

# Cloud-Point Curves of Polymer Solutions<sup>1a</sup>

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Received May 22, 1970

**ABSTRACT:** The behavior of the cloud-point curve for a polydisperse homopolymer in a single solvent is examined in the Flory–Huggins approximation, with particular attention to the neighborhood of the critical point. Depending on the molecular weight distribution of the polymer, the curve may exhibit a singularity in its first derivative at a three-phase point and the critical point may be physically unstable. The general conclusions obtained are reinforced and illustrated by some model calculations and by experimental data on solutions of polyethylene in diphenyl ether.

Cloud-point curves of polymer solutions (plots of precipitation temperature against solute concentration, hereafter designated as CPC's) sometimes display a more or less pronounced depression on the right-hand descending branch. Although this phenomenon is not new, attention was drawn to it only rather recently by Koningsveld<sup>2</sup> (who gives references to the earlier experimental work). He concluded on the basis of the experimental evidence as well as his calculations for several hypothetical polymer samples that the depression is due to high asymmetry in the molecular weight distribution.

In the present paper Koningsveld's conclusion is justified by an analytical study based on Flory–Huggins theory. Some unexpected effects in the critical region are also encountered, as will be seen below. The paper is divided into four sections. The general implicit equation of the CPC derived in the first section is used in the second section to discuss the relation between the CPC and the molecular weight distribution of the polymer. In the third section, the limiting form of the CPC for a polymer with "diverging" distribution (e.g., logarithmic normal) is examined. Finally, the last section contains a comparison of general conclusions with several particular computer examples as well as with some experimental data.

## I. General Implicit Equation of the CPC

Consider the polymer solution separated into the "principal" and "conjugate" liquid phases.<sup>3</sup> The volume fraction of P-mer  $\phi_P^c$  in the conjugate phase is given<sup>4</sup> by

$$\phi_P^c = \phi w(P)(Q + 1)[Q + \exp(-K\sigma P)]^{-1} \quad (1)$$

as follows from a material balance. Here  $\phi$  denotes the over-all mean volume fraction of the polymer in the solution,  $w(P)$  is the normalized polymerization degree (DP) distribution function (by weight) of the polymer,  $Q$  is the volume ratio of the conjugate to the principal

phase,  $K$  is a constant which takes the value  $K = +1$  if  $\phi^c > \phi^v$  and  $K = -1$  if  $\phi^c < \phi^v$  ( $\phi^c$  and  $\phi^v$  denoting the total volume fractions of polymer in two phases), and  $\sigma$  is the separation factor in the well-known equation

$$\phi_P^c/\phi_P^v = \exp(K\sigma P) \quad (2)$$

Being interested in the CPC, which is defined by the incipient formation of a second phase from the originally homogeneous solution, we may take the limit for  $Q \rightarrow 0$  of eq 1 and obtain a simple relation describing the distribution  $w^c(P)$  in the appearing phase

$$\lim_{Q \rightarrow 0} \phi_P^c/\phi \equiv w^c(P) = w(P) \exp(K\sigma P) \quad (3)$$

It is easy now to express<sup>5</sup> any statistical moment  $\nu_k$  of the distribution  $w^c(P)$  in terms of the parameter  $\sigma$  and the statistical moments  $\mu_i$  of the original distribution function

$$\nu_k = \int_0^\infty P^k w^c(P) dP = \int_0^\infty w(P) \sum_{i=0}^\infty [(K\sigma)^i P^{k+i}/i!] \cdot dP = \mu_k + \sum_{i=1}^\infty (K\sigma)^i \mu_{k+i}/i! \quad (4)$$

It should be emphasized that the distribution function  $w^c(P)$  is not normalized and its zeroth moment gives the volume fraction ratio between the two phases,  $\nu_0 = \phi^c/\phi$ . From eq 4 we also have the derivatives

$$\frac{d^n \nu_k}{d\sigma^n} = K^n \nu_{k+n} \quad (5)$$

Moreover, since the amount of the separated conjugate phase goes to zero, the parameters of the principal phase can be considered as identical with those characterizing the over-all system.

Under the assumptions made, the equilibrium condition for the two phases following from the Flory–Huggins theory<sup>4</sup>

$$\sigma(\phi' + \phi'')/2 + \phi'' - \phi' + (\phi'/P_n') - (\phi''/P_n'') + [1 - (\phi' + \phi'')/2] \ln [(1 - \phi'')/(1 - \phi')] = 0 \quad (6)$$

can be transformed into

$$F(\sigma, \phi) \equiv K\sigma(1 + \nu_0)/2 + (\nu_0 - 1) - (\nu_{-1} - \mu_{-1}) + [\phi^{-1} - (1 + \nu_0)/2] \ln [(1 - \phi\nu_0)/(1 - \phi)] = 0 \quad (7)$$

(5) K. Šolc, *Collect. Czech. Chem. Commun.*, **34**, 992 (1969).

(1) (a) Supported by the National Science Foundation; (b) on leave of absence from The Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, Prague, Czechoslovakia.

(2) (a) R. Koningsveld and A. J. Staverman, *J. Polym. Sci., Part A-2*, **6**, 349 (1968); (b) R. Koningsveld, Thesis, Leiden, 1967.

(3) This artificial distinction between two equivalent phases proves to be useful for further simultaneous treatment of both subcritical and supercritical branches of the CPC.

(4) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapter XIII.

which allows direct calculation of the CPC: for the given DP distribution of the polymer (which yields the moments  $\mu_i$ ) and a chosen volume fraction  $\phi$ , the physically significant root  $\sigma$  of eq 7 is found, eq 4 having been used to evaluate  $\nu_0$  and  $\nu_{-1}$ . Then the parameter  $\chi$  is calculated from the equation

$$2\chi\phi(\nu_0 - 1) = K\sigma + \ln[(1 - \phi)/(1 - \phi\nu_0)] \quad (8)$$

## II. Polymers with "Converging" Distribution

A distribution is here called "converging" if the series for  $\nu_0$  in eq 4 is convergent even for  $K\sigma > 0$ . This definition includes most distributions of practical interest, as mentioned later.

When the distribution function  $w(P)$  is not too asymmetric, eq 7 has a single nontrivial root  $\sigma$  which goes to zero as  $\phi$  approaches its critical value,<sup>6</sup>  $\phi_{\text{crit}} = (1 + P_w P_z^{-1/2})^{-1}$ . In this case the root  $\sigma$  is always positive when  $K$  is chosen in accord with common experience, i.e.,  $K = 1$  for  $\phi < \phi_{\text{crit}}$  and  $K = -1$  for  $\phi > \phi_{\text{crit}}$ . For these "normally" behaving polymers several relations including the known<sup>6</sup> one for  $\chi_{\text{crit}}$  can be derived from eq 4, 5, 7, and 8 by taking the limit for  $\sigma \rightarrow 0$  and  $\phi \rightarrow \phi_{\text{crit}}$

$$\chi_{\text{crit}} = 1/2(1 + P_z^{1/2}P_w^{-1})(1 + P_z^{-1/2}) \quad (9)$$

$$\left(\frac{d\sigma}{d\phi}\right)_{\text{crit}} = -4K \frac{P_w P_z^{-1/2}(1 + P_z^{1/2}P_w^{-1})^2}{3P_z + 2P_z^{1/2} - P_{z+1}} \quad (10)$$

$$\left(\frac{d\chi}{d\phi}\right)_{\text{crit}} = 1/2(1 + P_z^{1/2}P_w^{-1})^2(1 - P_w P_z^{-1}) \quad (11)$$

$$\left(\frac{d(\phi\nu_0)}{d\phi}\right)_{\text{crit}} = 1 - 4(P_w + P_z^{1/2})(3P_z + 2P_z^{1/2} - P_{z+1})^{-1} \quad (12)$$

$$\left(\frac{d^2\chi}{d\phi^2}\right)_{\text{crit}} = P_w^{-1}(1 + P_w P_z^{-1/2})^3 + (1 + P_z^{1/2}P_w^{-1})^3 \times \left[1 - \frac{4}{3} \left(\frac{P_w^2 P_z^{-1/2}(1 + P_z^{1/2}P_w^{-1})^2}{3P_z + 2P_z^{1/2} - P_{z+1}}\right)\right] \quad (13)$$

