his discussions concerning this work, and to Drs. S. Zacharius, G. ten Brinke, and C. Ryan for their aid in preparing this manuscript.

References and Notes

(1) G. Hadziioannou, J. W. Gilmer, and R. S. Stein, *Polym. Bull.*, **9**, 563 (1984).
(2) G. Hadziioannou and R. S. Stein, *Macromolecules*, **17**, 1059 (1984).
(3) C. L. Ryan, Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1979.
(4) S. L. Zacharius, Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1982.
(5) S. L. Zacharius, G. ten Brinke, W. J. MacKnight, and F. E. Karasz, *Macromolecules*, **16**, 381 (1983).
(6) L. P. McMaster, *Macromolecules*, *6*, 760 (1973).
(7) P. J. Flory, *J. Chem. Phys.*, **9**, 660 (1941); **10**, 51 (1942).
(8) M. L. Huggins, *J. Chem. Phys.*, **9**, 440 (1941); *Ann. N.Y. Acad. Sci.*, **43**, 1 (1942).
(9) A. J. Staverman and J. H. VanSanten, *Recl. Trav. Chim. Pays-Bas.*, **60**, 76 (1941).
(10) H. Tompa, "Polymer Solutions", Butterworth, London, 1956.
(11) R. Koningsveld and L. A. Kleintjens, *J. Polym. Sci., Polym. Symp.*, **61**, 221 (1977).
(12) R. Koningsveld, L. A. Kleintjens, and H. M. Schoffeleers, *Appl. Chem.*, **39**, 1 (1974).
(13) R. Koningsveld and L. A. Kleintjens, "NATO Advanced Study Institute on Polymer Blends and Mixtures", to be published.
(14) P. Debye and A. Bueche, *J. Chem. Phys.*, 18, 1423 (1950).
(15) R. Koningsveld and L. A. Kleintjens, *Pure Appl. Chem., Macromol. Suppl.*, 8, 197 (1973).
(16) R. Koningsveld, *Adv. Colloid. Interface Sci.*, **2**, 151 (1968).
(17) J. W. Kennedy, M. Gordon, and R. Koningsveld, *J. Polym. Sci., Part C*, **39**, 43 (1972).
(18) M. H. Onclin, L. A. Kleintjens, and R. Koningsveld, *Makromol. Chem. Suppl.*, **3**, 197 (1979).
(19) E. L. Atkin, L. A. Kleintjens, R. Koningsveld, and L. J. Fetters, *Makromol. Chem.*, **185**, 377 (1984).
(20) Th. G. Scholte, *Eur. Polym. J.*, **6**, 1063 (1970).
(21) P. J. Flory, *J. Am. Chem. Soc.*, **87**, 1833 (1965).
(22) M. L. Huggins, *J. Am. Chem. Soc.*, **86**, 3535 (1964).
(23) D. Patterson, *Rubber Rev.*, **40**, 1 (1967).
(24) R. Koningsveld, W. H. Stockmayer, J. W. Kennedy, and L. A. Kleintjens, *Macromolecules*, **7**, 73 (1974).
(25) S. G. Chu and P. Munk, *J. Polym. Sci., Polym. Phys. Ed.*, **15**, 1163 (1977).
(26) H. Tompa, *C. R. Reun. Annu. Soc. Chim. Phys.*, p 163, (1952).
(27) Th. G. Scholte, *J. Polym. Sci., Part A-2*, **9**, 1553 (1971).
(28) Th. G. Scholte, *J. Polym. Sci. Part C*, **39**, 281 (1972).
(29) E. A. Guggenheim, *Proc. R. Soc. London, Ser. A*, **183**, 213 (1944); *Trans. Faraday Soc.*, **44**, 1007 (1948).
(30) W. J. C. Orr, *Trans. Faraday Soc.*, **40**, 320 (1944).
(31) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).
(32) M. Smoluchowski, *Ann. Phys.*, **25**, 205 (1908).
(33) A. Einstein, *Ann. Phys.*, **33**, 1275 (1910).
(34) F. Zernike, Ph.D. Dissertation, University of Amsterdam, 1915; *Arch. Neerl. 3A*, 4, 74 (1918).
(35) R. Koningsveld and L. A. Kleintjens, *Macromolecules*, 4, 673 (1971).
(36) R. S. Stein, T. P. Russell, B. S. Morra, M. Wai, and J. W. Gilmer, "IUPAC—Structural Order in Polymers", F. Ciardelli and P. Giusti, Eds., Pergamon Press, New York, 1981, p 195.
(37) T. P. Russell, Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1979.
(38) J. W. Gilmer, Ph.D. Dissertation, University of Massachusetts, Amherst, MA, 1984.
(39) W. C. Kohler and R. W. Hendricks, *J. Appl. Phys.*, **50**, 1951 (1979).
(40) P. R. Bevington, "Data Reduction and Error Analysis for the Physical Sciences", McGraw-Hill, New York, 1969.
(41) R. Ullman, *J. Polym. Sci., Polym. Lett. Ed.*, **21**, 521 (1983).
(42) H. Yang, G. Hadziioannou, and R. S. Stein, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 159 (1983).
(43) E. L. Aktin, L. A. Kleintjens, R. Koningsveld, and L. J. Fetters, *Polym. Bull.*, **8**, 347 (1982).
(44) W. Patnode and W. J. Scheiber, *J. Am. Chem. Soc.*, **61**, 3449 (1939).

Zero-Shear Viscosity of Linear Polymer Solutions over a Wide Range of Concentration

Yoshiaki Takahashi,* Yoshinobu Isono,† Ichiro Noda, and Mitsuru Nagasawa

Department of Synthetic Chemistry, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan. *Received April 2, 1984*

ABSTRACT: The zero-shear viscosity data of poly(α-methylstyrene) solutions in good, poor, and Θ solvents covering wide ranges of polymer concentration and molecular weight were accumulated and analyzed on the basis of the scaling concept of de Gennes, in comparison with the other theories. The theory was found to be useful for understanding the viscosity behavior in the semidilute region. However, the theory is not applicable if the polymer concentration is higher than $\simeq$0.2 g/mL. The crossover point from the dilute to the semidilute region varies with solvent power.

