Shear Creep Studies of Narrow-Distribution Poly(*cis*-isoprene). III. Concentrated Solutions[1]

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Received May 26, 1972

ABSTRACT: In order to elucidate the behavior of the steady-state compliance J_e as function of polymer concentration, shear creep measurements were made on concentrated solutions of narrow-distribution poly(*cis*-isoprenes) with molecular weights M of 153,000 and 395,000 in chlorinated diphenyl, and also in a poly(*cis*-isoprene) of molecular weight 3100 as a solvent. In all the solutions studied, J_e is found to exhibit a rather complicated dependence on polymer concentration c. At high concentrations, J_e is independent of M and is proportional to c^{-3}. With decreasing c, J_e reaches to a maximum, then passes through a small minimum, and increases again. In the last region of c, J_e is approximately proportional to $c^{-1.5}$ and to M. The maximum and minimum in J_e are shifted toward lower values of c as the molecular weight is increased, but are not affected by the nature of solvent. In contrast to these properties of J_e, the pseudoequilibrium compliance J_{eN} decreases monotonously with increasing concentration as $J_{eN} \propto 1/c^2$, showing no complexity over the wide range of c from about 10 wt % to the undiluted state. The viscosity η_ζ and the maximum relaxation time $\tau_{m\zeta}$ at constant friction factor also varied monotonously as functions of c.

In a recent publication,[2] Einaga, *et al.*, found for concentrated solutions of narrow-distribution polystyrene in chlorinated diphenyl that the steady-state compliance J_e exhibits a somewhat complicated dependence on the concentration c. At low concentrations, J_e is approximately proportional to c^{-1}, whereas at high concentrations it is proportional to c^{-3}. The transition between these two types of c dependence occurs in a narrow range of c, describing an inverse-N-shaped curve. This behavior of J_e is in marked contrast to the gradual transition from c^{-1} to c^{-2} dependence which has been reported on polystyrene solutions in toluene by Graessley and Segal.[3] Thus, we find it worthwhile to study the creep behavior of concentrated polymer solutions with other combinations of polymer and solvent than the above and to clarify the behavior of J_e as a function of c. This paper describes a similar study on concentrated solutions of poly(*cis*-isoprene) in two solvents, a chlorinated diphenyl and a poly(*cis*-isoprene) liquid of low molecular weight.

Experimental Section

Materials. Three poly(*cis*-isoprene) samples designated as I-29, -6, and -31 were of the narrow-distribution type having weight-average molecular weights 3100, 153,000, and 395,000, respectively. Two samples, I-29 and -31, were selected from the samples used in the preceeding papers of this series,[4] and sample I-6 was newly prepared by the same method as described in part I.[4a] The chlorinated diphenyl was Aroclor 1248 supplied by the Monsanto Co.

The solutions designed as IA series were prepared by dissolving weighed amounts of poly(*cis*-isoprene), I-31 or I-6, and Aroclor in benzene and then evaporating the benzene in a freeze drier for 4 days. A preliminary test showed that the vaporization of Aroclor was negligible during the freeze-drying process. The polymer concentration c (grams per milliliter) was calculated from the weights of the components by assuming volume additivity. The validity of this assumption was demonstrated to an accuracy of 0.5% by dilatometry. The densities of the polymer and solvent were 0.904 and 1.454 at 25°, respectively. The solutions of poly(*cis*-isoprene) I-31 in Aroclor were designated as the IA-300 series, while those of I-6 were the IA-600 series. The last two figures of the sample code in Table I represent an approximate value of polymer concentration expressed in grams per 100 ml.

The solutions designated as series II were binary blends of poly(*cis*-isoprene) I-6 and -29, which were prepared by a method analogous to that above. The two digits attached to the sample code in Table II represent the weight per cent of I-6 in each sample.

All the solutions (and blends) contained 0.5% 2,2-methylenebis-1,4-methyl-6-*tert*-butylphenol as an antioxidant.

