

## Cross-Over Concentration in Polydisperse Polymer Solutions

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**ABSTRACT:** Correlation length and osmotic compressibility of blends of narrow distribution polystyrenes in benzene solutions were measured by dilute and semidilute regimes. Universal curves were obtained for correlation length and osmotic compressibility. These curves were the same as those of monodisperse polystyrenes. The cross-over concentration  $C^*$  of polydisperse systems can be calculated by the equation,  $1/C^* = \sum_i (w_i/C_i^*)$ , where  $w_i$  and  $C_i^*$  are the weight fractions and cross-over concentrations of  $i$ -th components, respectively.

**KEY WORDS** Cross-Over Concentration / Polydisperse / Correlation Length / Radius of Gyration / Osmotic Compressibility / Polystyrene /

The semi-dilute regime proposed by des Cloizeaux<sup>1</sup> is one of the most important concepts in the field of polymer solutions. The cross-over concentration  $C^*$  from the dilute regime to the semi-dilute regime is defined as the overlap threshold of the chain spheres of solute polymers. In monodisperse polymer solutions, this concentration is regarded as comparable to the average concentration inside the chain sphere.

In the semi-dilute regime, solution properties, such as correlation length  $\xi$  and osmotic pressure  $\Pi$ , become independent of the molecular weight  $M$  at the same reduced concentration  $C/C^*$ . Further, the concentration dependence of the scaled values by the value at the infinite dilution, such as  $\xi^2/\langle S^2 \rangle_{C \rightarrow 0}$  or  $(\partial\Pi/\partial C) M/RT \langle \langle S^2 \rangle \rangle$ : the mean square radius of gyration), can be expressed by universal functions of  $C/C^*$  through the whole range of dilute and semidilute regimes.

For monodisperse polymer solutions, the theoretical prediction by des Cloizeaux has been confirmed by many experiments.<sup>2</sup> Ex-

amples by us<sup>3</sup> are shown in Figures 1 and 2. However, for polydisperse polymer solutions, there are few studies. In polydisperse polymer solutions, the average concentration inside the chain sphere is not unique and the universality has not been examined.

In this report, the concentration dependence of  $\xi$  and  $\Pi$  for two peaks type—polydisperse systems is examined, and the universality and  $C^*$  for polydisperse systems are discussed.

### EXPERIMENTAL

Two peaks type—polydisperse samples were prepared by blending the standard polystyrenes (Toyo Soda MFG); F80 ( $M = 77.5 \times 10^4$ ) with F20 ( $M = 18.6 \times 10^4$ ) or F1 ( $M = 1.02 \times 10^4$ ). The F20/F80 blends were in the ratios 1:1 (ml), 10.1:1 (m10), and 99.8:1 (m100), respectively. The F1/F80 blends were in the ratios 0.998:1 (m1), 7.63:1 (m7), 49.5:1 (m50), and 247:1 (m250), respectively. The correlation length and osmotic compressibility,  $\partial\Pi/\partial C$ , in benzene solutions

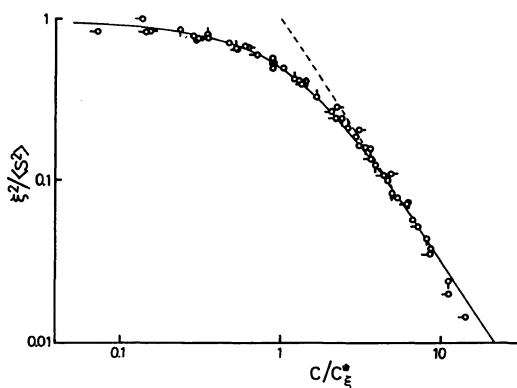


Figure 1. The universal curve of the correlation length of monodisperse polystyrenes in benzene.

