

Zero-Shear Viscosity of Block Copolymers in Semidilute Solutions

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ABSTRACT: The zero-shear viscosity η^0 of styrene-2-vinylpyridine diblock copolymers in semidilute solutions was measured in pyridine (a commonly good solvent), methyl ethyl ketone (MEK) (a commonly poor solvent) at 25°C, and in benzene (a selective solvent) at 11.4°C. It was found that the reduced zero-shear viscosity η_R^0 ($\equiv \eta_{sp}^0/C[\eta]$) is expressed as a universal function of $C[\eta]$ in all solvents, and the dependence of η_R^0 on $C[\eta]$ is determined by the exponent in the relationship between the radius of gyration and molecular weight of the block component which has the larger excluded volume, regardless of the solvent.

KEY WORDS Zero-Shear Viscosity / Block Copolymer / Scaling Theory / Solvent Effect /

The zero-shear viscosity η^0 of homopolymer solutions is discussed by classifying solutions into at least three concentration regions in terms of concentration C and degree of coil-overlapping C/C^* .^{1,2} Here, the critical concentration C^* , at which polymer chains begin to overlap with each other can be defined by

$$C^* = 3M / (4\pi \langle s^2 \rangle^{3/2} N_A) \quad (1)$$

where M is the molecular weight, $\langle s^2 \rangle$ is the mean square radius of gyration and N_A is Avogadro's number.

In dilute solutions where $C \ll 1$ and $C/C^* \ll 1$, the reduced zero-shear viscosity η_R^0 is given by

$$\begin{aligned} \eta_R^0 &\equiv \eta_{sp}^0 / C[\eta] = 1 + k' C[\eta] + \dots \\ &= 1 + k C/C^* + \dots \end{aligned} \quad (2)$$

where $\eta_{sp}^0 = (\eta^0 - \eta_s) / \eta_s$, η_s is the solvent viscosity, $[\eta]$ is the intrinsic viscosity, k' is the Huggins' constant, and $k = 3k' \Phi' / (4\pi N_A)$. Here, the last equation is obtained by assuming the Flory-Fox equation, $[\eta] = \Phi' \langle s^2 \rangle^{3/2} / M$ where

Φ' is the Flory viscosity factor.³

In semidilute solutions where $C \ll 1$, but $C/C^* \gg 1$, η_R^0 is given by a scaling law as⁴⁻⁶

$$\eta_R^0 \propto (C/C^*)^{(4,4-3\nu)/(3\nu-1)} \propto (C[\eta])^{(4,4-3\nu)/(3\nu-1)} \quad (3)$$

where ν is the exponent in the relationship between radius of gyration and molecular weight, $\langle s^2 \rangle \propto M^{2\nu}$. Here, the second equation is also derived assuming the Flory-Fox equation. Thus, η_R^0 is predicted to be expressed as a universal function of (C/C^*) or $C[\eta]$ in both the dilute and semidilute regions, and this theoretical prediction was confirmed by experiments as reported previously.^{5,6}

In block copolymer solutions, microphase separation occurs above a critical concentration even in commonly good solvents.⁷ Particularly, in selective solvents which dissolve a block chain, but not others, block copolymers form a strong three-dimensional macrolattice in solutions. Thus, viscosities of block copolymer solutions have been studied mainly in relation

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to the microphase-separated structures.^{8,9}

Measurements of viscosity, light scattering and small-angle neutron scattering revealed that a block copolymer does not assume intramolecular segregation and behaves like a homopolymer in dilute solutions.^{10–13} However, solution properties of block copolymers from dilute to microphase-separated regions are little known. In the present work, therefore, we measured η^0 of block copolymers in the intermediate or semidilute region between the dilute and microphase-separated regions to examine the applicability of the scaling law (eq 3), which is valid for homopolymers in semidilute solutions,^{5,6} to η^0 of block copolymer solutions.

EXPERIMENTAL

Samples

Samples used were styrene–2-vinylpyridine (SP) diblock copolymers, which were prepared *in vacuo* at -78°C by an anionic polymerization method with a sequential monomer addition technique. Details of the preparation and characterization of the block copolymers are reported in previous papers.^{13,14} The molecular characteristics of samples are listed in Table I.