Methods. Shear creep measurements were made with a torsion pendulum described in part I.[4a] A disk-shaped sample for the creep measurements was molded under pressure at room temperature, provided that the viscosity was sufficiently high to keep the sample shape stable more than an hour. Otherwise, the samples were treated as described in part II.[4b]

Results

Series IA. The creep master curve of each sample was constructed from a series of creep curves obtained at several temperatures by the usual procedure based on the time-temperature superposition principle. Figure 1 shows the creep master curves for the IA-300 series solutions, where a_T represents the shift factor for the time–temperature reduction. The subscript p represents that the creep compliance $J(t)$ has been multiplied by the eleasticity factor, $T\rho/T_0\rho_0$, where ρ and ρ_0 represent the densities at temperature T and a reference temperature T_0, respectively. The reference temperature here is $-15°$. The number attached to each curve represents the concentrations, in grams, of polymer I-31 per 100 ml of solution. Also shown in the figure are the master curves for the solvent Aroclor and the polymer I-31; the latter is essentially the reproduction of Figure 3 in part I.

At the initial stage of this study, we conducted the creep measurements at temperatures as low as $-70°$ to encompass the transition region of the creep curves. At low temperatures, however, the creep compliances $J(t)$ of the solutions of series IA were found to be dependent on the thermal history of test samples. For instance, $J(t)$ of a rapidly cooled sample sometimes became as small as one-tenth of $J(t)$ of a slowly cooled sample. Thus, in Figure 1, we omitted these low temperature data of $J(t)$ for the solutions. This type of anomaly was not found for pure poly(*cis*-isoprene) nor the solvent Aroclor.

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[1] Part V of a series on viscoelastic properties of narrow-distribution polymers.

[2] Y. Einaga, K. Osaki, M. Kurata, and M. Tamura, *Macromolecules*, 4, 87 (1971).

[3] W. W. Graessley and L. Segal, *ibid.*, 2, 49 (1969).

[4] (a) N. Nemoto, M. Moriwaki, H. Odani, and M. Kurata, *ibid.*, 4, 215 (1971); (b) N. Nemoto, H. Odani, and M. Kurata, *ibid.*, 4, 531 (1972).

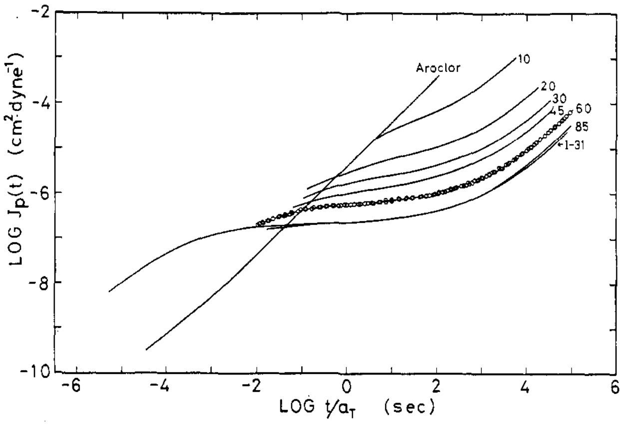

Figure 1. The creep master curves for sample I-31, Aroclor, and six solutions of the IA-300 series.

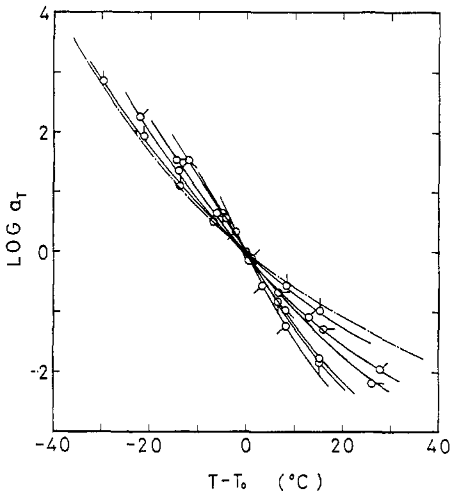

Figure 2. The semilogarithmic plot of a_T against $T - T_0$ with $T_0 = -15°$. Circles with pip up, IA-385; successive 45° rotation clockwise, IA-360, 345, 330, 320, and 310, respectively. The chain curve represents a_T of undiluted samples I-31 obtained in earlier measurements.[4a]

The shift factors a_T used for the time-temperature reduction are plotted semilogarithmically against $T - T_0$ in Figure 2. All the data points are well represented by the WLF-type equations as illustrated by the solid curves

$$\log a_T = -\frac{c_1(T - T_0)}{c_2 + T - T_0} \tag{1}$$

The values of c_1 and c_2 are summarized in Table I. The chain curve in the figure represents the WLF equation for sample I-31, which is derived from eq 2 in part I simply by modifying T_0 from -30 to $-15°$. A similar analysis of a_T has also been carried out for the IA-600 series solutions, yielding the values of c_1 and c_2 in Table I. The constant values, c_1 and c_2, for the solutions are, however, subjected to considerable error because of the lack of data points in the transition region. Therefore, further analysis of a_T based on the free volume theory is not attempted here.