Introduction

The polymer concentration (C) and molecular weight (M) dependences of the zero-shear viscosity η^0 of linear polymer solutions over a wide range of polymer concentration have been extensively studied.[1-4] Concerning the molecular weight dependence of η^0, it is well established that η^0 is proportional to $M^{3.4}$ if polymer coils are entangled with each other. Concerning the concentration dependence of η^0, however, the problem is more complicated, except in dilute solutions. There are two approaches to the analysis of the polymer concentration dependence of η^0. One is the approach from the dilute-solution side and the other one is the approach from the polymer-melt side.

In dilute solutions, it is well established that the zero-shear viscosity η^0 can be expressed by the expansion form

$$\eta_R{}^0 \equiv \eta_{sp}{}^0/C[\eta] = 1 + k'[\eta]C + ... \qquad (1)$$

in which k' is Huggins' constant and $\eta_{sp}{}^0 = (\eta^0 - \eta_s)/\eta_s$, η_s being the solvent viscosity. That is, $\eta_R{}^0$ is given as a function of $C[\eta]$ in dilute solutions. In more concentrated solutions, too, $C[\eta]$ has been used as an approximate reducing parameter of viscosity. Strictly speaking, however, the superposition of $\eta_R{}^0$ with respect to $C[\eta]$ is not perfect.[5] Utracki and Simha[6,7] proposed that $\eta_R{}^0$ may be expressed in terms of reduced concentration $\tilde{C} \equiv C/\gamma$, where γ is defined by $\gamma \propto k'[\eta]^{-1} \propto M^{-a_1}$. That is

---

† Present address: Department of Material Science and Technology, Technological University of Nagaoka, Kamitomioka-cho, Nagaoka 949-54, Japan.

0024-9297/85/2218-1002$01.50/0

$$\eta_R^0 = f(CM^{a_1}) \tag{2}$$

where a_1 is usually close to the Mark–Houwink–Sakurada exponent a in $[\eta] \propto M^a$. This relationship holds well up to 50% in a fairly large number of polymer–solvent systems.

In entangled regions, η^0 is practically determined by the number of entanglements per polymer molecule. If polymer coils are extensively entangled with each other so that each segment has equal probability for forming entanglement, the number of entanglements per polymer molecule is proportional to CM, independent of polymer conformation. In concentrated solutions, therefore, it is reasonable to assume that η^0 is proportional not only to $M^{3.4}$ but also to $C^{3.4}$ as long as the local frictional coefficient of polymer chain is maintained constant. Since the local frictional coefficient ω would be changed with polymer concentration as was first pointed out by Berry and Fox,[1] the polymer concentration dependence of η^0 in concentrated solutions should be expressed proportional to $(CM)^{3.4}\omega(\eta_s,T,C)$. Extending this idea to more dilute solutions, Berry et al.[8,9] proposed an equation to express the zero-shear viscosity in a wide range of polymer concentration

$$\eta^0 \propto \rho M_c(\alpha_\phi^2 CM/\rho M_c)^b \omega(\eta_s,T,C) \tag{3}$$

with

$$\begin{aligned} b &= 3.4, \quad CM > \rho M_c \\ &= 1.0, \quad CM < \rho M_c \end{aligned}$$

where M_c, ρ, and α_ϕ are the critical molecular weight in the undiluted state, the density of bulk polymer, and the expansion factor, respectively.

The viscosity behavior of linear polymers in so-called semidilute or moderately concentrated solutions may reasonably be explained by both theories if we empirically determine the parameters a_1 in the theory of Utracki and Simha and ω in the theory of Berry et al. However, their physical interpretations are not equivalent.

Recently, the scaling concept of de Gennes was applied to zero-shear viscosity of linear polymers in semidilute solutions.[10–13] In this theory, the elastic modulus of polymer network E and the reptation time of a polymer chain T_r in semidilute solutions are respectively given by

$$E \propto kT/\xi^3 \tag{4}$$

$$T_r \propto \eta_s(M/M_e)^3\xi^3/kT \tag{5}$$

where ξ is the correlation length and M/M_e is the number of blobs per polymer chain. The zero-shear viscosity η^0 ($\propto ET_r$) in the semidilute region is, therefore, given by

$$\eta^0 \propto \eta_s(M/M_e)^3 \tag{6}$$

This means that η^0 in semidilute solutions is determined by the number of entanglements per polymer chain as in most previous theories.[1–4] Considering the experimental facts and recent discussions,[14–16] however, the third power of M/M_e in eq 6 should be modified as the 3.4th power.

In the model of de Gennes, the number of entanglements per polymer molecule in the semidilute solution cannot be assumed proportional to CM, since the probability for forming entanglements is not uniform for all segments. In his theory, M/M_e is scaled by the degree of coil overlapping C/C^* and the excluded volume exponent ν ($\langle S^2\rangle \propto M^{2\nu}$) such as

$$M/M_e \propto (C/C^*)^{1/(3\nu-1)} \tag{7}$$

where C^* is the critical concentration at which polymer coils begin to overlap each other, that is

$$C^* = 3M/4\pi N_A\langle S^2\rangle^{3/2} \tag{8}$$

where N_A is Avogadro's number. Thus, η_R^0 is given by a universal function of C/C^* only, such as

$$\eta_R^0 \propto (C/C^*)^{(4.4-3\nu)/(3\nu-1)} \tag{9}$$

and this gives

$$\eta_{sp}^0 \propto M^{3.4}C^{3.4/(3\nu-1)} \tag{9'}$$

A feature of the scaling theory, in comparison with the other theories, is that the polymer concentration dependence of η^0 in the semidilute region is explicitly predicted from thermodynamic properties, i.e., $\langle S^2\rangle$ and ν. The scaling concept was found useful for understanding the thermodynamic properties of polymers in good solvents.[17–22] The purpose of this work is to examine the applicability of the scaling concept (eq 9) to the zero-shear viscosity η^0 of linear polymer solutions covering wide ranges of polymer concentration and molecular weight. Moreover, η^0 of a linear polymer in good solvents is higher than that in poor solvents in dilute solutions, whereas the situation is generally opposite if the polymer molecules are entangled. The reversal-phenomenon in η^0 vs. C plots in good and poor solvents has been reported and discussed by many authors.[2,23–26] The phenomenon is also discussed in this paper. For these purposes, it is essential to accumulate the data of the samples which have narrow molecular weight distributions and whose behavior in dilute solutions is well-known.