Solvents

Solvents used were pyridine, methyl ethyl ketone (MEK) and benzene. Pyridine and MEK of the specific grade of Kishida Chemical Co., were dried according to standard procedure. Benzene of the spectroscopic grade of Merck was used without further purification. Pyridine is a good solvent for both polystyrene (PS) (0.73) and poly(2-vinylpyridine) (P2VP) (0.73), MEK is a poor solvent for both PS (0.63) and P2VP (0.48), while benzene is a selective solvent which is good for PS (0.70) but as a θ -solvent for P2VP (0.5) at 11.4°C . Here, the values in parentheses denote the exponent a in the Mark–Houwink–Sakurada (MHS) equation, $[\eta] = KM^a$ for PS and P2VP

Table I. Molecular characteristics of styrene–2-vinylpyridine diblock copolymers

Sample code	$M_w \times 10^{-5}$	M_w/M_n^a	$C_s/\text{wt}\%^b$
SP-12	4.22	1.03	50
SP-23	10.9	1.03	51
SP-18	15.6	1.17	48

^a M_w/M_n were determined from GPC.

^b C_s denotes styrene content.

Table II. Solvent viscosity

Temp/ $^\circ\text{C}$	$\eta_s/\text{mPa s}$		
	Pyridine	MEK	Benzene
11.4			0.736
25.0	0.884	0.378	

in the respective solvents.¹³ The viscosities of these solvents η_s are listed in Table II.

Zero-Shear Viscosity Measurements

Weighed amounts of polymer sample and solvent were mixed, and the solutions were kept at about 40°C in an incubator for two weeks to be dissolved completely. The concentrations were converted to g cm^{-3} by assuming the additivity of specific volumes of polymer and solvent. The zero-shear viscosity η^0 was measured with capillary viscometers of Maron–Krieger–Sisko type¹⁵ and the Ubbelohde type in pyridine and MEK at 25°C , and in benzene at 11.4°C . The MHS equation of the diblock copolymer in benzene at 11.4°C was determined in this work.

RESULTS AND DISCUSSION

No shear-rate dependence of viscosity as reported in microphase-separated regions^{8,9} was observed for any sample solution measured in this work. Thus, the effects of microphase separation on the viscosity were not observed explicitly.

Figures 1–3 show double logarithmic plots of η_{sp}^0 vs. C in pyridine, MEK and benzene,

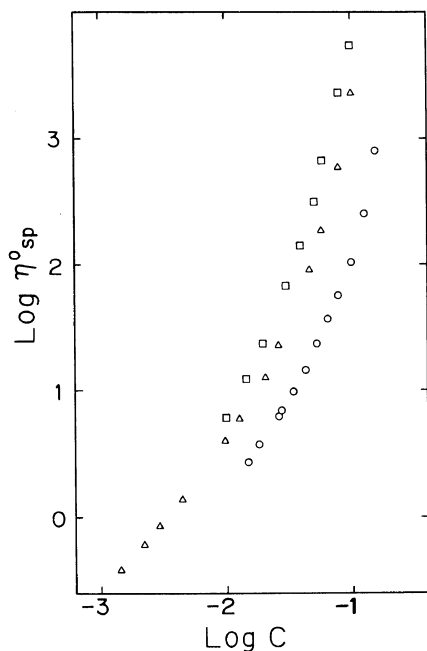


Figure 1. Concentration dependence of specific viscosity η_{sp}^0 in pyridine at 25°C. Symbols (○), (△), and (□) denote the data for samples SP-12, SP-23 and SP-18, respectively.

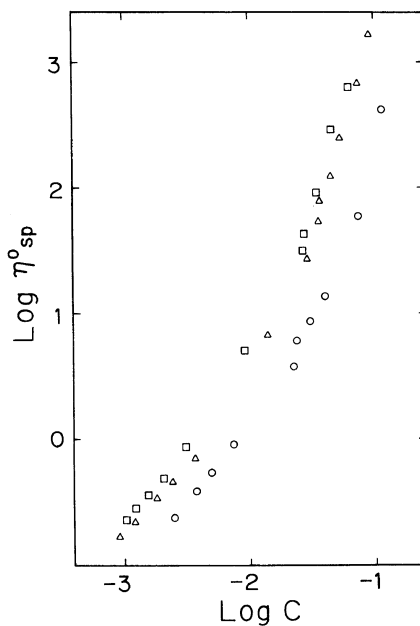


Figure 3. Concentration dependence of specific viscosity η_{sp}^0 in benzene at 11.4°C. Symbols are the same as in Figure 1.