Table I

Isothermal Viscosity η_T and Steady-State Compliance J_e of Concentrated Solutions of Poly(*cis*-isoprene) I-31 and I-6, in Aroclor at 0°

Code	c, g/ml	WLF constants[a] c_1	c_2	η_T, P	J_e cm²/dyn
I-31	0.920	7.02	104.5	4.38×10^8	1.27×10^{-6}
I-A-385	0.849	7.69	107.3	3.31×10^8	1.50×10^{-6}
I-A-360	0.600	10.7	124.6	1.17×10^8	4.82×10^{-6}
I-A-345	0.449	13.1	138.7	1.84×10^7	1.58×10^{-5}
I-A-330	0.300	24.2	197.2	5.37×10^6	1.50×10^{-5}
I-A-320	0.200	21.0	164.6	1.29×10^6	3.06×10^{-5}
I-A-310	0.100	10.3	59.4	6.03×10^5	9.40×10^{-5}
I-6	0.920	7.02	104.5	2.36×10^7	1.26×10^{-6}
I-A-680	0.798			1.25×10^7	2.25×10^{-6}
I-A-660	0.599			5.31×10^6	3.60×10^{-6}
I-A-653	0.530			3.65×10^6	3.10×10^{-6}
I-A-642	0.419			1.86×10^6	4.10×10^{-6}
I-A-630	0.300			4.44×10^5	6.65×10^{-6}
I-A-620	0.200			1.10×10^5	1.40×10^{-5}

[a] $T_0 = -15°$.

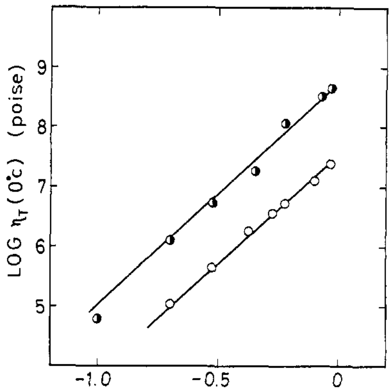

Figure 3. The logarithmic plot of the isothermal viscosity η_T against concentration c at 0°: (◐) solutions of the IA-300 series, (○) the IA-600 series.

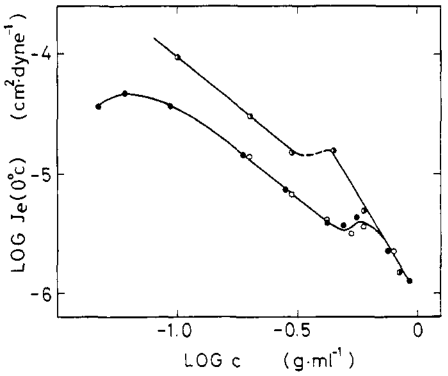

Figure 4. The logarithmic plot of the steady-state compliance J_e against c: (◐) solutions of the IA-300 series, (○) the IA-600 series, (●) the II series.

The viscosity η and the steady-state compliance J_e were calculated by the extrapolation method of Ninomiya.[5] The values obtained at 0° are given in Table I. The concentration dependences of these parameters, η and J_e, are illustrated in Figures 3 and 4, respectively, where the half-filled circles represent data for the IA-300 series and the open circles those for the IA-600 series. The meaning of the black circles in Figure 4 is explained in the next section. As may be seen from Figure 3, the viscosity η is proportional to the 3.5 power of concentration c in both series of solutions, indicating that all these systems are in a state of entanglement. For con-

(5) K. Ninomiya, *J. Phys. Chem.*, **67**, 1152 (1963).