Experimental Methods

The polymer samples used are poly(α-methylstyrenes) having narrow molecular weight distributions. Their molecular characteristics are listed in Table I.[27,28] The critical concentrations C^* in Table I were evaluated from eq 8 using the experimental values of radius of gyration in the respective solvent, which were previously determined by a light scattering method using the same series of samples.[27] Most data of η^0 used for discussion in this paper were already reported in previous papers.[23,28–30] The data listed in Table II were obtained in this work.

The zero-shear viscosity η^0 was measured by capillary viscometers of the Maron–Krieger–Sisko and Ubbelohde types and also by a Weissenberg rheogoniometer type R-17 of Sangamo Controls Ltd., equipped with a gap-servo system. The measurements were carried out at 30.0, 45.5, and 50.0 °C in α-chloronaphthalene (α-CN) (good solvent), at 30.0 °C in toluene (good solvent), at 25.0 and 30.0 °C in *trans*-Decalin (t-D) (poor solvent), at 10.0 °C in t-D (Θ solvent), at 40.0 °C in *n*-undecyl anisitate (*n*-UA) (Θ solvent), and at 50.0 °C in *n*-butyl benzyl phthalate (*n*-BBP) (Θ solvent), respectively. The solvent viscosities are listed in Table III.

Comparison of the Scaling Theory with Experimental Data

Figures 1–3 show double logarithmic plots of η_{sp}^0 vs. C for poly(α-methylstyrenes) with different molecular weights in Θ, poor, and good solvents, respectively. To compare those data with the scaling theory, they are replotted in the form of log η_R^0 vs. log (C/C^*) in Figures 4–6, respectively. The temperature differences in t-D (poor) and in good solvents affect the solvent viscosity and density but do not cause any detectable difference in the plots of Figures 5 and 6. The solid lines in these figures are given with the slopes calculated from eq 9 using the experimental values of ν, i.e., $\nu = 0.5$ (Θ) 0.55 (poor), and 0.58_5 (good), respectively.[27,28] The chain curves in these figures are calculated from eq 1 assuming the relationship $C/C^* = 3k'\Phi/4\pi N_A(C[\eta])$, that is

$$\eta_R^0 = 1 + k(C/C^*) + ... \tag{1'}$$

Table I
Samples and Their Characteristics

sample code	$10^{-6}M_w$	10^2C^*, g/cm³					[η], dL/g				
		a	*b*	*c*	*d*	*e*	*a*	*b*	*c*	*d*	*e*
αs-001	0.06	4.0_5					0.25_4				
αs-3	0.14_5	2.1_3					0.48_9				
αs-6	0.44_4	0.90_8					1.1_2				
αs-9	1.1_9	0.43_3					2.3_4				
αs-12	1.8_2	0.31_2					3.2_1				
αs-13	3.3_0	0.20_0					5.0_0				
α-001	0.0_6		7.0_2					0.17_9			
α-002	0.14_6	2.1_1	4.2_6		4.1_6	3.7_7	0.49_1	0.27_9		0.25_1	0.29_2
α-004	0.33_2	1.1_4				2.1_9	0.90_4				0.49_4
α-005	0.44_0	0.91_4	2.4_6			1.7_4	1.1_2	0.48_4			0.59_1
α-18	0.76	0.64_9					1.5_0				
α-19	1.4_9	0.36_5					2.7_7				
α-19A	1.6_5	0.33_7	1.2_7				2.9_8	0.93_8			
α-20	1.1_2	0.45_0			1.1_1	0.99_4	2.2_4			0.98_4	1.0_7
α-110	1.1_9			1.6_1		0.97_2			0.75		1.12
α-111	7.4_7			0.64_1					1.8_7		
α-112	1.8_2		1.2_1	1.3_0				0.98_5	0.91_4		
α-113	3.3_0			0.96_4		0.52_1			1.2_1		2.1_5

[a] Toluene, 30 °C (good), $\langle S^2 \rangle = 1.7_8 \times 10^{-18}M^{1.17}$,[13] $[\eta] = 7.0_6 \times 10^{-5}M^{0.74_4}$.[14] [b] cyclohexane, 35 °C (θ), $\langle S^2 \rangle = 8.4 \times 10^{-18}M$,[13] $[\eta] = 7.3 \times 10^{-4}M^{0.5}$.[14] [c] t-D, 10 °C (θ), $\langle S^2 \rangle = 8.0 \times 10^{-18}M$,[13] $[\eta] = 6.7 \times 10^{-4}M^{0.5}$.[14] [d] t-D, 25 °C (poor), $\langle S^2 \rangle = 2.6 \times 10^{-18}M^{1.1}$,[13] $[\eta] = 8.7_1 \times 10^{-5}M^{0.6_7}$.[14] [e] t-D, 30 °C (poor), $\langle S_2 \rangle = 2.7_5 \times 10^{-18}M^{1.1}$,[13] $[\eta] = 1.4_5 \times 10^{-4}M^{0.6_4}$.[14]