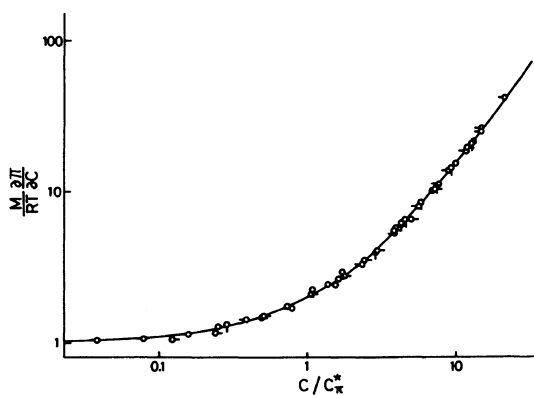


Figure 2. The universal curve of the osmotic compressibility of monodisperse polystyrenes in benzene.

at 33°C were measured by using a home-made light scattering photometer described previously.<sup>4</sup> Solutions were prepared at 60°C and left for a day. The solutions were clarified by filtration through a membrane filter (Toyo Roshi TM-4P) just before measurement.

### RESULTS

Figures 3 and 4 show the concentration dependence of the correlation length of the F20/F80 and F1/F80 blends, respectively. The solid curves are those of pure F20 and F80. The correlation length of F1 is too small to measure even at the dilute regime. The calculated value of  $\langle S^2 \rangle^{1/2}$  of F1 is about 3 nm,

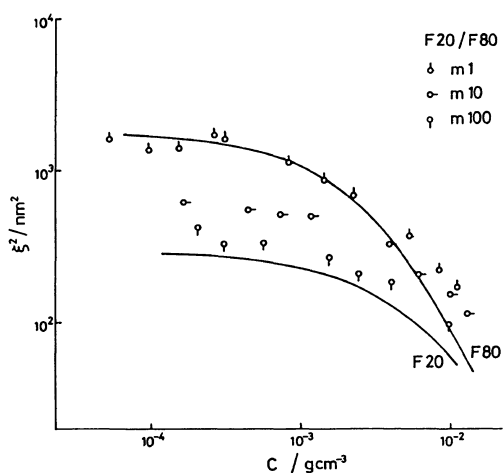


Figure 3. The correlation length of F20/F80 systems. Solid curves represent the values of pure F80 (upper) and F20 (lower), respectively.

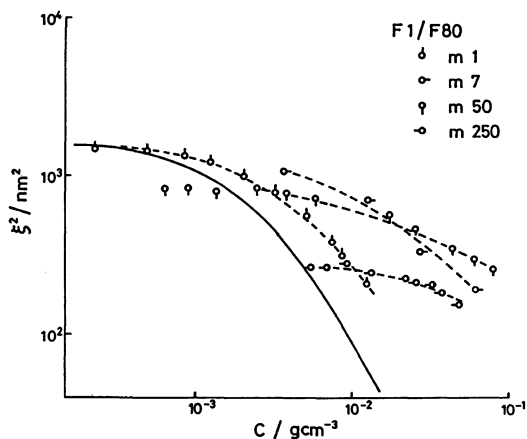
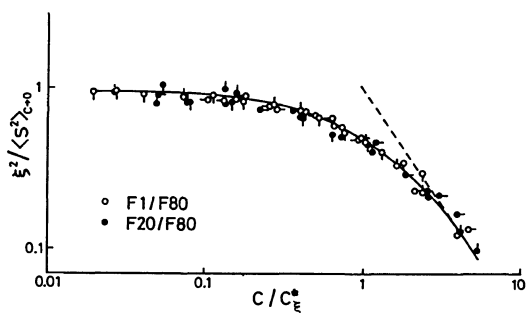