TABLE II

ISOTHERMAL VISCOSITY η_T, STEADY-STATE COMPLIANCE J_e, PSEUDOEQUILIBRIUM COMPLIANCE J_{eN}, AND MAXIMUM RELAXATION TIME τ_m OF BINARY BLENDS OF POLY(*cis*-ISOPRENES) I-6 AND I-29, AT −30°

Code	$M_w \times 10^{-4}$	w_2	T_0, °C	$\Delta \log t$	η_T, P	J_e, cm²/dyn	J_{eN}, cm²/dyn	τ_m, sec
I-6	15.3	1.00	−30.0	0	2.64×10^9	1.39×10^{-6}	1.95×10^{-7}	1.26×10^4
II-80	12.3	0.800	−34.4	0.384	5.70×10^8	2.47×10^{-6}	3.60×10^{-7}	3.54×10^3
II-60	9.28	0.599	−35.1	0.444	1.39×10^8	4.72×10^{-6}	5.12×10^{-7}	2.91×10^3
II-53	8.24	0.530	−36.3	0.540	6.64×10^7	3.99×10^{-6}	7.40×10^{-7}	1.48×10^3
II-45	7.06	0.450	−36.8	0.580	3.55×10^7	4.24×10^{-6}	9.50×10^{-7}	6.66×10^2
II-30	4.80	0.300	−38.0	0.673	5.97×10^6	8.18×10^{-6}	2.41×10^{-6}	1.96×10^2
II-20	3.31	0.200	−39.3	0.780	1.10×10^6	1.60×10^{-5}	4.83×10^{-6}	7.66×10^1
II-10	1.80	0.100	−39.6	0.800	1.15×10^5	4.01×10^{-5}	1.56×10^{-5}	1.92×10^1
II-7	1.28	0.0645				5.18×10^{-5}		
II-5	1.06	0.0501				3.98×10^{-5}		
I-29	0.31	0	−39.9	0.820	3.56×10^3	1.96×10^{-8}		2.89×10^{-2}

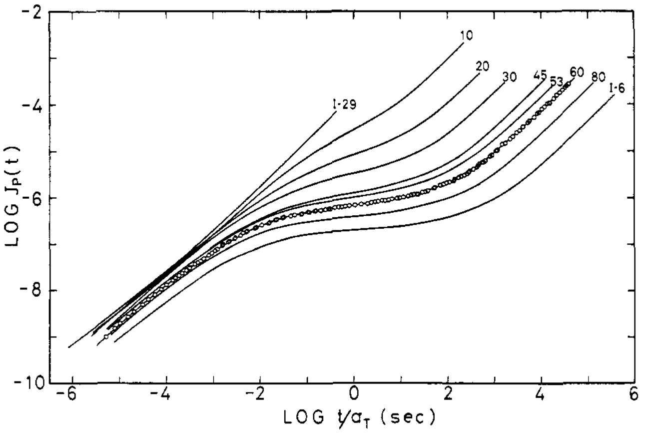

Figure 5. The creep master curve of samples I-6, I-29, and their binary blends with the indicated values of the weight per cent w_2 of I-6.

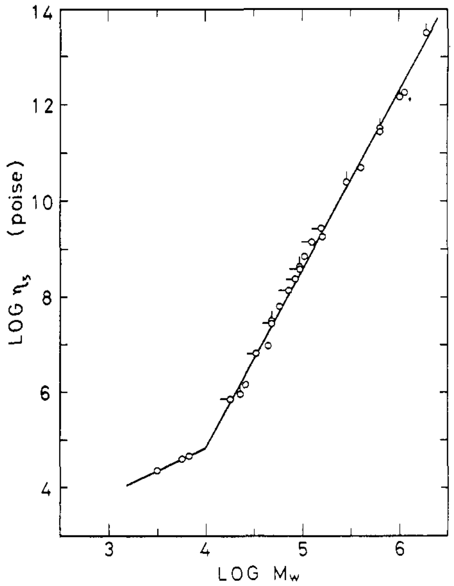

Figure 6. The logarithmic plot of η_ζ at constant friction factor against M_w: (O) earlier data for narrow-distribution samples,[4] (pip up) data of Holden,[6] (pip left) present work.