Table II
Zero-Shear Viscosity

sample code	solv	T, °C	C, g/dL	η^0, P
α-002	α-CN	45.5 (good)	23.1	5.30×10^0
			14.6	1.05×10^0
			8.80	3.01×10^{-1}
			7.44	2.23×10^{-1}
			4.74	1.04×10^{-1}
			2.97	6.43×10^{-2}
α-20	α-CN	45.5 (good)	10.2	5.13×10^1
			7.08	1.10×10^1
			4.21	1.76×10^0
			2.38	4.77×10^{-1}
			1.81	2.90×10^{-1}
α-002	*trans*-Decalin	25.0 (poor)	24.7	1.13×10^1
			13.2	1.25×10^0
			7.64	2.57×10^{-1}
			5.33	1.11×10^{-1}
			3.26	5.33×10^{-2}
α-20	*trans*-Decalin	25.0 (poor)	9.68	2.70×10^2
			5.93	1.76×10^1
			3.73	1.34×10^0
			2.14	1.95×10^{-1}
			1.30	8.40×10^{-2}
α-001	*n*-UA	40.0 (Θ)	38.9	1.82×10^3
			33.5	3.33×10^2
			30.9	1.72×10^2
			30.1	1.51×10^2
			26.7	6.52×10^1
α-002	*n*-UA	40.0 (Θ)	38.3	4.19×10^4
			28.9	1.80×10^3
			27.7	1.32×10^3
			26.1	8.16×10^2
			23.7	3.66×10^2

Table III
Zero-Shear Viscosities of Solvents

temp, °C	η_s, cP				
	α-CN	toluene	t-D	*n*-UA	*n*-BBP
10.0					
25.0			1.88		
30.0	2.82	0.522	1.76		
40.0				10.7	
45.5	1.88				
50.0	1.65				15.5

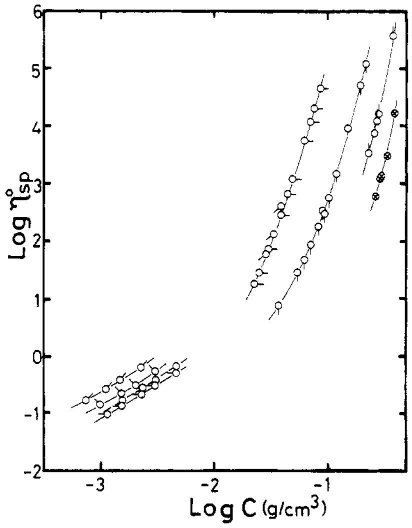

Figure 1. Polymer concentration dependence of zero-shear specific viscosity η_{sp}^0 in Θ solvents (*n*-UA, *n*-BBP, t-D): α-001 (⊗), α-19A (○), α-112 (○), α-002 (○), α-110 (○), α-113 (○), α-005 (○), α-111 (○).

The values of *k′* are assumed to be 0.8 (Θ), 0.7 (poor), and 0.35 (good). The Flory coefficient Φ slightly depends on the excluded volume effect[28,31] but can be safely assumed constant for each polymer–solvent system. In Θ and poor solvents (Figures 4 and 5) all experimental data of η_R^0 are well expressed by a unversal function of C/C^*, as predicted from eq 1′ and 9. The crossover between dilute and semidilute regions takes place at $C/C^* \simeq 2$ in Θ solvents and at $C/C^* \simeq 4$ in poor solvents.

Figures 7–9 show the double logarithmic plots of $\eta_{sp}^0/M^{3.4}$ against *C* in Θ, poor, and good solvents, respectively. The chain curves and the solid lines were calculated from eq 1 and 9′, respectively, using the experimental values of *ν*. In Figures 7 and 8 it can be pointed out that $\eta_{sp}^0/M^{3.4}$ is different with molecular weight in dilute solutions but the data converge on a universal line of eq 9′ as the concentration increases.

In Θ and poor solvents, therefore, it can be concluded that the viscosity of linear polymer solutions crosses over from the dilute region to the entangled region at a critical value of C/C^* and the polymer concentration dependence of viscosity in the semidilute region can be explained by the scaling theory. Although there are more detailed ar-

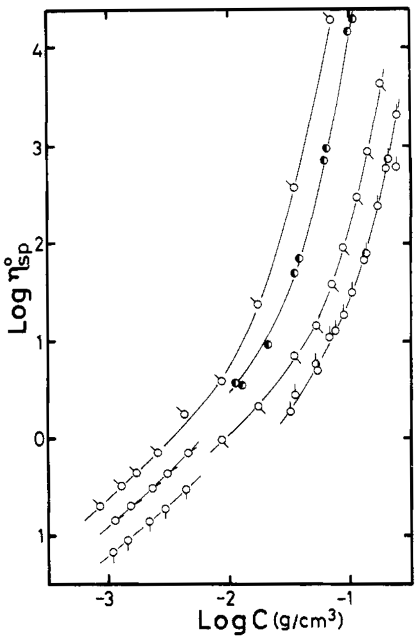

Figure 2. Polymer concentration dependence of zero-shear specific viscosity $\eta_{sp}{}^0$ in poor solvents (t-D): α-002 (○), α-20 (◐), α-004 (○), α-110 (○), α-005 (○), α-113 (○).

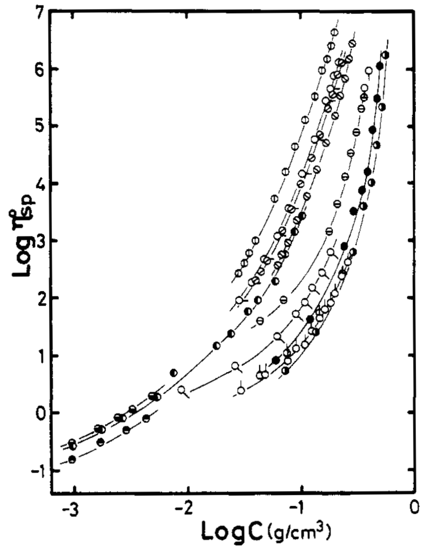

Figure 3. Polymer concentration dependence of zero-shear specific viscosity $\eta_{sp}{}^0$ in good solvents (toluene and α-CN): αs-001 (◑), αs-13 (○), α-18 (⊖), αs-3 (●), α-002 (○), α-19 (⊖), αs-6 (⊖), α-004 (○), α-19A (○), αs-9 (○), α-005 (○), α-20 (◐), αs-12 (○).

guments based on the scaling concept in poor solvents,[32] those theories need not be brought in to explain the present experimental data.