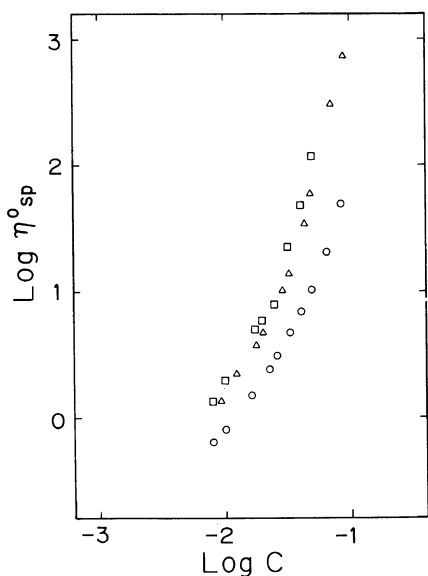


Figure 2. Concentration dependence of specific viscosity η_{sp}^0 in MEK at 25°C. Symbols are the same as in Figure 1.

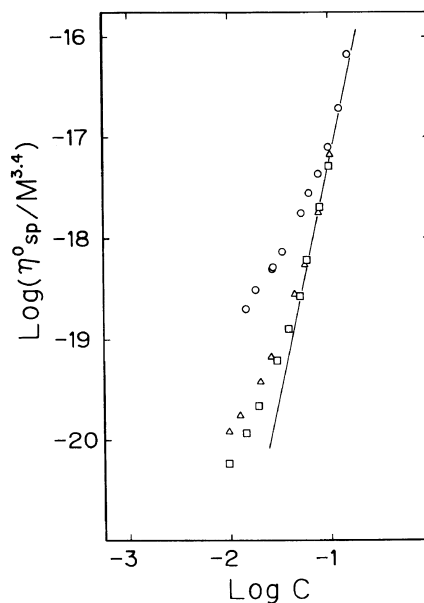


Figure 4. Double logarithmic plots of $\eta_{sp}^0/M^{3.4}$ vs. C in pyridine. Symbols are the same as in Figure 1.

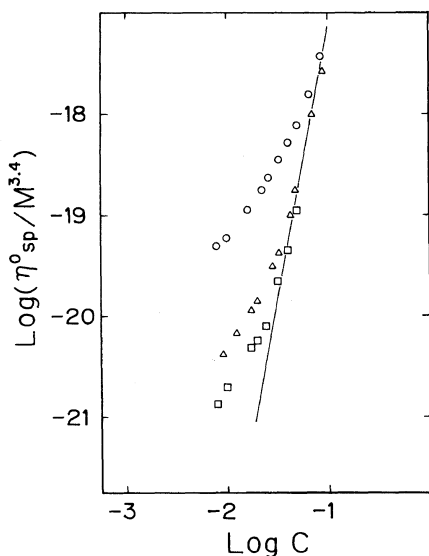


Figure 5. Double logarithmic plots of $\eta_{sp}^0/M^{3.4}$ vs. C in MEK. Symbols are the same as in Figure 1.

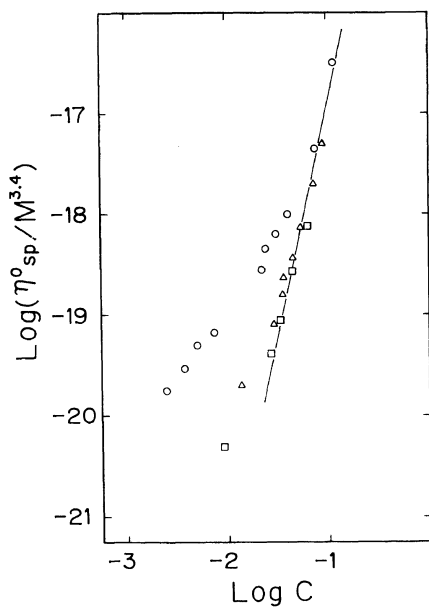


Figure 6. Double logarithmic plots of $\eta_{sp}^0/M^{3.4}$ vs. C in benzene. Symbols are the same as in Figure 1.

