Cloud-Point Curves of Polymers with Logarithmic-Normal Distribution of Molecular Weight

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ABSTRACT: In the Flory–Huggins approximation, the cloud-point curves (CPC's) of polymers with a true logarithmic-normal distribution of molecular weight show a peculiar behavior. Independently of the averages x_n, x_w, etc., the precipitation threshold is at $\varphi = 0$ and $\chi = \frac{1}{2}$, and the subcritical branch of CPC follows the simple relation $2\chi = (1 - \varphi)^{-1}$. The metastable branch of CPC is identical with the spinodal, i.e., $2\chi = (1 - \varphi)^{-1} + (\varphi x_w)^{-1}$, and it passes through the critical point which is never thermodynamically stable. Along both of these branches, the polymer concentrations in the two equilibrium phases are identical although the molecular weight distributions of the polymers contained in the two conjugate phases vastly differ. CPC's exhibit a triple point at which two incipient phases of different compositions are at equilibrium with the principal phase. This behavior is caused by an infinitesimal yet significant amount of material with $x \rightarrow \infty$. By cutting off the high molecular end of the distribution, the threshold gradually relaxes to $\chi > \frac{1}{2}$ and $\varphi > 0$, while the metastable region diminishes and the triple point moves to lower concentrations and lower values of χ. However, the general character of the CPC, in particular the existence of a "depression" on it, remains the same, unless the cut-off value becomes too low. The results indicate that the low-concentration part of CPC left of the "depression", provided there is any, is very sensitive to minute amounts of high molecular weight material, while being almost independent of the low-order averages x_n, x_w, etc., commonly used to characterize samples.

One of the intricate problems in the theory of phase equilibria of simple Flory–Huggins quasi-binary systems are the cloud-point curves (CPC) of polydisperse polymers with "diverging" distributions of molecular weight. This term was suggested[1] for analytical distributions which converge with $x \rightarrow \infty$ *slower* than any exponential $\exp(-\sigma x)$ does where σ is a positive parameter. Hence, such distributions, multiplied by a factor $\exp(\sigma x)$, diverge with $x \rightarrow \infty$ for *any* positive value of σ no matter how small it might be

$$\lim_{x \rightarrow \infty} w(x) \exp(\sigma x) = \infty \tag{1}$$

$$\text{for all } \sigma > 0$$

For large enough k, the statistical moments μ_k

$$\mu_k = \int_0^\infty w(x) x^k \mathrm{d}x \tag{2}$$

of "diverging" distributions grow faster than the factorial term (k!). A classical example of this type is the logarithmic-normal (LN) distribution, here employed in the Wesslau form

$$w_{\mathrm{LN}}(x) = (x\beta\pi^{1/2})^{-1} \exp[-\beta^{-2} \ln^2 (x/x_0)] \tag{3}$$

$$0 < x$$

where $x_0 = (x_w x_n)^{1/2}$ and $\exp(\beta^2/2) = x_w/x_n = x_z/x_w = \ldots.$ The statistical moments of this distribution are given by the fast-growing expression

$$\mu_{k,\mathrm{LN}} = x_0{}^k \exp(k^2\beta^2/4) \tag{4}$$

On the other hand, the exponential distribution

$$w_{\mathrm{E}}(x) = t^{u+1}\Gamma^{-1}(u + 1)x^u \exp(-tx) \tag{5}$$

is classified as "converging" since for $\sigma < t$ (where t is a positive parameter), its product with $\exp(\sigma x)$ converges to zero as x grows to infinity. Similarly, every discrete distribution consisting of a mixture of species with finite chain lengths (such as, e.g., hypothetical distributions employed in computer simulations) is "converging" since for large k, its moments μ_k will grow slower than (k!).

The reason for making a distinction is a very different behavior of CPC equations (and, consequently, of the CPC's themselves) for these two types of distributions. In the case of "converging" distributions, the equation for CPC (as well as for the precipitation threshold which is a special point of the CPC) poses no particular problems and can be numerically solved.[1–5] On the other hand, for "diverging" distributions such a trivial approach fails because the equations in the commonly employed form contain terms diverging to infinity.[3,4] Obviously this does not imply that the CPC's for such polymers would not exist; it only means that they cannot be obtained in a conventional way.

The first attempt to solve this problem was done by Koningsveld and Staverman[3,4] in their extensive numerical study of CPC's of polymers with various hypothetical distributions of molecular weight. The CPC indicating the incipient phase separation (corresponding to the fraction size 0) was determined by extrapolation of numerical data obtained by solving the equilibrium equations for fraction sizes different from 0. This indirect method formally eliminated the difficulties since the "diverging" character of the distribution caused problems only in the limit for zero fraction size, i.e., for the CPC itself. The calculated CPC's showed a distinct depression, or dip, in the critical region which strongly contrasted with smooth dependence found for polymers with exponential distributions. Also, perhaps not surprisingly, all investigated CPC's turned out to be greatly dependent upon the average degrees of polymerization and the "polydispersity" x_w/x_n.