In good solvents, however, the situation is more complicated. In Figure 6, $\eta_R{}^0$ appears to disagree with the prediction of eq 9. If the molecular weights of samples are low, the experimental data do not fit the theoretical line at all. Only if the molecular weights are high do the data converge on the theoretical line of eq 9 but the agreement is found only in a limited range. The data again deviate from the theoretical line as the polymer concentration increases further. In Figure 9, too, agreement between the experimental data and the scaling theory is found in a limited range. All experimental data appear to converge on the theoretical line except the data for low molecular weight samples but the data again deviate from the theoretical line as the polymer concentration increases further.

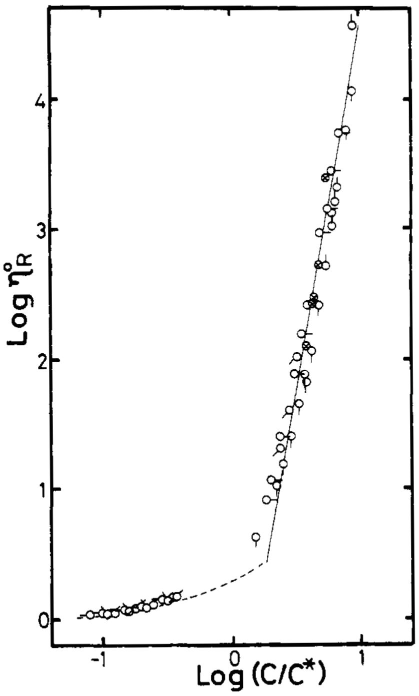

Figure 4. Double logarithmic plots of reduced viscosity $\eta_R{}^0$ vs. degree of coil overlapping (C/C^*) in Θ solvents. Symbols are the same as in Figure 1. The chain curve denotes the calculated values of eq 1′. The solid line denotes the slope calculated from eq 9 ($\eta_R{}^0 \propto (C/C^*)^{5.8}$).

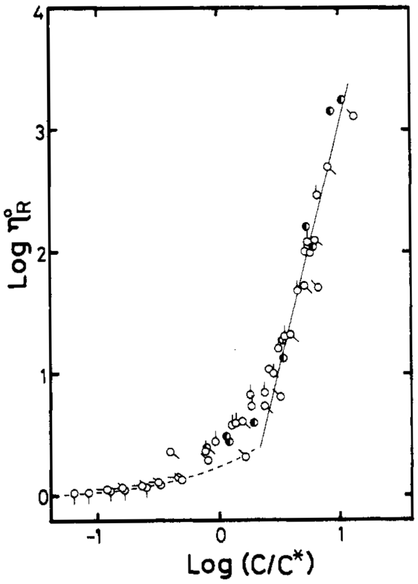

Figure 5. Plots of log $\eta_R{}^0$ vs. log (C/C^*) in poor solvents. Symbols are the same as in Figure 2. The chain curve and the solid line denote eq 1′ and 9 ($\eta_R{}^0 \propto (C/C^*)^{4.2_3}$).

If we carefully inspect the data in Figures 6 and 9, however, we can point out that all experimental data can be well explained if we assume a three-regime model: the dilute (D), semidilute (S), and concentrated (C) regions as shown in Figure 10. Equation 1 is valid in D and the model of Berry and Fox is applicable in C, as discussed later, while eq 9 is valid in region S. The crossover between the dilute and semidilute regions is found to take place at $C/C^* \simeq 10$ in Figure 6. The boundary between D and S in Figure 10 was given assuming $C/C^* = 10$. In Figure 9, the deviation of experimental data from the scaling theory at higher concentrations is found to occur at a critical concentration C^{**} independent of molecular weight. The boundary between S and C is shown by a shaded area

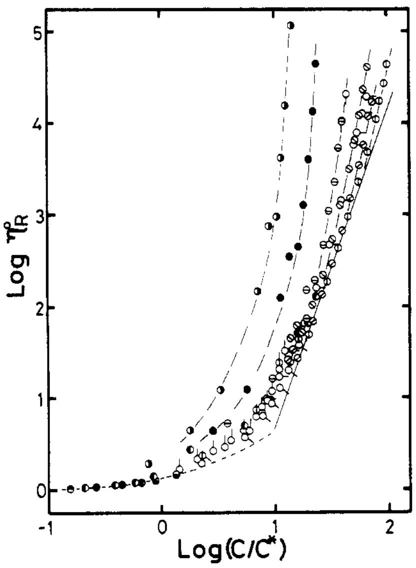

Figure 6. Plots of log η_R^0 vs. log (C/C^*) in good solvents. Symbols are the same as in Figure 3. The chain curve and the solid line denote eq 1′ and 9 ($\eta_R^0 \propto (C/C^*)^{3.5}$), respectively. The broken lines denote deviations from eq 1′ and 9.

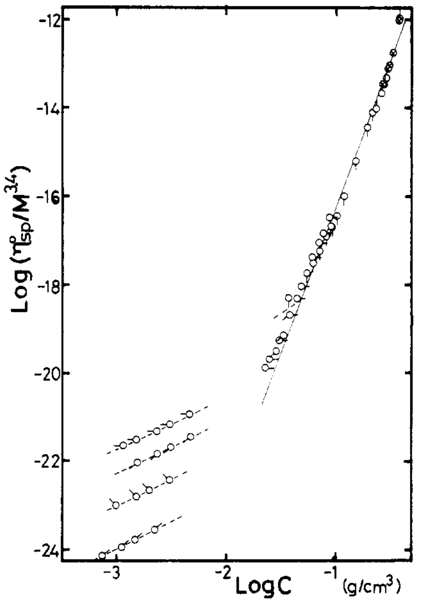

Figure 7. Double logarithmic plots of $\eta_{sp}^0/M^{3.4}$ vs. C in Θ solvents. Symbols are the same as in Figure 1. The chain curves denote the values calculated from eq 1. The solid line shows the slope calculated from eq 9′ ($\eta_{sp}^0/M^{3.4} \propto C^{6.8}$).

assuming $C^{**} \simeq 0.2$ g/mL in Figure 10. Here, we would like to note that the excluded volume effect also disappears in the viscosity of 0.2 g/mL.[9,18,22] Low molecular weight samples ($M < 1.5 \times 10^5$) do not show the S region. The boundary between D and C regions for low molecular weight samples is shown by a broken line, assuming that the critical concentration for η^0 varies with $CM = \rho M_c$ and $M_c = 2.8 \times 10^4$.