In the above equations, the usual definitions of average degrees of polymerization are employed; i.e.,

$$P_w = \mu_1/\mu_0; P_z = \mu_2/\mu_1; P_{z+1} = \mu_3/\mu_2, \text{ etc.} \quad (13a)$$

All the equations are valid independently of the direction from which the critical point is approached, which excludes in general any singularity in the CPC or its shadow curve<sup>7</sup> at the critical point. However, eq 10 does signal the possibility of anomalous behavior: the parameter  $\sigma$ , positive by definition, can be larger than zero around  $\phi = \phi_{\text{crit}}$  according to eq 10 only if the denominator  $S$  is positive (unless we change the value assigned to  $K$ )

$$S \equiv 3P_z + 2P_z^{1/2} - P_{z+1} > 0 \quad (14)$$

The same conclusion follows from comparison of eq 11 and 13 with the derivatives taken along the spinodal, which is given by the equation<sup>2,9</sup>

(6) W. H. Stockmayer, *J. Chem. Phys.*, **17**, 588 (1949).

(7) The term "shadow curve" was introduced by Koningsveld<sup>2b,8</sup> for the coexistence curve of the CPC. In our nomenclature, it represents the plot  $\chi^{-1}$  vs.  $\phi\nu_0$  (whereas the CPC corresponds to  $\chi^{-1}$  vs.  $\phi$ ).

(8) R. Koningsveld, *Pure Appl. Chem.*, **20**, 271 (1969).

(9) R. Koningsveld and A. J. Staverman, *J. Polym. Sci., Part A-2*, **6**, 325 (1968).

$$2\chi_{sp} = (1 - \phi)^{-1} + \phi^{-1}P_w^{-1} \quad (15)$$

and defined as the line separating the unstable and metastable regions in the two-phase area. While the first derivative  $(d\chi_{sp}/d\phi)_{\text{crit}}$  is identical with relation 11,<sup>2a</sup> the second derivative is different

$$\left(\frac{d^2\chi_{sp}}{d\phi^2}\right)_{\text{crit}} = P_w^{-1}(1 + P_w P_z^{-1/2})^3 + (1 + P_z^{1/2}P_w^{-1})^3 \quad (16)$$

As long as  $S$  is positive, then  $(d^2\chi_{sp}/d\phi^2)_{\text{crit}} > (d^2\chi/d\phi^2)_{\text{crit}}$ , and the spinodal passing through the critical point and there touching the CPC remains inside the two-phase region. But as soon as  $S$  turns to negative values, the CPC is predicted to "jump" inside the spinodal area, which is physically impossible. The critical point thus shows singular behavior for a special group of distributions with  $S = 0$ , and is certainly physically inconsistent for  $S < 0$ . While the condition of eq 14 is always satisfied for some types of distributions (e.g., Schulz-Zimm type), it may not be for others. Since in the latter anomalous case more than one root of eq 7 is present, it will be discussed later.

Although  $\chi$  is a function of  $\sigma$  (see eq 8),  $(d\chi/d\phi)_{\text{crit}}$  is independent of  $(d\sigma/d\phi)_{\text{crit}}$  as long as the latter quantity is finite, which explains why the parameter  $S$  does not appear in eq 11. From eq 11 it follows that the critical point always occurs either at the top (for monodisperse polymer) or on the right-hand branch (for polydisperse polymer) of the CPC, in agreement with the recent conclusions of Gordon, Chermin, and Koningsveld<sup>10</sup> as well as with the experimental evidence. For a very polydisperse polymer with a Schulz-Zimm distribution,  $(d\chi/d\phi)_{\text{crit}}$  decreases with increasing molecular weight down to the limiting value  $1/4$ . On the other hand, with  $P_w$  constant the derivative  $(d\chi/d\phi)_{\text{crit}}$  increases with increasing polydispersity from zero to  $[1 + (2/P_w)^{1/2}]^2/4$ . Equation 12 gives the ratio of the increments in the volume fractions on the shadow curve and the CPC due to a common increment in  $\chi$  at the critical point. It can be shown by inspection that this derivative is always negative provided condition 14 is satisfied, which means that the shadow curve and the CPC must arrive at the critical point from opposite sides. For a polydisperse polymer with a Schulz-Zimm distribution,  $[d(\phi\nu_0)/d\phi]_{\text{crit}}$  is always larger than the limiting value  $-1$  for monodisperse polymer, indicating that the shadow curve is always steeper than the CPC at the critical point. From eq 13, a characteristic value

$$P_{z+1}^{\#} = 3P_z + 2P_z^{1/2} - \frac{4}{3}P_w^2 P_z(1 + P_z^{1/2}P_w^{-1})^2(P_w^2 + P_z^{3/2})^{-1} \quad (17)$$

can be found which determines the shape of the CPC at the critical point: if the distribution is not too asymmetric so that  $P_{z+1} < P_{z+1}^{\#}$  (as in the Schulz-Zimm case) the plot  $\chi^{-1}$  vs.  $\phi$  is convex upward at  $\phi = \phi_{\text{crit}}$ . On the other hand, if  $3P_z + 2P_z^{1/2} > P_{z+1} > P_{z+1}^{\#}$ , the curvature is of the opposite sign; however, we have not been

(10) M. Gordon, H. A. G. Chermin, and R. Koningsveld, *Macromolecules*, **2**, 207 (1969).