respectively. In Figures 4–6, the data in Figures 1–3 are replotted in the double logarithmic form of $\eta_{sp}^0/M^{3.4}$ vs. C , where the data at the lower concentration were neglected since we were interested in the high concentra-

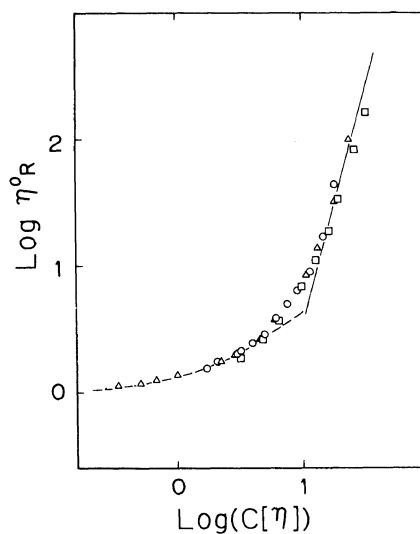


Figure 7. Double logarithmic plots of η_R^0 vs. $C[\eta]$ in pyridine. Symbols are the same as in Figure 1. The broken curve and solid line denote eq 2 with $k'=0.35$ and eq 3 with $\nu=0.58$, respectively.

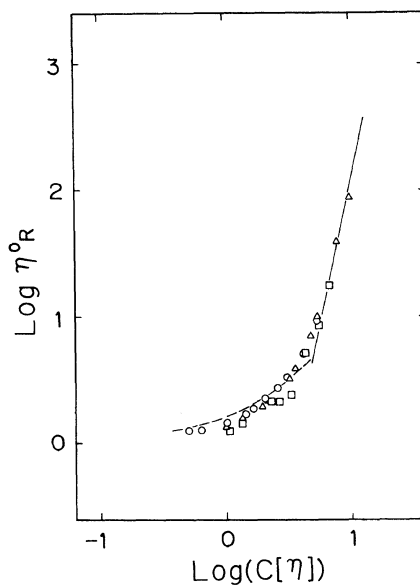


Figure 8. Double logarithmic plots of η_R^0 vs. $C[\eta]$ in MEK. Symbols are the same as in Figure 1. The broken curve and solid line denote eq 2 with $k'=0.7$ and eq 3 with $\nu=0.53$, respectively.

tion region. These figures show that the data of $\eta_{sp}^0/M^{3.4}$ converge on a straight line at high concentrations, and hence the 3.4th power law

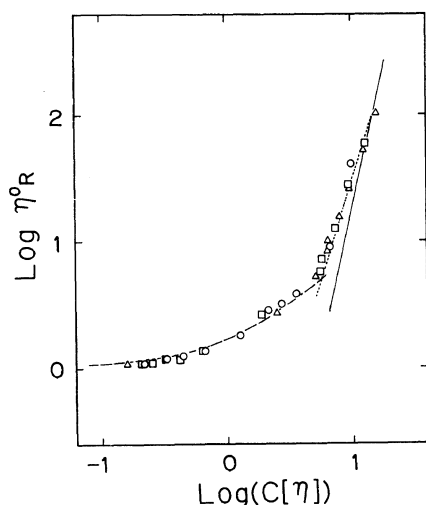


Figure 9. Double logarithmic plots of η_R^0 vs. $C[\eta]$ in benzene. Symbols are the same as in Figure 1. The broken curve and solid line denote eq 2 with $k'=0.7$ and eq 3 with $\nu=0.55$, respectively. The dotted line denotes eq 3 assuming $\nu=0.58$.