Thus, the viscosity behavior in good solvents can be understood by the same model as thermodynamic properties if we take into account the semidilute region. However, the semidilute region in viscosity behavior is much narrower than that in thermodynamic properties.[19-22] The crossover value of C/C^* between dilute and semidilute solutions in good solvents is about 2 in thermodynamic properties, whereas it is about 10 in viscosity. The difference may be caused by the difference in the effect of entanglement on both properties.

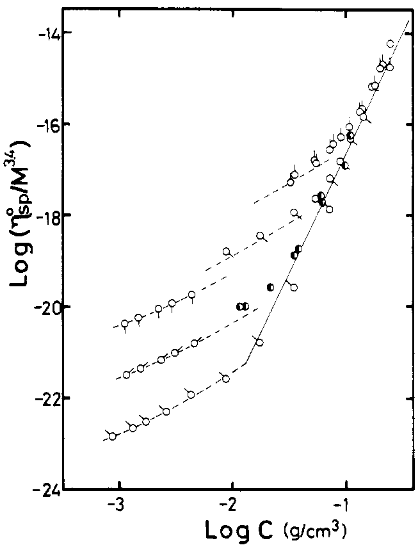

Figure 8. Plots of log ($\eta_{sp}^0/M^{3.4}$) vs. log C in poor solvents. Symbols are the same as in Figure 2. The chain curves and the solid line denote eq 1 and 9′ ($\eta_{sp}^0/M^{3.4} \propto C^{5.2_3}$), respectively.

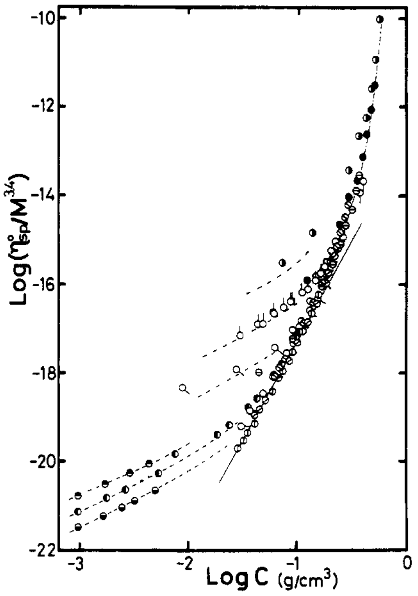

Figure 9. Plots of log ($\eta_{sp}^0/M^{3.4}$) vs. log C in good solvents. Symbols are the same as in Figure 3. The chain curves and the solid line denote eq 1 and 9′ ($\eta_{sp}^0/M^{3.4} \propto C^{4.5}$), respectively.

Discussion

Analyzing the molecular weight and polymer concentration dependence data of η^0 in 12 polymer–solvent systems, Utracki and Simha[6,7] showed that the exponent a_1 in eq 2 is 0.47 in Θ solvents but increases with solvent power as in the case of exponent a. Since a simple average of a_1 in good solvents appears to be in the vicinity of 0.73, the results of Utracki and Simha may mean that η_R^0 in most polymer–solvent systems can be given as a universal function of $C^{2.1}M$ in Θ solvents and of $C^{\sim 1.4}M$ in good solvents. Onogi and Masuda et al.[33,34] also reported that the relationship $\eta^0 \propto C^\alpha M^\beta$ with a constant ratio of α/β holds for several polymer–solvent systems. The ratio α/β also has a close correlation with the exponent a. They showed that α/β is nearly 2 in Θ solvents but lower in good solvents (ca. 1.4). Besides these two works, a few works with similar results have been published.[24,25,35] Considering that the polymer concentration range employed for superposition of data in the present work is narrower than those in the previous works, the present conclusion (η_R^0

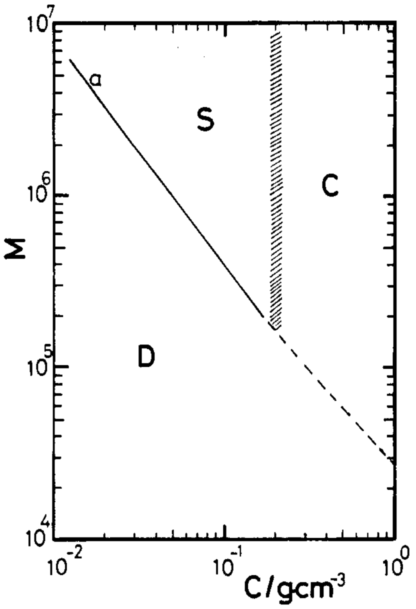

Figure 10. Molecular weight–concentration diagram for viscosity of poly(α-methylstyrene) in good solvents. D, S, and C stand for dilute, semidilute, and concentrated regions, respectively.

is a function of C^2M in Θ and of $C^{1.33}M$ in good solvents) seems to be in very good agreement with the former empirical relationships. Moreover, the scaling theory satisfactorily predicts not only the universal parameter for η_R^0 but also its function form (eq 9) in the semidilute solution, whereas no previous theories could do it.

Here, it should be noted that, since $[\eta]$ is approximately proportional to $(C^*)^{-1}$ for the present samples, as can be seen in Table I, there is no detectable difference in Figures 4–6 even if we plot the data using $C[\eta]$ instead of C/C^* as in many previous works.