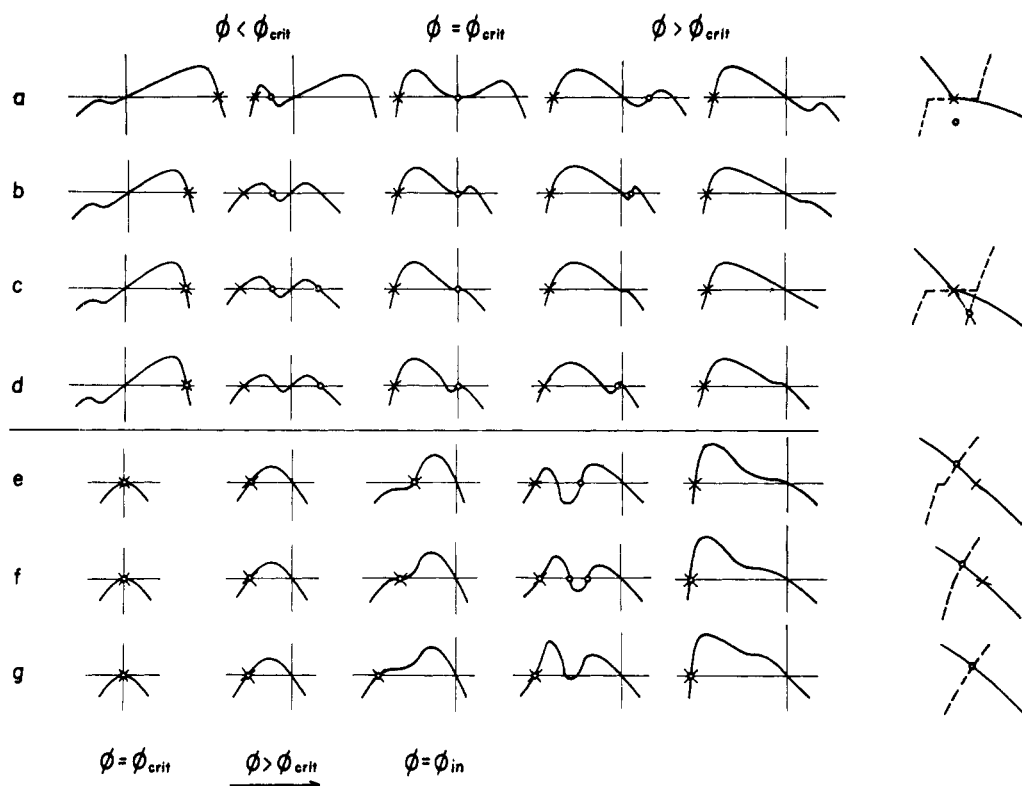


Figure 1. Plots of the function  $[F(\sigma)]_{\phi=\text{const}}$ , eq 7, against  $\sigma$  for solutions at several concentrations of polymers with varying molecular weight distributions. Within each row of graphs, the polymer concentrations  $\phi$  increase from left to right according to scales appearing above the figure for the first four rows and below the figure for the last three rows. In each graph the intersection of axes is at the origin, where trivial inflection points have not been exhibited, for reasons of simplicity. Each row corresponds to a different value of the distribution parameter  $S$ , eq 14, as follows: row a,  $S \ll 0$ ; row b,  $S \rightarrow 0^-$ ; row c,  $S = 0$ ; row d,  $S \rightarrow 0^+$ ; row e,  $S \rightarrow S^{*-}$ ; row f,  $S = S^*$ ; row g,  $S \rightarrow S^{*+}$ . Special roots of eq 7 are marked as follows:  $\circ$ , critical root;  $\times$ , physically significant root. The last column shows schematic CPC's and shadow curves for some of the distributions:  $\circ$ , critical points;  $\times$ , triple points.

able to decide generally whether this case can ever have physical meaning or not.

Sometimes it is observed that eq 7 has more than one nontrivial root  $\sigma$ . Although some of them may be negative, the additional roots must not be discarded just because of their negative sign. Since  $\sigma$  appears in eq 4 and 7 always in a product with  $K$ , a negative root  $\sigma$  obtained with an assumed  $K$  means that eq 7 has also a positive root of the same absolute value as the negative one, when  $-K$  is used for its solution. The negative sign of a root can thus simply indicate that our estimate of whether  $\phi^c < \phi$  or  $\phi^c > \phi$  was wrong. In order to admit the physical significance of such a root, the absolute "milestone" meaning ascribed to the critical concentration must be abandoned, and the possibility of separating a more concentrated conjugate phase from a solution with supercritical concentration (or a less concentrated conjugate phase from a solution with subcritical concentration) must be accepted. To decide which root is physically significant, the Flory–Huggins molar free enthalpy of mixing  $\Delta G^M$  of our closed isothermal system with incipient separation of the second phase can be considered. Since the amount of the separated conjugate phase is infinitesimally small  $\Delta G^M$  depends only on the composition of the principal phase and the parameter  $\chi$ ; i.e.,  $\Delta G^M = \Delta G^M(\phi, \chi)$ . At constant  $\phi$  we have an increasing function  $\Delta G^M = \Delta G^M(\chi)$ , where  $\chi$  in turn depends on  $\sigma$  through eq 8

and 4. Hence to find the minimum value of  $\Delta G^M$ , corresponding to the stable state, that root  $\sigma$  has to be chosen which yields the lowest value of  $\chi$ .

In general, only one of the roots goes to zero when  $\phi$  approaches its critical value,  $\phi \rightarrow \phi_{crit}$ ; it will be called the critical root. All the relations derived previously for the simple (critical) root, eq 9–13, are again valid for it, but this root may not have any physical meaning. On the other hand, the other roots are not particularly related to the critical concentration and, in general, they are not zero at  $\phi = \phi_{crit}$ . The complexity of the equations involved impedes direct analysis of all the roots. However, it is possible to discuss their behavior by means of the known properties of the function  $F = F(\sigma, \phi)$ , defined as the left-hand side of eq 7. In the following discussion  $K$  will be arbitrarily chosen positive,  $K = +1$ , for the whole interval of  $\phi$ , to avoid the switching of roots when passing through critical concentration. It should be kept in mind that a negative root thus corresponds to a conjugate phase which is more dilute than the principal one, while the positive root describes the opposite case. The pattern of the function  $[F(\sigma)]_{\phi=\text{const}}$  will be examined as to dependence on the concentration  $\phi$  and on the parameter  $S$  characterizing the asymmetry of the distribution  $w(P)$ . When these two variables change, physical significance will switch at certain points from one root  $\sigma_1$  to another  $\sigma_2$ , but the computed  $\chi$  surface must be always continu-

ous. This requirement of continuity together with some knowledge about  $F(\sigma, \phi)$  (see Appendix I) allows the following conclusions about the roots and the CPC to be drawn.

$S < 0$ . When the DP distribution is very asymmetric,  $S \ll 0$  (Figure 1a), the  $F$  function for  $\phi = \phi_{\text{crit}}$  shows a flat minimum touching the origin and therefore must have two different noncritical roots  $\sigma_1$  and  $\sigma_2$ . As  $\phi$  decreases, for example, a critical root  $\sigma_{\text{crit}}$  appears which is negative, *i.e.*, of a sign opposite to that normally expected, and is always without physical meaning. By the shift rule (see Appendix I), further decrease of  $\phi$  causes the critical root together with the negative noncritical root to disappear, leaving a single positive noncritical root for  $\phi \ll \phi_{\text{crit}}$ . The CPC consists of two noncritical branches,<sup>11</sup> each corresponding to one noncritical root. They meet each other at a *triple point*  $\phi_t$ , characterized by the condition  $\chi_1 = \chi_2$  for  $\phi = \phi_t$ . However, because  $\sigma_1 \neq \sigma_2$  we find  $(d\chi_1/d\phi) \neq (d\chi_2/d\phi)$  and  $\phi_1^c \neq \phi_2^c$ . At this characteristic point the CPC appears to be broken and the shadow curve shows a discontinuity; *i.e.*, the principal phase and two different conjugate phases are in equilibrium. The difference in the derivatives for  $\phi = \phi_t$  is

$$\phi \left[ \left( \frac{d\chi_1}{d\phi} \right)_t - \left( \frac{d\chi_2}{d\phi} \right)_t \right] = \frac{\phi_1^c - \phi_2^c}{(1 - \phi)(\phi_1^c - \phi)(\phi_2^c - \phi)} + (\phi_1^c - \phi)^{-2} \ln \frac{1 - \phi}{1 - \phi_1^c} - (\phi_2^c - \phi)^{-2} \ln \frac{1 - \phi}{1 - \phi_2^c} \quad (18)$$

which indicates that the slope of the CPC is steeper when  $\phi_t$  is approached from the left than when approached from the right. The CPC thus shows a distinct depression in the neighborhood of the triple point. The critical point is found *under* the CPC; it has no relation to the noncritical branches and no physical meaning, and the spinodal does not touch the CPC. Both  $\phi_t > \phi_{\text{crit}}$  or  $\phi_t < \phi_{\text{crit}}$  can occur. With  $S$  increasing to zero, usually one of the noncritical roots  $\sigma$  for  $\phi = \phi_{\text{crit}}$  moves toward zero (the positive one in Figure 1b) which results in the critical point approaching the corresponding noncritical branch of the CPC extended beyond the triple point.