centrated solutions of polymers, the isothermal viscosity often varies as a power of c much higher than 3.5. For example, in the case of polystyrene in Aroclor at about 30°, the quantity $d \log \eta / d \log c$ reaches a value as high as 15 at very high concentrations.[2] This is, of course, due to the fact that in the vicinity of the glass-transition point, the addition of solvent gives rise to a rapid increase in the free volume of the system. In the case of Figure 3, however, the temperature involved is far above the glass-transition temperatures of polymer and solvent, −72 and −50°, and the thermal coefficients of the two components are not very different from each other, *i.e.*, 0.78×10^{-3} for the polymer and 1.03×10^{-3} for the solvent. Thus, the free volume factor may not affect the concentration dependence of the isothermal viscosity.

Figure 4 shows the double-logarithmic plot of J_e *vs.* c. In contrast to the simple power dependence of η on c, the compliance J_e exhibits a rather complicated dependence on c. J_e first decreases approximately in proportion to $c^{-1.5}$ with increasing c, reaches a minimum and then a maximum, and again decreases in proportion to c^{-3}. This type of concentration dependence of J_e is essentially the same as that first pointed out by Einaga, *et al.*, on polystyrene solutions in Aroclor.[2] However, in the present solutions, the maximum is located at a concentration further in the entanglement region than it is in the latter solutions, and the height of the maximum is considerably lower. As for the molecular weight dependence, J_e is approximately proportional to M at low concentrations and is independent of M at high concentrations.

Series II. In order to test the effect of the solvent nature on J_e, we carried out an analysis of the creep behavior, similar to the above, on binary blends of poly(*cis*-isoprenes) I-6 and I-29. In this case, the latter polymer I-29 may be regarded as the solvent. The creep master curves of these systems constructed with the aid of the time–temperature reduction are shown in Figure 5, where the circles represent the original data points for the sample II-60. The shift factor a_T can be fitted to eq 1 either by assigning composition-dependent values to c_1 and c_2 with a fixed value of T_0, or by assigning a composition-dependent value to T_0 with $c_1 = -8.20$ and $c_2 = 89.5$. Table II shows the values of T_0 in the latter choice. The procedure used for determination of T_0 has already been explained in part I.[4a]

The isothermal viscosity η_T and steady-state compliance J_e evaluated at −30° are summarized in Table II. For two samples, II-7 and II-5, the creep measurements were preformed only at −39.2 and −44.6°, respectively; hence, a_T was left undetermined. Thus, the creep compliance J_e obtained at these temperatures was converted to the values at −30° as shown in Table II, but not the viscosity η.

The viscosity at constant friction factor, η_ζ, was calculated from η_T as

$$\log \eta_\zeta = \log \eta_T - \Delta \log t \tag{2}$$

where $\Delta \log t$ represents the horizontal distance between two master curves, one of I-6 and the other of the solution con-

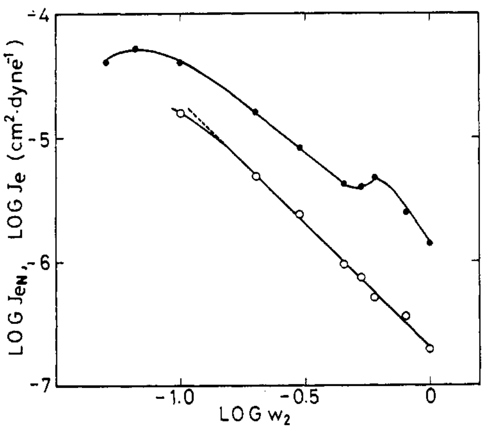

Figure 7. The steady-state compliance J_e and the pseudoequilibrium compliance J_{eN} plotted against w_2 on a double logarithmic scale: (●) J_e, (○) J_{eN}.

cerned, in the transition zone. The values of $\Delta \log t$ are also included in Table II. The double-logarithmic plot of η_ζ against the weight-average molecular weight is illustrated in Figure 6, where the data for narrow-distribution samples are also shown for the sake of comparison.[4,6] The present data of blend samples are well fitted to a straight line of the slope 3.7 ± 0.1, confirming that samples II-10 to II-80, are in a state of entanglement.