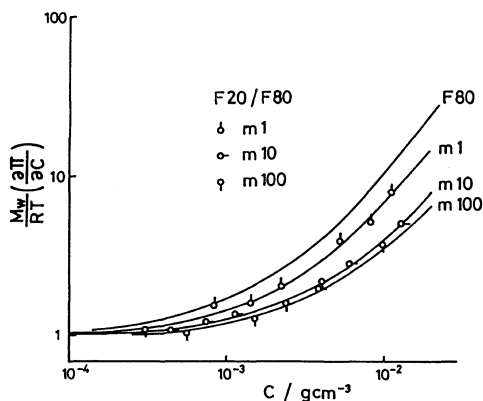
Figure 4. The correlation length of F1/F80 systems. The solid curve represents the value of pure F80.

which is negligibly small compared with the correlation length of the F1/F80 blend in the whole experimental range. The correlation length decreases with increase of concentration in all samples as in the case of monodisperse samples. The correlation length of blended samples is between those of the components in the dilute regime and becomes larger than both of them in the semi-dilute regime.

As shown in Figure 5, the reduced correlation length by the value at the infinite dilution ( $\equiv \langle S^2 \rangle_{C \rightarrow 0}$ ),  $\xi^2 / \langle S^2 \rangle_{C \rightarrow 0}$ , can be



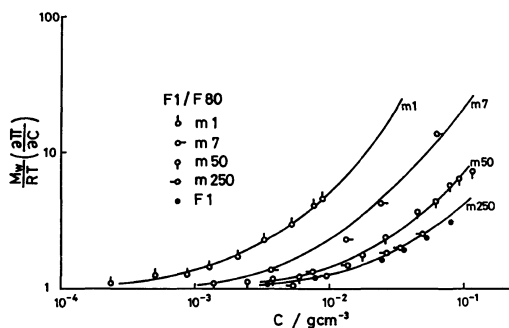
**Figure 5.** The universal curve of the correlation length of polystyrene blends in benzene. Symbols are the same as in Figures 3 and 4. Closed and open symbols represent F20/F80 and F1/F80 systems, respectively.



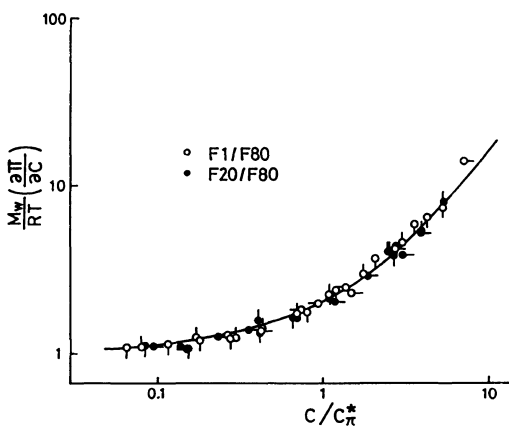
**Figure 6.** The osmotic compressibility of F20/F80 systems. The top solid curve represents the value of pure F80. The value of pure F20 is the same as that of m100.

superposed on a universal curve for both blends of F20/F80 and F1/F80, by reducing the concentration  $C$  to  $C/C_{\xi}^*$ . The reducing factor  $C_{\xi}^*$  was determined so as to give the best expression to the universal curve. This universal curve is identical to that of mono-disperse systems.

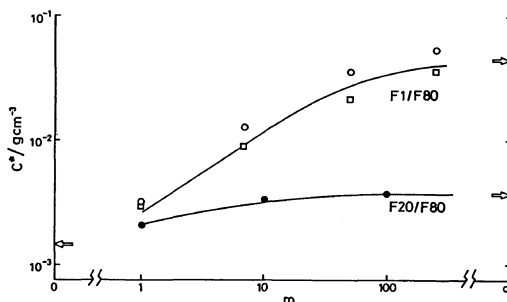
Figures 6 and 7 show the concentration dependence of the reduced osmotic compressibility  $(\partial \Pi / \partial C) \bar{M}_w / RT$  of F20/F80 and F1/F80 blends, respectively. The solid curve in Figure 6 is that of pure F80. The reduced osmotic compressibility of pure F20 is the same as that of the m100 blend. As shown in Figure 8, the concentration dependence of the



**Figure 7.** The osmotic compressibility of F1/F80 systems.



**Figure 8.** The universal curve of the osmotic compressibility of polystyrene blends in benzene. Symbols are the same as in Figure 5.