$S = 0$ . At this particular distribution the first four derivatives  $(\partial^n F / \partial \sigma^n)$  at  $\sigma = 0$  for  $\phi = \phi_{\text{crit}}$  are zero, and the function  $F$  here usually shows a flat inflection (provided that the fifth derivative is not zero). This permits a continuous transition of one noncritical branch of the CPC into the critical one. Let us follow the example given in Figure 1c, where the point of inflection occurs on the descending branch of the  $F$  function. In accordance with the shift rule, when  $\phi$  decreases from  $\phi = \phi_{\text{crit}}$  the point of inflection will develop into a minimum and maximum, yielding thus two critical roots. They differ from the other critical roots only in that the "rate" of their approach to zero with  $\phi \rightarrow \phi_{\text{crit}}$  goes to infinity as follows from eq 10 or from eq A-5 as well as on purely geometrical grounds.

(11) A branch of the CPC is called *critical* if it corresponds to the critical root and *noncritical* if it corresponds to a noncritical root. At the same time its position with respect to the critical concentration  $\phi_{\text{crit}}$  is expressed by the term *sub-* or *super-critical*. However, these terms must not be understood as strictly as in case of the single root: *e.g.*, the subcritical branch may be extended beyond the critical concentration.

Around  $\phi = \phi_{\text{crit}}$  as well as in the whole supercritical region the negative noncritical root is physically significant, but when  $\phi$  decreases into the subcritical region it is the positive critical root which gains physical meaning while both the negative roots finally disappear. The subcritical branch of the CPC can be therefore denoted as the critical one and the critical point is now located on its portion extended beyond the triple point. On the other hand, for  $S$  close to zero but negative, Figure 1b, the positive root which also has physical meaning in the subcritical region cannot approach zero with  $\phi \rightarrow \phi_{\text{crit}}$  because of the required shape of  $F$  function at the origin, and the corresponding branch of the CPC is thus the noncritical one. The sign of the fifth derivative (A-4) decides which branch of the CPC is approached by the critical point: if

$$P_{z+2} < (15P_z^2 + 20P_z^{3/2} + 6P_z)/(3P_z + 2P_z^{1/2}) \quad (19)$$

then the subcritical branch becomes critical at  $S = 0$ . On the other hand, if  $P_{z+2}$  is larger than the right-hand side of relation 19, it is the supercritical branch which is transformed into the critical one at  $S = 0$ .

In the very rare but possible case that both the fourth and fifth derivatives  $(\partial^n F / \partial \sigma^n)$  at  $\sigma = 0$ ,  $\phi = \phi_{\text{crit}}$  are simultaneously zero (*i.e.*,  $S = 0$  and  $P_{z+2}$  is equal to the right-hand side of relation 19), the  $F$  function usually shows a very flat maximum or minimum, depending on the sign of the sixth derivative. This possibility has not been analyzed in detail because of its rarity and complexity. If the sixth derivative is negative [*i.e.*,  $P_{z+3} < \psi(P_z)$ , where the function  $\psi(P_z)$  follows from the sixth derivative], it seems that both noncritical roots are here transformed into the critical ones at the same time that  $S$  becomes zero. The critical point thus approaches directly the triple point, and its emergence on the CPC is accompanied by the disappearance of the discontinuity in the first derivative of the CPC. Denoting by  $S^*$  the value of the parameter  $S$  at which the triple point disappears from the CPC for the given class of distributions, we here have  $S^* = 0$ . However, this case is very rare, as remarked above; usually the situation develops as described below.

$S > 0$ . When  $S$  crosses zero both the shape of  $[F(\sigma)]_{\phi=\phi_{\text{crit}}}$  around  $\sigma = 0$  and the orientation of the critical root are suddenly changed as compared with  $S < 0$  (Figure 1b,d). The  $F$  function now shows a flat maximum at the origin for  $\phi = \phi_{\text{crit}}$  and the critical root is positive for  $\phi < \phi_{\text{crit}}$  and negative for  $\phi > \phi_{\text{crit}}$  as would be normally expected. The rest of the  $F$  function at  $\phi = \phi_{\text{crit}}$  as well as the whole function for  $\phi \neq \phi_{\text{crit}}$  do not show any discontinuous change, and the values of the physically significant roots change smoothly (which preserves the continuity of the  $\chi$  surface); however, the switch in orientation of the critical root causes the previous noncritical positive root now to become the critical one; *i.e.*, it goes to zero when  $\phi \rightarrow \phi_{\text{crit}}$ . It is not yet stable enough and it disappears for  $\phi \gg \phi_{\text{crit}}$  but it is physically significant in a part of the subcritical region. The critical point is still located on the critical branch of the CPC beyond the triple point; *i.e.*, without physical meaning. By further increase of  $S$ , it moves along the critical branch toward and above the triple point. At a particular value  $S$  (which depends on the type of distribution) it appears right at the triple point and

thereafter it has a real physical meaning although the CPC remains “broken.”

$S = S^*$ . The condition for the final disappearance of the triple point must include the continuous transition of the remaining noncritical branch of the CPC into the already present critical branch. This is possible if the  $F$  function shows a nontrivial point of inflection with horizontal slope located on the  $\sigma$  axis at some non-zero value of  $\sigma$ . In the example followed in Figure 1e–g, the subcritical branch corresponds to the critical root, so that the point of singularity  $\phi_c$  is located in the supercritical region. According to the shift rule, the point of inflection occurring on the ascending branch of the  $F$  function on the  $\sigma$  axis at the concentration  $\phi = \phi_{in.} = \phi_c^*$  for  $S = S^*$  (Figure 1f) splits into three roots with increasing concentration. From the relation

$$\left(\frac{\partial \chi}{\partial \sigma}\right)_\phi = -\phi^{-1}(\nu_0 - 1)^{-2} \left(\frac{\partial F}{\partial \sigma}\right)_\phi \quad (20)$$

from the difference equation for  $\Delta \chi$  of two close roots<sup>7</sup> and from the known sign of  $(\partial F / \partial \sigma)_\phi$  at the central root, it can be concluded that the root with the largest absolute value is always physically significant, while the other two roots again disappear upon further change of  $\phi$ . At this particular distribution  $S^*$ , all three roots can be considered as the critical ones, since they were formed by splitting of the critical root. However, when the distribution is changed infinitesimally the point of inflection shifts away from the  $\sigma$  axes. Again three different roots can be observed in about the same concentration region as before, and the outer one has physical meaning but now it can be identified as the critical or noncritical root according to its behavior for  $\phi \rightarrow \phi_{crit.}$  For example, if the distribution is less asymmetric,  $S > S^*$ , the point of inflection moves upward, thus leaving physical meaning to the critical root (Figure 1g), whereas the opposite is true for a more asymmetric distribution (Figure 1e). As shown in Appendix I, the requirement of a point of inflection with these properties defines a special group of distributions, and in the considered  $\chi$ - $\phi$ - $w(P)$  space<sup>12</sup> such a distribution  $w^*(P)$  is unique. Its CPC is already smooth, continuous in the first derivative, and the whole CPC can be considered as corresponding to the critical root. However, because of the discontinuity of  $(d\sigma/d\phi)$  at  $\phi = \phi_c^*$  discontinuities persist in  $(d^2\chi/d\phi^2)$  and  $[d\chi/d(\phi\nu_0)]$ . The shadow curve is continuous but has a discontinuity in its first derivative. It is probably impossible to find a closed relation giving the criterion for  $w^*(P)$ . The only way we know is by location of a point of inflection with a horizontal slope: for a given distribution  $w(P)$ , the  $F$  function at the point of inflection,  $F_{in.}$ , should be calculated (see Appendix I). Only if  $F_{in.} = 0$  does the given distribution  $w(P)$  correspond to the required  $w^*(P)$ . In that case the  $\chi$  parameter is simply

$$2\chi^* = (\phi_c^* \nu_1)^{-1} + (1 - \phi_c^* \nu_0)^{-1} \quad (21)$$

which resembles the relation for  $\chi_{crit.}$  Though not established in general, it appears that a similar criterion can be used to ascertain whether a given distribution  $w(P)$  is more or less asymmetric than  $w^*(P)$ : if the

(12) Here  $w(P)$  represents a series of distribution functions of the same type differing only in the value of some parameter affecting their asymmetry.

