

# Experimental test of mean field theory for critical points of polymer mixtures

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The critical value of the effective interaction parameter,  $\chi_{cr}^{eff}$ , and the critical concentration  $\phi_{cr}$  have been studied experimentally as a function of the degree of polymerization of the components in a mixture of polymers for the first time. The results are compared with the predictions of the mean field theory and of a numerical simulation.

Critical phenomena associated with various phase transitions are being studied widely in low-molecular substances and mixtures<sup>1</sup> and also in solutions of polymers (see Refs. 2 and 3, for example). In the most general class of mixtures, mixtures of polymers [if the partial degree of polymerization  $r_i$  ( $i = 1, 2$ ) of one or two components is 1, these mixtures correspond to solutions of polymers or to low-molecular mixtures], there is the question of the position of the stratification critical points  $\chi_{cr}$  and  $\phi_{cr}$  as a function of  $r_i$  of the two components. Up to this point, there has been only a single theory which predicts this dependence: the Flory-Huggins-Scott mean field theory.<sup>4-6</sup> The predictions of this theory were recently tested by a Monte Carlo simulation, and a marked discrepancy with the predictions of the mean field theory was found.<sup>7,8</sup> In this letter we are reporting an experimental study of the  $r_i$  dependence of

the parameters of the critical points of mixtures of short-chain polymers. We compare the experimental results with the predictions of the Flory-Huggins-Scott theory and the numerical simulation.

In the experiments we used mixtures of polypropyleneglycol ( $r_1$  up to 21) and polyethyleneglycol ( $r_2$  up to 91) with a narrow molecular-mass distribution  $M_w/M_n = 1.11-1.34$ ). The effective values of the Huggins interaction parameter,  $\chi^{eff}$ , were determined from the measured phase diagrams of the mixtures.<sup>9</sup> Their temperature dependence is described well by

$$\chi^{eff} = a + b/T,$$

where the coefficients  $a$  and  $b$  depend on  $r_i$ . The values of  $\chi_{cr}^{eff}$  were found from the values of  $\chi^{eff}$  corresponding to the upper critical temperature for stratification. The temperature was monitored within  $\pm 0.1$  K. The critical concentrations were measured by the direct method of the ratio of phase volumes.

The Flory-Huggins-Scott theory predicts the following dependence of  $\chi^{cr}$  or  $r_i$  (Refs. 4-6 and 10):

$$\chi_{cr}^{FHS} = \frac{1}{2} (r_1^{-1/2} + r_2^{-1/2})^2. \quad (1)$$

Figure 1 compares  $\chi_{cr}^{eff}$  with  $\chi_{cr}^{FHS}$ . Expression (1) gives a fairly good description of the experimental values of  $\chi_{cr}^{eff}$  at large values of  $r_i$  ( $r_i \gtrsim 20$ ). The values of  $\chi_{cr}^{eff}$  are systematically higher than  $\chi_{cr}^{FHS}$ , but the difference is slight, about 3%. Such a small ratio contradicts the results of a simulation on a lattice of polymer mixtures with approximately the same values of  $r_i$ , according to which the difference would be about 100% even in the absence of vacancies.<sup>7,8</sup> A possible reason for the pronounced discrepancy

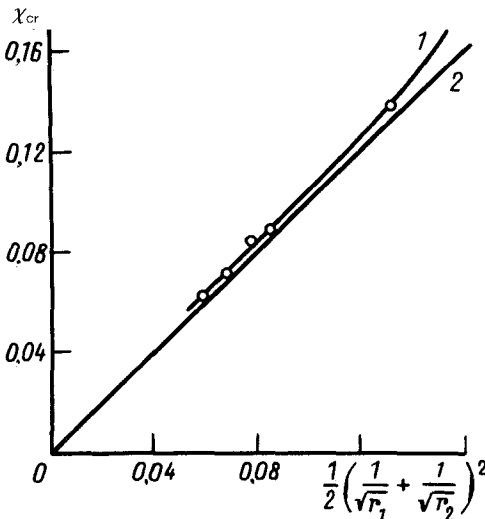


FIG. 1. Plots of (1)  $\chi_{cr}^{eff}$  and (2)  $\chi_{cr}^{FHS}$  according to Eq. (1) versus the degrees of polymerization.

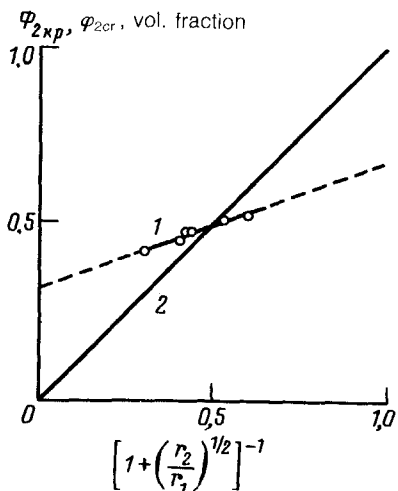


FIG. 2. 1—Behavior of the critical volume fraction of polyethyleneglycol,  $\phi_{2cr}$ ; 2—theoretical behavior [expression (2)].

between the experimental results and the simulation is that the simulation was carried out on a cubic lattice, which does not reflect the continuous nature of the actual system, while the equations of the FHS theory can be derived outside lattice models.<sup>2</sup>

As  $r_i$  decreases (below about 20), the difference between  $\chi_{cr}^{eff}$  and  $\chi_{cr}^{FHS}$  increases, reaching a value of about 10% at the smallest  $r_i$  values of the components studied; i.e., the FHS theory for  $\chi_{cr}$  becomes inapplicable at small values of  $r_i$ .

In this theory, another parameter of the critical point—the critical concentration—is given by

$$\phi_{2cr} = [1 + (r_2/r_1)^{1/2}]^{-1}. \quad (2)$$

This formula describes the experimental data correctly only in the particular case of symmetric mixtures ( $r_1 = r_2$ ); it does not agree with experimental data for asymmetric mixtures (Fig. 2). The experimental data can be approximated well by the function

$$\phi_{2cr} = s [1 + (r_2/r_1)^{1/2}]^{-1} + (1 - s) / 2,$$

where the slope  $s$  differs from 1 [as in expression (2)], having a value of  $0.335 \pm 0.032$ .

The reason why the dependence of the critical concentration on the degree of polymerization of the polymers is weaker than predicted by the theory appears to lie in the polarity of the components and the ability of the end groups to form hydrogen bonds. The critical concentration in this case should be determined to a greater extent by the strong intermolecular interaction than by the lengths of the chains, so the dependence on the chain length weakens.

The Flory-Huggins-Scott theory ignores correlation effects which arise in the case of a strong intermolecular interaction, so it cannot correctly describe the  $r_1$  depen-

dence of the critical concentration. The theory must accordingly be developed further to incorporate correlation effects, particularly for short chains with end groups which are special cases in terms of energy.

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