is based on this theory of Graessley, *et al.* Their equation is

$$J_e = [\alpha_1/(1 + \alpha_2 CM)](J_e)_R \quad (4)$$

where α_1 and α_2 are constants, independent of C, M, and temperature. $(J_e)_R$ is the value calculated from the Rouse theory.[34] From eq 4 we can obtain J_e/M^2 as a universal function of CM as in eq 2 and 3, since $(J_e)_R \propto M/C$. The calculated curves obtained from eq 4 with $\alpha_1 = 7.45 \times 10^{-1}$ and $\alpha_2 = 7.12 \times 10^{-6}$ agree with our experimental results at the limits of low and high entanglement densities as shown in Figure 7. However, a disagreement is found in the middle range. If we modify their theory according to the present experimental results, J_e may be expressed as

$$J_e \propto (1/\nu)RT \propto M/CRT \text{ for (CM)} < C_c^J M \quad (5)$$

$$J_e \propto (1/\nu)ERT \propto 1/C^2RT \text{ for (CM)} \geqslant C_c^J M \quad (6)$$

where ν is the number of polymer per volume, R is the gas constant, T is the absolute temperature, and E is the average number of entanglement per molecule. Equations 5 and 6 are the same as eq 2 and 3.

The above experimental results appear to mean that the elastic element governing the elasticity of linear polymer solution changes from individual molecules to chain segments between entanglement points at the transition point. This definition of the critical point or M_c^J has a clear physical meaning and can be experimentally determined from J_e *vs.* M or J_e *vs.* C relationship without ambiguity. Here, however, it is to be noted that M_c^J should not be considered equal to the molecular weight per entanglement (M_e), which is usually determined from the relaxation modulus at the plateau region in stress relaxation curves. M_e for undiluted poly(α-methylstyrenes) was previously found to be 1.2×10^4.[16] (This value for M_e appears to be a little lower than the values accepted for most polymers.[4]) If we accept this value for M_e, the critical entanglement number per molecule for entanglement network formation is about 11. Thus, the above conclusion means that even though there are several entanglements per molecule, so that the viscosity of the sample is determined by entanglement, the elasticity of the sample may be governed by the relaxation modes of the molecule in the viscous medium if the molecular weight is lower than M_c^J, as was discussed by Ferry.[4] If the entanglement number per molecule is beyond the critical number for the J_e–M relationship the relaxation modes of individual molecule cease to contribute and, instead, the relaxation modes of the segments between entanglements may become predominant.

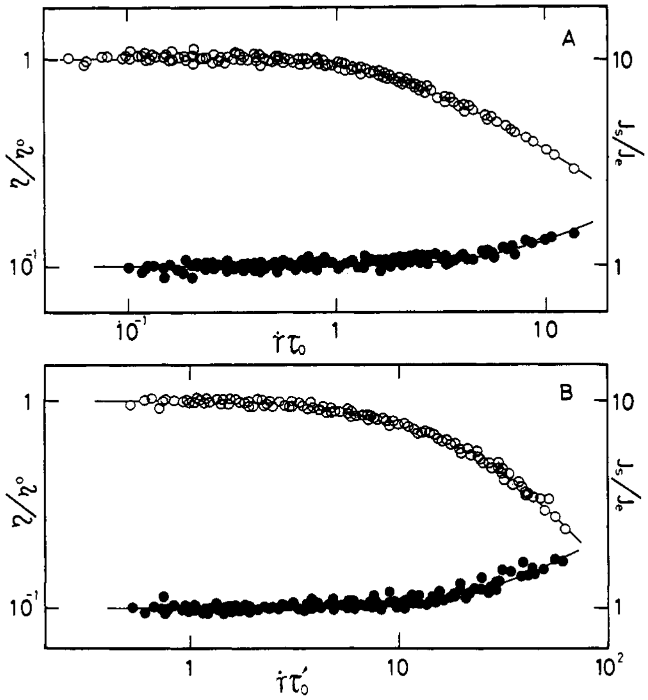

Figure 10. Superpositions of reduced steady shear viscosity η/η^0 (○) and compliance J_s/J_e (●) with respect to shear rate. Part A denotes the superposition in the range of low concentration and/or low molecular weight, whereas part B denotes that in the range of high concentration and/or high molecular weight.

Moreover, it is sometimes pointed out that the entanglement junctions must surely occur with a wide range of complexities and, hence, of lifetimes. Particularly if the entanglement junctions in networks extending throughout the solution are discussed, such complex natures of entanglement should be carefully taken into account, because, for example, there might be a possibility that the critical molecular weights change with experimental conditions. In this paper, we analyzed our data neglecting such complexities. This assumption may be justified by the facts that not only the shear stress but also the normal stress difference reaches a constant value at low shear rates but also that the observed critical values appear to be independent of the solvent used and temperature, so long as good solvents are employed. At least, however, it should be noted that the network discussed here is not a real network, but the transition from the "Rouse-like" behavior to the "network-like" behavior is meant.