$F$  function has no point of inflection with horizontal slope in the physically reasonable ranges of the variables  $\sigma$  and  $\phi$ , or if it shows such a point which however satisfies at the same time the relations

$$\begin{aligned} F_{in.} &\geq 0 \\ -2K\nu_1\nu_2^{-1}(\nu_0 - 1)^{-1} \left(\frac{\partial^3 F}{\partial \sigma^3}\right)_{\phi=\phi_{in.}} &= \\ 3\frac{\nu_2}{\nu_1} + 2\frac{\nu_2^{1/2}}{\nu_1^{1/2}} - \frac{\nu_3}{\nu_2} &> 0 \end{aligned} \quad (22)$$

then the CPC is smooth, while in other cases it has a triple point.

### III. Polymers with “Diverging” Distribution

All considerations so far have been restricted to “converging” distributions, defined as those which yield a convergent series in eq 4 for  $\nu_0$  with  $K\sigma > 0$ . This type includes all cases where the highest molecular weight present is finite (soluble polymer samples, and hypothetical polymers the distributions of which are generated by computer) as well as some infinitely extended mathematical distributions the moments of which diverge slowly as compared with the factorial (e.g., Schulz–Zimm type). On the other hand, it does not include the mathematical logarithmic–normal distribution with its extremely diverging moments. Although the consideration of such a distribution might seem to be of little practical interest at first sight, it represents a limiting case of many real distributions. By exaggerating one characteristic property—in this case the asymmetry—its effect can be revealed easily and the kind of behavior shown which is to be expected with real distributions of that type.

Let us consider a series of distributions  $W(P)$  which are created by cutting off the tail of some diverging distribution  $w(P)$  at  $P_{max}$ , and then observe the limiting behavior for  $P_{max} \rightarrow \infty$ . This procedure entitles us to use previous relations 4 and 7, since the distributions  $W(P)$  are in general converging. We are interested especially in three quantities in the subcritical region of concentrations ( $K = +1$ )

$$\begin{aligned} \nu_{-1} - \mu_{-1} &= \sum_{i=1}^{\infty} \sigma^i \mu_{i-1} / i! = \\ &\sigma \left[ 1 + \sum_{i=1}^{\infty} \sigma^i \mu_i (i+1)^{-1} / i! \right] \end{aligned} \quad (23a)$$

$$\nu_0 - 1 = \sum_{i=1}^{\infty} \sigma^i \mu_i / i! \quad (23b)$$

$$\nu_1 - \mu_1 = \sum_{i=1}^{\infty} \sigma^i \mu_{i+1} / i! = \sigma^{-1} \sum_{i=2}^{\infty} i \sigma^i \mu_i / i! \quad (23c)$$

From the definition of diverging distributions and the physical requirement of a finite  $(\nu_0 - 1)$  it follows that for  $P_{max} \rightarrow \infty$  the parameter  $\sigma$  must go to zero<sup>5</sup> not only at the critical concentration but along the entire left branch of the CPC

$$\lim_{P_{max} \rightarrow \infty} \sigma = 0 \quad (24b)$$

Thus  $\sigma = 0$  necessarily represents the only physically possible noncritical root of eq 7 in the subcritical re-

gion. So far we cannot say anything about  $(\nu_0 - 1)$  except that it is either larger than zero or approaches zero much more slowly than  $\sigma$  does, due to the eq 23b. With this in mind it is noted immediately from eq 23a and 23c that

$$\lim_{P_{\max} \rightarrow \infty} (\nu_{-1} - \mu_{-1}) = 0 \quad (24a)$$

$$\lim_{P_{\max} \rightarrow \infty} (\nu_1 - \mu_1) = \infty \quad (24c)$$

However, the equation of the limiting CPC obtained by substitution of eq 24a,b into eq 7

$$(\nu_0 - 1) + [\phi^{-1} - 1/2(\nu_0 + 1)] \ln \frac{1 - \phi\nu_0}{1 - \phi} = 0 \quad (25)$$

has only a single trivial root  $\nu_0 = 1$ . The left branch of the CPC is thus given simply by a reciprocal relation

$$\lim_{P_{\max} \rightarrow \infty} (2\chi) = \lim_{\substack{\sigma \rightarrow 0 \\ \nu_0 \rightarrow 1}} \phi^{-1}(\nu_0 - 1)^{-1} \times \left[ \sigma + \ln \frac{1 - \phi}{1 - \phi\nu_0} \right] = (1 - \phi)^{-1} \quad (26)$$

and it is independent of any other properties of the distribution than just its divergence. For  $\phi \rightarrow 0$ ,  $\chi$  approaches  $1/2$ , which is the same as observed for a monodisperse polymer with  $P \rightarrow \infty$ . The amount of material with  $P \rightarrow \infty$  is here obviously large enough to avoid the normally observed increase of  $\chi$  with  $\phi \rightarrow 0$ . For  $\phi > 0$ ,  $\chi^{-1}$  as a function of  $\phi$  drops faster for diverging distributions, as expected, than for monodisperse polymer with  $P \rightarrow \infty$ . Along all this noncritical branch, eq 24a,c as well as

$$\lim_{P_{\max} \rightarrow \infty} \nu_0 = 1 \quad (27)$$

are valid. The concentration and the number-average  $P_n^c$  of the conjugate phase approach those of the principal phase, while its weight-average  $P_w^c$  grows to infinity. On the other hand, because of the negative  $K$  there is no reason for similar anomalous behavior of the right-hand branch of the CPC, provided  $S > 0$ ; therefore  $\sigma$  is generally nonzero and only for  $\phi \rightarrow \phi_{\text{crit}}$  does it approach zero. Polymer with a diverging distribution will thus never show a smooth CPC since the critical root cannot have physical meaning in the whole interval of  $\phi$ , no matter how small the "polydispersity"  $P_w/P_n$  may be.