In Table II, it can be observed that the zero-shear viscosity η^0 of the same sample at the same concentration markedly varies with solvents. This means that the local frictional coefficient is important for discussing the viscosity behavior of polymer solutions and melt. In the scaling theory, the lcoal frictional coefficient is taken into account as the proportionality factor in eq 5, 6, or 9 and is assumed to be independent of polymer concentration in the semidilute solutions, where polymer coils are entangled but C is still low. Hence eq 9 corresponds to the structure factor of eq 3, neglecting the local frictional factor $\omega(\eta_s,T,C)$. In very good solvents ($\nu = 0.6$) eq 9 predicts η^0 as a function of $C^{1.25}M$, whereas, in the structure factor of eq 3, η^0 is given as a function of $C^{0.75}M$ if we assume $\alpha_\phi^2 \propto C^{-0.25}$.[9,18] In Θ solvents, moreover, $\eta^0 = f(C^2M)$ from eq 9, whereas $\eta^0 = f(CM)$ in the structure factor of eq 6. That is, in the theory of Berry et al. the number of entanglements per molecule is assumed proportional to CM (neglecting expansion factor) and the local frictional coefficient ω is assumed to vary with polymer concentration, whereas in the scaling theory, the former is given as proportional to $C^{1/(3\nu-1)}M$ and ω is assumed to be independent of polymer concentration. Both theories may be two extreme cases. Considering the fact that good agreement between eq 9 and experiments can be found without assuming any parameter and also the fact that the thermodynamic properties of polymer solutions in the semidilute region can be explained by using the same model, it is our present opinion that the scaling theory is more reasonable for understanding the viscosity behavior in the semidilute region. In concentrated solutions, the approach of Berry and Fox may be most reasonable.

In different solvents, the proportionality coefficient in eq 9 cannot be assumed equal. The local frictional coefficient in eq 3 may be equivalent to the rupture energy of an entanglement (strength of entanglement) proposed by Isono et al., in a previous paper.[23] In those two treatments, it is assumed that the viscosity of polymer solutions in the entangled region is determined by the number of entanglements per molecule and ω or the strength of entanglement, respectively. The local frictional coefficient seems to imply that the friction between a polymer chain and its environment is distributed over the whole chain, whereas the strength of entanglement means that the overall friction is assigned to entanglement points. It was pointed out in the previous paper that the strength of entanglement is stronger in poor solvents than in good solvents. The situation may be opposite to the solvent effect on the excluded volume effect in dilute solutions. Comparison of Figures 4–6 shows that the critical value of C/C^* at the crossover from the dilute to the semidilute region becomes higher in the order of solvent power, in agreement with the above speculation.

Due to this change in C/C^* with solvent power in addition to the higher polymer concentration dependence of $\eta_{sp}{}^0$ in poor solvents than in good solvents, it is expected that $\eta_{sp}{}^0/M^{3.4}$ in poor solvents would become generally higher than in good solvents in the entangled region, though it is opposite in dilute solutions. This speculation is well accounted for by comparing Figure 9 with Figures 7 and 8.

References and Notes

(1) Berry, G. C.; Fox, T. G. *Adv. Polym. Sci.* **1968**, 5.
(2) Graessley, W. W. *Adv Polym. Sci.* **1974**, 16.
(3) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(4) Vinogradov, G. V.; Mulkin, A. Ya. "Rheology of Polymers"; Mir Publishers: Moscow, 1980.
(5) Simha, R.; Zakin, L. *J. Colloid Sci.* **1962**, *17*, 270.
(6) Utracki, L.; Simha, R. *J. Polym. Sci., Part A* **1963**, *1*, 1089.
(7) Simha, R.; Utracki, L. *J. Polym. Sci., Part A-2* **1967**, *5*, 853.
(8) Berry, G. C.; Nakayasu, H.; Fox, T. G. *J. Polym. Sci., Part A-2* **1979**, *17*, 1825.
(9) Hager, B. L.; Berry, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 911.
(10) De Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(11) De Gennes, P. G. *Macromolecules* **1976**, *9*, 587, 594.
(12) Adam, M.; Delsanti, M. *J. Phys. (Paris)* **1982**, *43*, 549.
(13) Adam, M.; Delsanti, M. *J. Phys. (Paris)* **1983**, *44*, 1185.
(14) Doi, M. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 265.
(15) Takahashi, M.; Masuda, T.; Nakamura, H.; Onogi, S. *Polym. Prepr., Jpn.* **1983**, *32*, 2361.
(16) Osaki, K.; Nishizawa, K.; Kurata, M. *Nihon Reoroji Gakkaishi* **1982**, *10*, 169.
(17) Des Cloizeaux, J. *J. Phys. (Paris)* **1975**, *36*, 281.
(18) Daoud, M.; Cotton, J. P.; Farnoux, B., Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P. G. *Macromolecules* **1975**, *8*, 804.
(19) Noda, I.; Kato, N.; Kitano, T.; Nagasawa, M. *Macromolecules* **1981**, 14 668
(20) Des Cloizeaux, J.; Noda, I. *Macromolecules* **1982**, *15*, 1505.
(21) Higo, Y.; Ueno, N.; Noda, I. *Polym. J.* **1983**, *15*, 367.
(22) Noda, I.; Higo, Y.; Ueno, N.; Fujimoto, T. *Macromolecules* **1984**, *17*, 1055.
(23) Isono, Y.; Nagasawa, M. *Macromolecules* **1980**, *13*, 862.
(24) Ferry, J. D.; Grandine, L. D. Jr.; Udy, D. C. *J. Colloid Sci.* **1953**, *8*, 529.
(25) Gandhi, K. S.; Willimas, M. C. *J. Polym. Sci., Part C* **1971**, *35*, 211.
(26) Simha, R.; Chan, F. S. *J. Phys. Chem.* **1971**, *75*, 256.
(27) Kato, T.; Miyaso, K.; Noda, I.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 777.
(28) Noda, I.; Mizutani, K.; Kato, T.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1970**, *3*, 787.
(29) Sakai, M.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1972**, *5*, 786.
(30) Kajiura, H.; Ushiyama, Y.; Fujimoto, T.; Nagasawa, M. *Macromolecules* **1978**, *11*, 894.