B. At Finite Shear Rates. The shear rate dependence of J_s is one of the important problems in the molecular rheology, though the physical meaning of the shear rate dependence of J_s is not absolutely clear. In diluted solutions, the shear rate dependence of J_s may be due to deformation of polymer coil, whereas, in concentrated solutions, it may be caused by both deformation of polymer coil and change in entanglement density, though, besides, changes in the hydrodynamic interaction between segments and others due to high shear rate are also likely.[35] Thus, it is understandable that the effective entanglement density decreases to zero and J_s approaches the proportionality to M/C at the limit of high shear rate even in

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TABLE III
MOLECULAR WEIGHT AND CONCENTRATION DEPENDENCES OF ψ_{12}^0, τ_0, and J_e

$CM < 1.35 \times 10^5$	$CM \geqslant 1.35 \times 10^5$
$\psi_{12}^0 \propto \eta^{02}M/CRT$	η^{02}/C^2RT
$\tau_0 \propto \eta^0 M/CRT$	η^0/C^2RT
$J_e \propto M/CRT$	$1/C^2RT$

concentrated solutions (*i.e.*, in $C \geqslant C_c^J$), as can be seen in Figure 8.

At moderately high shear rates, the region of $J_s \propto 1/C^2$ still remains, but deviation from the universal line is observed at higher concentrations. In that region, J_s is proportional to C^{-n} $(0 < n < 2)$ and depends on molecular weight. This deviation from the universal line of $J_s \propto 1/C^2$ is due to the change in the effective entanglement density, which would occur from the highly entangling chains first. That is, the change in the effective entanglement density due to high shear rate was given by Graessley as[36]

$$E = E_0 g(\theta)$$

where $\theta = (1/2)\dot{\gamma}\tau = (1/2)\dot{\gamma}(\eta/\eta^0)\tau_0$ and E_0 is the value of E at zero shear rate. The function $g(\theta)$, which gives the rate of change in E with $\dot{\gamma}$, was calculated by Graessley. Therefore J_s is given by

$$J_s(\dot{\gamma}) \propto (1/\nu)E_0RTg(\theta) \qquad (7)$$

Although the absolute values of θ cannot be estimated in the range of $J_s \propto 1/C^2$ and, hence, quantitative comparison between eq 7 and experiments is not possible, the qualitative features of the shear rate dependence of J_s in Figure 8 can well be explained by eq 7.

In the region of $J_e \propto C^{-1}$, it was reported that the superposition of η and J_s with respect to molecular weight, polymer concentration, and temperature can be carried out by applying the theory of Rouse,[34] Bueche,[37] and Zimm.[38] Superposition of the present data is shown in Figure 10A, in which the shift factor τ_0 $(12/\pi^2)(\eta^0M/CRT)$ is used. Concerning the superposition of η and J_s in the region of $J_e \propto C^{-2}$, it can be speculated from the above discussion that the superposition would be successful if we use the shift factor $\tau_0' = K\eta^0/C^2RT$ where K is a constant. The superposition results are shown in Figure 10B, where $K = 10^6$ cgs is arbitrarily used. Our shift factors for concentrated and dilute solutions agree with the values of Graessley and Segal[26] who reported this superposition first.

As a summary, the polymer concentration and molecular weight dependences of J_e, τ_0, and ψ_{12}^0 $(= \lim(\dot{\gamma}\rightarrow 0)\ (P_{11} - P_{22})/\dot{\gamma}^2)$ are shown in Table III. Except for the numerical factors, we believe that these relationships agree with most experimental results reported previously. However, it is to be noted that these relationships hold only for monodisperse polymers. From the table, moreover, it can be pointed out that J_e is proportional to τ_0/η^0 over the whole concentration range. Since τ_0 can be speculated from the shear rate dependence of η, it may be possible to speculate relative values of J_e from the data on shear rate dependence of η alone.

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Structure of Silane Adhesion Promoter Films on Glass and Metal Surfaces

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Received July 7, 1972

ABSTRACT: The films of vinyl-, γ-chloropropyl, *p*-chlorophenylethyl-, and γ-aminopropyltrialkoxysilane deposited on glass and metal surfaces from polar and nonpolar solvents were examined using contact angle measurements, internal reflection infrared spectroscopy, ellipsometry, and scanning electron microscopy. These studies showed the films to be polysiloxane coatings, part of which could be easily rinsed from the surface by organic solvents or water. Contact angle determinations on the remaining, strongly held material indicate it to be an open polymeric structure since it was easily penetrated by the wetting liquids. Ellipsometric measurements showed the films from nonpolar solvents to be relatively thick (>1000 Å) and resistant to desorption. The films from polar solvents were generally less than 100 Å thick and easily disrupted by polar liquids. However, the scanning electron microscopy study revealed that over the continuous films measured ellipsometrically there were discrete, widely separate patches of deposit. The significance of these findings to the use of trialkoxysilanes as adhesion promoters is discussed.

The adhesion of polymers to glass and metals can be significantly improved by applying certain trialkoxysilanes to the adherend surface.[1,2] These "silanes" are especially effective in improving the resistance of the bond to attack by moisture. In order to explain their adhesion-promoting effect, it has been suggested that these agents form a chemical link between the adhesive and adherend.[1,3] Other workers hold to the view that the silane affects the mechanical properties of the adhesive near the interface.[2,4,5] At present no theory provides a complete explanation of the adhesion-promoting action. One is inclined to believe that both mechanical and chemical effects are involved.

The work reported here was designed to determine the structure of the films of various silane adhesion promoters on glass and metal surfaces deposited by evaporation from polar and nonpolar solvents. It is hoped that this informa-

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