When  $S > 0$ , the right-hand branch of the CPC is the critical one, as mentioned above, while the left branch corresponds to the noncritical root  $\sigma = 0$ . For this case, some simple relations can be obtained analytically. When  $\phi_{\text{crit}}$  is approached from the left side,  $\chi$  and its derivative are obtained from eq 26

$$\lim_{\phi \rightarrow \phi_{\text{crit}}(-)} \chi = 1/2(1 + P_z^{1/2}P_w^{-1}) \quad (28)$$

$$\lim_{\phi \rightarrow \phi_{\text{crit}}(-)} \frac{d\chi}{d\phi} = 1/2(1 + P_z^{1/2}P_w^{-1})^2 \quad (29)$$

while for the right branch eq 9 and 11 can be applied. The noncritical left branch of the CPC arrives at the critical concentration at a higher value of  $\chi^{-1}$  and with a steeper slope than the critical right-hand one. Its physical meaning thus extends beyond the critical con-

centration, and a triple point is found with  $\phi_t > \phi_{\text{crit}}$  and  $\chi_t^{-1} < \chi_{\text{crit}}^{-1}$ . The critical point is not a stable state. The spinodal goes beside the CPC, but its subcritical branch appears as the continuation of the supercritical branch of CPC. The triple point can be located approximately by linear extrapolation of both branches in  $\chi^{-1} - \phi$  coordinates. The displacement between the critical point and the triple point is then

$$\phi_t - \phi_{\text{crit}} \simeq P_z^{-1/2}(1 + P_z^{-1/2})(1 + P_z^{1/2}P_w^{-1})^{-1} \times [(1 + P_z^{-1/2})^2 - (1 - P_wP_z^{-1})]^{-1} \quad (30)$$

$$\chi_{\text{crit}}^{-1} - \chi_t^{-1} \simeq 2\{(1 + P_z^{1/2})(1 + P_z^{1/2}P_w^{-1}) \times [(1 + P_z^{-1/2})^2(1 - P_wP_z^{-1})^{-1} - 1]\}^{-1} \quad (31)$$

while the angle between two branches is

$$\gamma \simeq \arctan \left[ 2 \frac{(1 + P_z^{-1/2})^2 - (1 - P_wP_z^{-1})}{(1 + P_z^{-1/2})^2 + 4(1 - P_wP_z^{-1})} \right] \quad (32)$$

Both points approach each other as the molecular weight increases, and the displacement in  $\chi^{-1}$  is especially sensitive to the ratio  $P_w/P_z$ : it gets smaller as  $P_w/P_z$  increases to unity. For sufficiently high  $P_z$ ,  $\gamma$  is given approximately as

$$\gamma \simeq \arctan [2P_w(5P_z - 4P_w)^{-1}] \quad (33)$$

which indicates that  $\gamma$  increases with increasing  $P_w/P_z$  (i.e., increasing "homogeneity") to a limiting value of about  $63^\circ$ . The shadow curve shows very unusual behavior: for  $P_{\max} \rightarrow \infty$  its right-hand branch approaches the corresponding left branch of the CPC, i.e., it is found on the opposite side of the triple point than normally would be expected. Since both phases differ only in weight and higher averages of DP but are approximately of the same concentration and density, a rather difficult phase separation can be expected in this region. The shadow curve always has a discontinuity at the triple point.

The validity of eq 30-33 is confined, however, to the condition  $S > 0$ . For example, with the Wesslau distribution,<sup>13</sup> for which

$$P_w/P_n = P_z/P_w = P_{z+1}/P_z = \dots = \epsilon > 1 \quad (34)$$

$$P_w = P_0\epsilon^{1/2}$$

the values  $P_0$  are unrestricted only if  $\epsilon \leq 3$ ; otherwise they have to satisfy the relation

$$P_0 < 4\epsilon^{-3/2}(\epsilon - 3)^{-2} \quad (35)$$

and they soon get unreasonably small. The minimum value of  $P_w/P_z$  compatible with  $S > 0$  is thus about one-third which yields the minimum angle  $\simeq 10^\circ$  from eq 33. For the Wesslau distribution, the general statement ascribing the critical root to the supercritical region can also be confirmed by means of eq 19. We may start from any Wesslau distribution with  $S > 0$  (e.g.,  $\epsilon \leq 3$ ) and vary its shape continuously until the condition  $S = 0$  is reached; then relation 19 between  $P_{z+2}$  and  $P_z$  can be examined. The simplest way is to increase the polydispersity index  $\epsilon$  beyond 3 at constant  $P_0$  until

(13) H. Wesslau, *Makromol. Chem.*, **20**, 111 (1956).

$$4\epsilon^{-3/2}(\epsilon - 3)^{-2} = P_0 \quad (36)$$

When  $P_{2+2}$  and  $P_2$  are now expressed in terms of  $\epsilon$  only and substituted into condition 19, an inequality

$$\epsilon^2 < \frac{60 + 40(\epsilon - 3) + 6(\epsilon - 3)^2}{12 + 4(\epsilon - 3)} \quad (37)$$

is obtained which obviously is not satisfied for any  $\epsilon > 3$ . Therefore, it can be concluded that for a polymer sample with a Wesslau distribution the supercritical branch of the CPC corresponds to the critical root.

Unfortunately for  $S < 0$  no similar analytical treatment is available, since we do not know the other non-critical root for  $\phi > \phi_c$ . We can only state qualitatively that all the typical features mentioned above are maintained here: the absence of the critical point, the depression of the CPC and the discontinuity in the shadow curve at the triple point, and the identity of shadow curve and CPC for  $\phi < \phi_c$ .

#### IV. Comparison with Model Calculations and Other Data

**Model Ternary System Solvent (1)–Monomer (2)–Polymer (3).** A ternary system was chosen for the demonstration of the anomalous CPC with a triple point, since in this case the  $\chi$  surface can be constructed in three-dimensional space. The temperature dependence of binodials (*i.e.*, horizontal sections of the  $\chi$  surface) in similar systems has been thoroughly investigated by Tompa<sup>14</sup> and other authors, and a detailed review is given by Koningsveld,<sup>2b</sup> however, it has apparently not been realized that vertical sections of the same  $\chi$  surface generated by planes passing through  $\phi_1 = 1$  (*i.e.*, the CPC's) sometimes do not contain the critical point while showing a singularity and, moreover, that this kind of behavior can also be generally observed in multicomponent systems. When the critical point is plotted in Tompa's<sup>15</sup> CPC constructed from binodials for a ternary system of solvent, polymer with  $P = 768$  and polymer with  $P = 10,950$ , it obviously falls under the CPC, but this fact apparently either went unnoticed or was attributed to numerical errors.

Our model polymer consists of two fractions,  $P_2 = 1$  and  $P_3 = 25$ , with no mutual thermodynamic interaction,  $\chi_{23} = 0$ , and the interaction polymer–solvent is assumed to be the same for both  $P_2$  and  $P_3$ ,  $\chi_{12} = \chi_{13} = \chi$ . The CPC's in Figure 2 were computed for  $w_3 = \phi_3/(\phi_2 + \phi_3)$  ranging from  $\approx 3 \times 10^{-5}$  to  $\approx 6 \times 10^{-2}$  by the method given in Appendix II. In order to cover such a broad range a logarithmic scale was used for  $w_3$  thus distorting binodials but not changing the CPC. The planes of constant  $w_3$  are drawn parallel in Figure 2 and the axis  $w_3$  represents the direction of changing asymmetry  $S$ . The locus of critical points on individual CPC's, called the critical line, sinks with decreasing  $w_3$ , passes through a minimum at  $w_3 \approx 9.4 \times 10^{-3}$ , then increases again to a maximum at  $w_3 \approx 4.2 \times 10^{-4}$  and arrives at  $w_3 = 0$  with  $\chi = 2$ . It can be shown that both extremes correspond to  $S = 0$ . At first the critical line is located on the  $\chi$  surface and the critical points have a real meaning, though the CPC's already show triple points.