for η^0 of homopolymers in entangled regions also holds for the block copolymer solutions where the concentration is high enough. Figures 7–9 show the viscosity data replotted in the double logarithmic form of η_R^0 vs. $C[\eta]$. These figures show that η_R^0 of a block copolymer is expressed as a universal function of $C[\eta]$ in both dilute and semidilute solutions in the same way as that of homopolymer. Moreover, η_R^0 of the block copolymer in pyridine is in good agreement with that of PS in good solvents.⁶ This result is consistent with the fact that the reduced osmotic pressure of the SP block copolymer in pyridine is in good agreement with that of PS in a good solvent as will be reported elsewhere.¹⁶

Now, let us compare quantitatively the data with eqs 2 and 3. In the dilute region, η_R^0 is in good agreement with eq 2 as shown by the broken lines, if the values of k' are assumed to be 0.35 in pyridine and 0.7 in MEK and benzene. These values are in good agreement with those of homopolymers in good and poor solvents, respectively.

To compare the experimental data in

semidilute solutions with eq 3, we need the ν values in these solvents, which can be calculated by assuming $\nu=(a+1)/3$ from the exponent a in the MHS equation. Although they slightly differ from the actual ν values, the difference does not significantly affect the following discussion.

MHS equations in these solvents are given by¹³

$$[\eta] = 9.8 \times 10^{-5} M_w^{0.73} \quad (\text{in pyridine at } 25^\circ\text{C})$$

$$[\eta] = 3.5 \times 10^{-4} M_w^{0.59} \quad (\text{in MEK at } 25^\circ\text{C})$$

$$[\eta] = 1.5 \times 10^{-4} M_w^{0.67} \quad (\text{in benzene at } 11.4^\circ\text{C})$$

The third relationship was obtained in the present work. The ν values calculated from the above relationships are 0.58, 0.55, and 0.53 in pyridine, benzene and MEK, respectively. The slopes of straight lines in Figures 7–9 were calculated from eq 3 using these ν values. The dependences of η_R^0 on $C[\eta]$ in pyridine (a commonly good solvent) and MEK (a commonly poor solvent) agree with those predicted by eq 3 with $\nu=0.58$ and 0.53, respectively, whereas the dependence of η_R^0 on $C[\eta]$ in benzene (a selective solvent) is lower than that predicted by eq 3 with $\nu=0.55$.

The critical concentration C_c for the microphase separation depends on the molecular weight of block copolymer and temperature T . Hashimoto *et al.* presented the following experimental relationship among them.⁷

$$C_c \propto TM^{-1/2} \quad (4)$$

This means that C_c increases with temperature and decreasing molecular weight. For the present block copolymer in a commonly good solvent, almost the same relationship was found, as will be reported elsewhere.¹⁷ By using the relationship, C_c is found to be around 0.1 gcm^{-3} for the highest molecular weight sample (SP-18) in pyridine. Since eq 4 appears to be valid regardless of solvent power⁷, we may assume that C_c in MEK and benzene is not significantly different from that in pyridine.

Thus, a few data at high concentrations in Figures 7—9 are considered to be above C_c . However, Figure 7 reveals that eq 3 is valid even above C_c in pyridine. This implies that the microphase-separated structures are too weak to affect η^0 in the concentration region slightly higher than C_c .

Although the dependence of η_R^0 on $C[\eta]$ in benzene is not explained by eq 3 as mentioned above, it is in good agreement with eq 3 if we assume $\nu=0.58$ for PS in a good solvent as shown by the dotted line in Figure 9. Moreover, it is to be noted that the dependence of η_R^0 on $C[\eta]$ in MEK also can be explained by eq 3 assuming $\nu=0.54$ for PS in MEK. Here, we do not show the calculated line because the two ν values, which are for the SP block copolymer in MEK and for PS in MEK, are so close that both calculated lines are almost the same. As mentioned above, η^0 in pyridine (a commonly good solvent) is explained by eq 3. Thus, these results in the three solvents indicate that the dependence of η_R^0 on $C[\eta]$ is determined by the exponent ν of block component which has the larger excluded volume, regardless of the solvent.

Finally, it is to be noted that the $C[\eta]$ values at the crossover from dilute to semidilute regions are about 4, 6 and 10 in MEK, benzene and pyridine, respectively, as shown in Figures 7—9. They increase with the mean solvent power for the block copolymer indicated by the exponent ν . This result is the same as observed for homopolymer solutions.⁵

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