Figure 7 shows the double-logarithmic plot of J_e against w_2, the weight fraction of I-6. At the two lowest values of w_2, J_e shows a tendency to diminish with decreasing concentration. At higher concentrations, J_e exhibits the same dependence on c as that shown in Figure 4.

The weight fraction w_2 of I-6 can be readily converted to the concentration c in grams per milliliter by multiplying by 0.920, the density at 0°. The data for J_e in Figure 7, which are obtained at $-30°$, are then adjusted to the values at 0° by multiplying the rubber elasticity factor $^{243}/_{273}$, and replotted against c in Figure 4 as shown by the black circles. As is seen from the figure, this plot for series II is nicely superimposed on that for the IA-600 series, indicating that the behavior of J_e is independent of the solvent nature.

The pseudoequilibrium compliance J_{eN} may be calculated as[7]

$$J_{eN} = \int_a^b L(\tau)\mathrm{d} \ln \tau \qquad (3)$$

where $L(\tau)$ is the retardation spectrum. In our calculation, $L(\tau)$ was derived from the master curves in Figure 5 by the second approximation of Schwarzl and Staverman;[8] the integral limits a and b were taken to encompass the maximum of $L(\tau)$ appearing at the end of the transition zone. The values of J_{eN} thus obtained are shown by open circles in Figure 7. In contrast to the complicated behavior of J_e, the quantity J_{eN} varied uniformly as a power of concentration, $J_{eN} \propto 1/w_2{}^2$, over the whole range of w_2 studied.

Finally, the maximum relaxation time τ_m was also evaluated by the method of Murakami and Tobolsky[9] after the creep master curves were converted to the master curves for the relaxation modulus. The results, given in Table II, vary by about the third power of w_2 over the range of w_2 studied. The maximum relaxation time $\tau_{m\zeta}$ at constant friction factor can be evaluated from τ_m with the aid of an equation analogous to eq 2. The values of $\tau_{m\zeta}$ thus obtained also show a simple power dependence on w_2, though this is not reproduced here.

Discussion

In the preceeding paper,[4b] we showed that J_e of narrow-distribution poly(*cis*-isoprenes) displays a rather sharp break at $M_b = 50{,}000$ as plotted logarithmically against M. This value of M_b is about five times larger than the critical entanglement molecular weight, $M_c = 10{,}000$. At $M < M_b$, J_e is approximately proportional to M, whereas at $M > M_b$, J_e is independent of M. On the other hand, η_ζ and $\tau_{m\zeta}$ are both proportional to the 3.7 power of M over the whole range of M greater than M_c, showing no break in the M dependence at M_b. Returning to the present case of concentrated solutions of poly(*cis*-isoprene), we may adopt the following relationship as a criterion for the entanglement formation

$$w_2 M_c(w_2) = 10{,}000 \qquad (4)$$

where w_2 represents the weight fraction of the polymer in solutions. Then, the critical entanglement molecular weight is 100,000 at $w_2 = 0.1$ and 143,000 at $w_2 = 0.07$. The molecular weights of the present samples I-6 and I-31 exceed these critical values. In other words, all the present solutions but II-5 are classified as entangled systems according to the criterion of eq 4. Now, the present study reveals that in the field of entanglement, J_e displays a rather complicated transition from $c^{-1.5}$ dependence to c^{-3} dependence, whereas η_ζ and $\tau_{m\zeta}$ display uniform power dependences. The concentration ranges where the transition in J_e occurs are $w_2 =$ 0.4–0.5 for I-6 and 0.3–0.4 for I-31, which are higher by about a factor of 7–10 than the values $w_2 = 0.06$ and 0.03 determined by eq 4. This factor 7–10 roughly corresponds to the ratio of M_b/M_c mentioned above. Thus, we may conclude that there is a basic relation between the two phenomena, the inverse-N-shaped transition in the $\log J_e$ *vs.* $\log c$ plot and the break at M_b in the $\log J_e$ *vs.* $\log M$ plot.

Acknowledgment. This work was supported in part by a grant for scientific research (Shiken Kenkyu, No. 50,160 in 1970) from the Ministry of Education of the Japanese Government.

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(9) A. V. Tobolsky and K. Murakami, *J. Polym. Sci.*, **40**, 443 (1956).