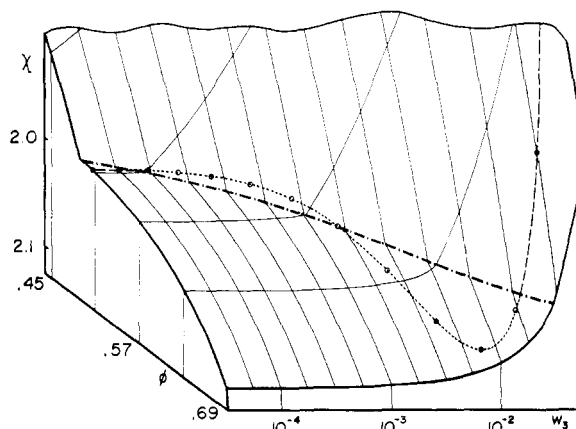


Figure 2. A portion of the  $\chi$  surface for the ternary system solvent (1); monomer,  $P = 1$  (2); polymer,  $P = 25$  (3). Sections of the surface parallel to the  $\chi$ – $\phi$  plane (bold full curves) indicate CPC's. Several sections parallel to the  $\chi$ – $w_3$  plane are shown (thin full curves) to aid visualization. Note that the concentrations  $w_3$  of the third component are on a logarithmic scale. Critical line, in unstable region, – – –; in stable region, — —; critical points, open circles; three-phase line, — · — · —.

However, with decreasing  $w_3$  the critical line approaches the three-phase line, crosses it at  $w_3 \approx 2 \times 10^{-2}$  and submerges under the  $\chi$  surface, losing at the same time physical stability. Down to  $S = 0$  (*i.e.*, to the minimum of the critical line) the critical points are located on the extended subcritical branches of the CPC. By further decrease of  $w_3$ , they move under the surface from the subcritical branch to the supercritical one and reach it at the maximum of the critical line. Then they approach the three-phase line along the supercritical branch until they emerge on the surface. For  $w_3 \lesssim 8 \times 10^{-5}$  they again have physical meaning, being located on the supercritical surface. The three-phase line, representing the locus of points which are in equilibrium with two different phases, also shows two extrema, each at an intersection with the critical line. These points correspond to double plait points on the binodials for that particular  $\chi$ , and the three-phase equilibrium here degenerates into a two-phase one. If  $\chi$  changes in proper direction, the double plait point develops into a new physically significant binodal located on the old one, and the three-phase line is formed by the points of intersection of these two binodials.

The equilibrium compositions of the CPC obtained by the direct method were checked numerically with Koningsveld's method for computing binodials,<sup>2</sup> with very good agreement. It should be noted that here, too, the choice of a particular branch of CPC by the critical point at  $S = 0$  complies with condition 19.

When the DP of the polymer component  $P_3$  is decreased, the region of  $w_3$  with  $S$  nonpositive gets smaller until at  $P_3 \approx 15.645$  it degenerates into a point at  $w_3 \approx 4.95 \times 10^{-3}$  where  $S = 0$ . Not surprisingly, at this point we find also  $P_{2+2}$  equal to the right-hand side of relation 19, indicating that  $S^* = 0$ . Since  $S$  is non-negative for all  $w_3$  at  $P_3 \approx 15.645$ , the  $\chi$  surface here must be smooth without any three-phase region. However, when  $P_3$  is increased beyond the above value at  $w_3 \approx 4.95 \times 10^{-3}$ , the parameter  $S$  becomes negative,

(14) H. Tompa, *Trans. Faraday Soc.*, **45**, 1142 (1949).

(15) H. Tompa, "Polymer Solutions," Academic Press, New York, N. Y., 1956, p 215.

both critical branches of the CPC are simultaneously transformed into the noncritical branches, and the three-phase region appears on the  $\chi$  surface. The ternary system with  $P_3 \simeq 15.645$  is thus the last one without a three-phase region, as long ago found also by Tompa<sup>14</sup> through his analysis of binodials.

**Model System Solvent-Polydisperse Polymer.** In his thesis and some of his papers, Koningsveld<sup>2</sup> gives the CPC's and shadow curves computed for several different types of hypothetical polymer by the extrapolation method.

For polymers with Schulz-Zimm distributions, both curves are smooth and their slopes at the critical point agree with relations 11 and 12. On the other hand, all the polymers with logarithmic-normal distribution, including two bimodal samples, show a singularity in the first derivative of the CPC. The slope of the right-hand branch of the CPC agrees with eq 11 for  $\epsilon \leq 3$ , but obviously not for  $\epsilon = 10$ , which is in accord with condition 35. The behavior involving the noncritical root can hardly be expected to be in quantitative agreement with the derived relations, since the upper limit of the DP distribution generated in the computer is finite and the noncritical root is thus larger than zero. This explains why the slope of the left-hand branch of CPC and the angle  $\gamma$  are not so large as predicted by eq 29 and 32. The shadow curves tend to turn toward the subcritical branch of the CPC, especially the one corresponding to the most asymmetric distribution  $w_1$  ( $\epsilon = 10$ ) which turns left and goes almost parallel with the CPC. This shadow curve also shows an obvious discontinuity at the triple point. The zero displacement between the critical point and the triple point following from Koningsveld's data is possibly due to low accuracy of the extrapolation method in the critical region and to his tacit assumption that the critical point be located on the CPC. The validity of the apparently controversial eq 24a and 24c is supported by the behavior of the polymer  $w_1$ : at subcritical concentration, a plot of the number-average DP of the separated phase  $P_n''$  against the fraction size shows a maximum and  $P_n''$  decreases as the fraction size becomes very small, while  $P_w''$  at the same time sharply increases.

**Comparison with the Experimental Data.** The system polyethylene-diphenyl ether investigated in detail by Koningsveld<sup>2</sup> seems to be especially convenient for comparison with the expressions obtained since it closely follows Flory-Huggins thermodynamics,<sup>2b</sup>  $\chi$  being approximately concentration independent as assumed in this paper. With the typical long-tail DP distribution of linear polyethylene, we can expect the data to be comparable with the relations for diverging distributions, *i.e.*, without a critical point and with a triple point on the CPC. The CPC's of all three samples really do show a dip, indicating the possible presence of the triple point, and their almost linear left branches reach to unusually low concentrations (about 1%). The estimated shadow curves tend to turn to the left above the point of intersection with CPC, as expected. Also, the dip is obviously deeper for the less polydisperse sample L30-7-6 than for L30-0-7, which is seemingly unreasonable but in accord with eq 32. The third sample L30-5-1 cannot be included in the comparison since its parameter  $S$  is very probably negative.

Taking into account these experimental data and the known long-tail DP distribution of linear polyethylene, we believe that the intersection of the CPC with the shadow curve corresponds to a triple point rather than to a critical point, which should be located at a lower concentration under the CPC. With this supposition, better agreement would be obtained between  $M_z$  calculated from  $M_w$  and  $\phi_{crit}$ , and  $M_z$  experimentally observed for samples L30-0-7 and L30-7-6.

On the other hand, with respect to present methods and experimental errors involved, it is not always easy to decide whether a CPC has a critical point, a triple point, or both of them, on the basis only of direct experimental evidence. Only if the second derivative of the experimental CPC is negative in the critical region it is obvious that the CPC has a critical point but no triple point. Otherwise several observations could give the answer. (1) Any discontinuity in the slope of the CPC and in the shadow curve itself indicates the presence of a triple point. If this discontinuity happens to be at the intersection of the CPC and the shadow curve, the critical point is unstable. Otherwise, the CPC has both critical and triple points, the critical point being located at the intersection. (2) At the triple point, three phases are in equilibrium. Thus, upon cooling an originally homogeneous solution with just the concentration  $\phi = \phi_t$ , two conjugate phases appear at the same time at  $\chi = \chi_t$ . The three-phase region certainly also occurs in the neighborhood of  $\phi_t$ , the only difference being that the second and third phases appear consecutively instead of simultaneously upon cooling. We believe that the statement can be reversed, and that the presence of a three-phase region close to the CPC indicates the presence of a triple point on the CPC. However, the experimental points of the CPC and more especially of the shadow curve (obtained by extrapolation from phase-equilibria data) are usually too scattered to allow an unambiguous interpretation, and a small three-phase region could easily be overlooked. While separation into three phases has been experimentally observed in quasi-ternary mixtures<sup>2b</sup> (*e.g.*, diphenyl ether and two polyethylene fractions with mol wt 25,000 and 540,000) no such observation has yet been reported for a single fraction or an unfractionated polymer. Only very exact and detailed experimental results can be expected to prove beyond any doubt that a triple point can occur on the CPC for real polymers with "natural" DP distributions.