1008 *Macromolecules* **1985**, *18*, 1008–1015

(31) Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958**, *29*, 311.
(32) Daoud, M.; Jannink, G. *J. Phys.* (*Paris*) **1976**, *37*, 973.
(33) Onogi, S.; Kimura, S.; Kato, T.; Masuda, T.; Miyanaga, N. *J. Polym. Sci., Part C* **1966**, *15*, 381.
(34) Masuda, T. Dissertation, Kyoto University, Kyoto, Japan, 1973.
(35) Johnson, M. F.; Evans, W. W.; Jordan, I.; Ferry, J. D. *J. Colloid Sci.* **1951**, *6*, 377.

Viscoelastic Properties of Binary Blends of Narrow Molecular Weight Distribution Polystyrenes. 2

Hiroshi Watanabe, Takashi Sakamoto, and Tadao Kotaka*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received August 27, 1984*

ABSTRACT: Viscoelastic properties of binary blends of narrow distribution polystyrenes with low and high molecular weight (designated as 1-chain and 2-chain, respectively) were examined. In the blends the 2-chains entangle with themselves, only when the weight fraction w_2 of the 2-chain has exceeded a critical value w_c. Then, such blends exhibit a boxlike relaxation spectrum with the characteristic time τ_{22} and intensity P_{22} at the long-time end. For the blends with the molecular weight of the 2-chain M_2 sufficiently larger than that (M_1) of the 1-chain, the τ_{22} is proportional to $w_2^{1.5}M_2^{3.5}$ and P_{22} to w_2^2. The behavior is similar to that of ordinary concentrated solutions. In such blends, a wedgelike spectrum with the characteristic time τ_{12} ($\propto w_2^0M_1^3M_2^2$) appears on the intermediate time scale. In terms of the concepts of reptation and tube renewal, this process may be attributed to the renewal of the tubes composed of the 1-chains. On the other hand, for the blends with M_2 close to M_1, the τ_{22} and P_{22} become proportional to $w_2^0M_2^{3.5}$ and w_2^1, respectively, and the wedgelike spectrum on the intermediate time scale becomes less prominent. Namely, the 2-chains relax before the renewal of the tubes composed of the 1-chains completes.

Introduction

Binary blends of polymers having narrow molecular weight distributions (MWD) are one of the simplest model systems for examining the effect of polydispersity on the viscoelastic properties. Extensive studies have been carried out by various authors on such binary blends, and some of the earlier results were summarized, for example, in the monograph by Ferry[1] and in the review by Graessley.[2] Recently, some workers[3–5] including ourselves[6] reexamined this problem on the basis of the "tube model"[7–11] and proposed some new blending laws.[3–6,12]

In such an attempt,[6] we described linear viscoelastic properties of binary blends consisting of narrow MWD polystyrenes of short and long chains (hereafter designated as 1- and 2-chains, respectively) with molecular weights M_1 and M_2 differing at least 10 times. For such blends, there was a critical value w_c for the content w_2 of the 2-chain corresponding to the onset of entanglements among the 2-chains. Thus, in what we called *dilute* blends[6] with w_2 below w_c, first the relaxation of entanglements among 1-chains took place, and that of entanglements among the 1- and 2-chains prevailed at long times. Then, the blends behaved as dilute solutions of 2-chains dissolved in 1-chains. On the other hand, in *concentrated* blends with w_2 well above w_c, the relaxation of 1–2 entanglements appearing at intermediate times was followed by the relaxation of entanglements among the 2-chains at sufficiently long times. Then, the blends behaved just as concentrated solutions of 2-chains.

We interpreted these results on the basis of the tube model incorporating not only the concept of *reptation*,[7–11] but also *contour length fluctuation*,[13,14] and *tube renewal processes*.[14,15] On this basis we concluded that the relaxation of the 1–2 entanglements appearing at intermediate times is due to the renewal of tubes composed of 1-chains to release the constraints imposed on 2-chains. We also concluded that the relaxation of the 2–2 entanglements at long times proceeds by reptation accompanying contour length fluctuation of the 2-chains, while the 1-chains are simply acting as solvent at this stage.

Table I
Characteristics of Polystyrene Samples

code	$10^{-3}M_n$	$10^{-3}M_w$	$10^{-3}M_z$	$10^{-3}M_{z+1}$
L36	36.3	38.9	41.6	44.6
L83[a]	82.7	88.6	96.1	107
L161[a]	161	172	183	197
L294[a]	294	316	341	373

[a] Supplied from Toyo Soda Mfg. Co., Ltd.

To generalize the above-mentioned tube-theory concept on the relaxation modes in binary blends,[6] we extended this study to the blends having relatively small M_2/M_1 ratio. To this end, we prepared a series of binary blends consisting of monodisperse polystyrenes with M_2/M_1 ratio ranging from 2 to 8 and with varying blending ratio. Then, we studied their linear viscoelastic properties. In this paper, we present the results and discuss possible relaxation mechanisms on the basis of the tube model employed in the previous study.[6]

Experimental Section

Anionically polymerized narrow MWD polystyrene (PS) samples were used. The characterization of the samples was carried out on a gel permeation chromatography (GPC; Toyo Soda, Ltd., Model HLC-801A) equipped with a triple-detector system consisting of a built-in refractometer, a UV monitor (Toyo Soda, Ltd., Model UV-8), and a low-angle laser light scattering photometer (Toyo Soda, Ltd., Model LS-8). Chloroform was the elution solvent, and commercially available narrow MWD PS (Toyo Soda, Ltd., TSK PS samples) were used as elution standards. Table I shows the characteristics of the samples. Each sample has an approximately logarithmic-normal MWD.

To prepare binary blends, we chose an L294 sample as component 2 (longer chain) and others as component 1 (shorter one). Prescribed amounts of the two PS samples were dissolved in benzene to make a 5 wt % solution. The solution was freeze-dried for 12 h and further dried at about 80 °C under vacuum for 24 h. The dried blend was then molded at about 170 °C with a

0024-9297/85/2218-1008$01.50/0