**Figure 9.**  $C^*$  as a function of the blend ratio,  $m$ . Symbols are denoted as follows: (●) F20/F80; (○) F1/F80 ( $C_{\xi}^*$ ); (□) F1/F80 ( $C_{II}^*$ ). The solid curves were obtained using eq 1.

reduced osmotic compressibility also can be superposed on a universal curve in both F20/F80 and F1/F80 blends by reducing the

concentration  $C$  to  $C/C_H^*$ . The reducing factor  $C_H^*$  was also determined so as to give the best expression to the universal curve. This universal curve is identical to that of monodisperse systems.

$C_\xi^*$  and  $C_H^*$  determined experimentally are plotted in Figure 9 as a function of the blending ratio. The values of  $C_\xi^*$  and  $C_H^*$  increase gradually with increase of the low molecular weight component.  $C_\xi^*$  and  $C_H^*$  coincide with each other for F20/F80 blends. But for F1/F80 blends,  $C_\xi^*$  is slightly larger than  $C_H^*$ .

## DISCUSSION

The experimental results shown in Figures 5 and 8 mean that the same scaling law is applicable to both the monodisperse and blend systems. In the original derivation by des Cloizeaux, systems were polydisperse and the number average degree of polymerization  $N$  was determined by a suitable choice of temperature and interaction parameters of the magnetic system. The value of  $N$  was fixed and independent of concentration, but the distribution of chain length was not fixed and did not remain the same shape at all concentrations. Nevertheless, the experimental results suggest that the same scaling law with the des Cloizeaux's theory seems to hold without regard to the dispersity of chain length.

If the above suggestion is true,  $C^*$  in polydisperse systems must be the overlap threshold. For polydisperse systems, the overlap threshold  $C^*$  ( $\equiv$  the cross-over concentration) is defined as follows,

$$C^* = \frac{\sum_i M_i n_i}{\sum_i V_i n_i} = \frac{1}{\sum_i w_i / C_i^*}, \quad (1)$$

where  $M$  is the molecular weight,  $V$  is the volume of the chain sphere,  $n$  is the number of polymer molecules,  $w$  is the weight fraction and the suffix  $i$  indicates the  $i$ -th species. The calculated curves of  $C^*$  by using eq 1 are represented by the solid curves in Figure 9. In these calculations, the value of  $C_i^*$  was eval-

uated from the concentration dependence of the correlation length of monodisperse systems of the  $i$ -th species except for F1. Since the correlation length of F1 could not be measured, the value of  $C^*$  of F1 was evaluated from the concentration dependence of osmotic compressibility. The observed and calculated values of  $C^*$  are in good agreement in the F20/F80 systems. For F1/F80 systems, though the calculated values are slightly smaller than the observed values, the calculated curve represents well the tendency of the experimental results. These results indicate that the previous suggestion that des Cloizeaux's scaling law for the concentration dependence is applicable without regard to the dispersity may be true.

It is interesting that  $1/C^*$  is proportional to the intrinsic viscosity  $[\eta]$ , since  $[\eta]$  is proportional to  $\langle S^2 \rangle^{3/2}/M$ . From eq 1, next relation is derived.

$$\frac{1}{C^*} = \sum_i \frac{1}{C_i^*} w_i \sim \sum_i [\eta]_i w_i = [\eta] \quad (2)$$

This equation predicts that  $[\eta]^{-1}$  is a good measure for  $C^*$  not only in monodisperse systems but also in polydisperse ones. This proportional relation between  $1/C^*$  and  $[\eta]$  is useful for the estimation of  $C^*$  of any polydisperse system. The weight averaged molecular weights are better than the number averaged molecular weights in the estimation of  $C^*$  as also in the case of  $[\eta] \sim M$  relation for polydisperse samples.<sup>5</sup>

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