**Acknowledgment.** The author wishes to express his sincere thanks to Professor W. H. Stockmayer for his stimulating discussions and continuous interest in this work. The author also wishes to thank Dr. R. Koningsveld for attracting his attention to this problem, and for his useful comments.

## Appendix I

The following relations can be derived for the function  $F(\sigma, \phi)$ .

(1) For  $\sigma = 0$ , the derivatives are

$$\left(\frac{\partial F}{\partial \sigma}\right)_\phi = \left(\frac{\partial^2 F}{\partial \sigma^2}\right)_\phi = 0 \quad (\text{A-1})$$



$$\left(\frac{\partial^3 F}{\partial \sigma^3}\right)_\phi = \frac{1}{2} K P_w^3 \left[ \frac{P_z}{P_w^2} - \left( \frac{\phi}{1 - \phi} \right)^2 \right] \quad (\text{A-2})$$

$$\left(\frac{\partial^4 F}{\partial \sigma^4}\right)_{\phi=\phi_{\text{crit}}} = P_w P_z (P_{z+1} - 3P_z - 2P_z^{1/2}) \quad (\text{A-3})$$

$$\left(\frac{\partial^5 F}{\partial \sigma^5}\right)_{\phi=\phi_{\text{crit}}} = \frac{1}{2} K P_w P_z (3P_{z+2} P_{z+1} - 10P_{z+1} P_z - 15P_z^2 - 40P_z^{3/2} - 18P_z) \quad (\text{A-4})$$

Provided  $K = +1$ , the function  $F(\sigma)$  at constant  $\phi$  and  $\sigma \rightarrow 0$  is a nondecreasing one if  $\phi < \phi_{\text{crit}}$  and a non-increasing one if  $\phi > \phi_{\text{crit}}$ , and in both cases it has a point of inflection at the origin. At the critical concentration,  $\phi = \phi_{\text{crit}}$ , even the third derivative is zero and the function has usually either a flat maximum or minimum, depending on the sign of  $S = 3P_z + 2P_z^{1/2} - P_{z+1}$ . Only for a particular group of distributions characterized by  $S = 0$  can the function  $F$  show here a flat inflection.

(2) When  $|\sigma|$  is large enough, the function  $F(\sigma)$  takes negative values. However,  $\sigma$  must be smaller than  $\sigma'$  where

$$\sum_{i=1}^{\infty} (\sigma')^i \mu_i / i! = \phi^{-1} - 1$$

(3) The function  $F(\sigma)$  has at least one extremum. The shift of the  $\sigma$  coordinate of the extremum with changing  $\phi$  satisfies the relation

$$\frac{d\sigma_{\text{extr}}}{d\phi} \left( \frac{\partial^2 F}{\partial \sigma^2} \right)_\phi = \frac{K\phi\nu_1(\nu_0 - 1)^2}{2(1 - \phi)(1 - \phi\nu_0)^2} \quad (\text{A-5})$$

Thus with increasing  $\phi$  the maxima move to lower  $\sigma$  and the minimum to higher  $\sigma$ . The "rate" of their movement is the higher the flatter the extrema. According to this "shift rule," the central minimum, if present, absorbs the right maximum on increase (and the left maximum on decrease) of concentration  $\phi$ .

(4) The function  $F(\sigma)$  sometimes has a nontrivial point where  $(\partial F / \partial \sigma)_\phi = (\partial^2 F / \partial \sigma^2)_\phi = 0$  (point of inflection with a horizontal slope). For a given distribution  $w(P)$ , this can happen only at a particular concentration  $\phi = \phi_{\text{in}}$ , satisfying the relation

$$\phi / (1 - \phi\nu_0) = \nu_2^{1/2} \nu_1^{-3/2} \quad (\text{A-6})$$

in which the value of  $\sigma$  to be used is the root of the equation

$$K\sigma - (\nu_0 - 1)[\nu_1^{-1} + \nu_2^{1/2} \nu_1^{-3/2}] + \ln [1 + (\nu_0 - 1)\nu_2^{1/2} \nu_1^{-3/2}] = 0 \quad (\text{A-7})$$

If in addition the function  $F(\sigma, \phi)$  is required to be zero at this point of inflection (*i.e.*,  $\sigma$  and  $\phi$  should comply with eq A-6, A-7, and 7), a condition is imposed on the

distribution  $w(P)$  itself which can only rarely be satisfied.

## Appendix II

Several precautions should be observed when solving the equilibrium equation for the CPC.

(1) Since the moments  $\mu_k$  of a distribution increase rapidly with  $k$  (especially when the average molecular weight of the polymer is high), only "reduced" moments  $\mu_k'$  and  $\sigma'$  were stored in the computer

$$\mu_k' = \sum_i w_i (P_i / C)^k / k! \quad (\text{A-8})$$

$$\sigma' = \sigma C \quad (\text{A-9})$$

where  $C$  is a constant of the order of the average DP. This transformation avoids overflow in the computer and at the same time allows the computation of moments, *e.g.*

$$\nu_0 = 1 + \sum_{k=1}^{\infty} \sigma^k \mu_k / k! = 1 + \sum_{k=1}^{\infty} (\sigma')^k \mu_k' \quad (\text{A-10})$$

(2) In order to ensure sufficient accuracy, some terms in eq 7 were sometimes combined so as to cancel large quantities of opposite sign

$$K\sigma(1 + \nu_0)/2 - (\nu_{-1} - \mu_{-1}) = \frac{1}{2} \sum_{i=3}^{\infty} (K\sigma)^i \mu_{i-1} (i - 2) / i! \quad (\text{A-11})$$

$$(\nu_0 - 1) + [\phi^{-1} - \frac{1}{2}(\nu_0 + 1)] \ln \frac{1 - \phi\nu_0}{1 - \phi} = -x^2(\nu_0 - 1) \left[ \frac{1}{12} + \frac{1}{12}x + \frac{3}{40}x^2 + \dots + \frac{1}{2}(n+1)(n+2)^{-1}(n+3)^{-1}x^n + \dots \right] \quad (\text{A-12})$$

where  $x = \phi(\nu_0 - 1)/(1 - \phi)$ .

The computation of a point on the CPC at the concentration  $\phi$  for the given distribution is then simple: taking into account the expected shape of the  $F$  function, we find the roots of eq 7 (using eq 4 for computing  $\nu_0 - 1$ , plus eq A-11 and A-12) and then compute the physically significant  $\chi$  from eq 8. When the convergence of the series in eq 4 is too slow the moments  $\nu_k$  can be computed as integrals

$$\nu_k = \int_0^{\infty} P^k \exp(K\sigma P) w(P) dP \quad (\text{A-13})$$

This direct calculation of the CPC is much faster than the method which has been used previously;<sup>2</sup> the solving of equilibrium conditions for several finite fractions excluded from a solution with the concentration  $\phi$  and extrapolation of results to zero fraction size.