The disadvantage of extrapolation to the zero fraction size, however, is its inherent inaccuracy particularly in the region of low concentrations and for polymers with LN distribution.[3,4] Fortunately the numerical extrapolation can be avoided by solving directly the CPC equation, as suggested by Koningsveld and Chermin for exponential distributions[6] and later generalized by this author.[1] In agreement with the above results, our analysis[1] showed that the CPC's of polymers with a true "diverging" distribution always exhibit a depression which physically corresponds to the triple point, i.e., to a point on the CPC where *three* phases of different compositions are at equilibrium. Our other conclusions, however, contradicted the numerical data of Koningsveld and Staverman. In particular, the subcritical branch of the CPC was predicted to follow the exceedingly simple limiting form

$$2\chi = (1 - \varphi)^{-1} \tag{6}$$

and to be superimposed onto its shadow curve, independently of the average degrees of polymerization.

To resolve the above controversy, we present in this paper an analysis of CPC's for polymers with LN distribution. By choosing a specific type of "diverging" distribution, the previously given admittedly rather intuitive arguments can be presented with much more rigor. They are further supported by several numerical examples.

Sometimes we will find it convenient to replace the true LN distribution extending up to infinity by a distribution conforming to eq 3 only within a certain interval of chain lengths

$$\begin{aligned} w_{\mathrm{Q}}(x) &\propto w_{\mathrm{LN}}(x) && \text{if } x_{\min} < x < x_{\max} \\ w_{\mathrm{Q}}(x) &= 0 && \text{otherwise} \end{aligned} \tag{7}$$

By placing an upper limit $x_{\max}$ to the chain length considered for the calculation, the originally "diverging" distribution is converted into a "converging" distribution which is easier to deal with. This modified distribution $w_{\mathrm{Q}}(x)$ will be referred to as a *quasi-LN* distribution.

General Cloud-Point Curve Equation

In the Flory–Huggins approximation with concentration-independent parameter χ, the CPC equation for the system single solvent-polydisperse polymer takes the form[1,5]

$$F(\varphi,\sigma) \equiv \tfrac{1}{2}K\sigma(1+\nu_0) - (\nu_{-1} - \mu_{-1}) + (\nu_0 - 1) + [\varphi^{-1} - \tfrac{1}{2}(1+\nu_0)] \ln \frac{1-\varphi\nu_0}{1-\varphi} = 0 \tag{8}$$

Here φ is the volume fraction of the polymer in solution, μ_k are statistical moments of the original normalized chain length distribution $w(x)$ defined by eq 2, ν_k are statistical moments of the distribution of the polymer contained in the incipient phase

$$\nu_k = \int_0^\infty w(x) x^k \exp(K\sigma x)\mathrm{d}x \tag{9}$$

and σ is the familiar nonnegative parameter describing the distribution of the polymer species of chain length x between the concentrated ($''$) and dilute ($'$) phases[7]

$$\varphi_x''/\varphi_x' = \exp(\sigma x) \tag{10}$$

The constant K can assume values +1 or −1, depending upon whether the incipient phase is more or less concentrated than the principal phase.

Sometimes it is more convenient to consider the expanded form of the CPC equation.[1] The series representation of ν_k is obtained by expansion of the exponential in eq 9

$$\nu_k = \mu_k + \sum_{i=1}^{\infty} (K\sigma)^i \mu_{k+i}/i! \tag{11}$$

One can always combine the first two terms of the CPC eq 8 to yield

$$\tfrac{1}{2}K\sigma(1+\nu_0) - (\nu_{-1} - \mu_{-1}) = \tfrac{1}{2} \sum_{i=3}^{\infty} (K\sigma)^i \mu_{i-1}(i-2)/i! \tag{12}$$

On the other hand, the simple expanded form of the remaining two terms of eq 8

$$\nu_0 - 1 + \left[\frac{1}{\varphi} - \frac{\nu_0 + 1}{2}\right] \ln \frac{1-\varphi\nu_0}{1-\varphi} = -\tfrac{1}{2}\gamma^2(\nu_0 - 1)M(\gamma) \qquad |\gamma| < 1 \tag{13a}$$

where

$$\gamma \equiv \varphi(\nu_0 - 1)/(1-\varphi)$$

$$M(\gamma) \equiv \sum_{n=0}^{\infty} \frac{(n+1)}{(n+2)(n+3)} \gamma^n \tag{13b}$$

can be used only if $|\gamma|$ of eq 13 is smaller than unity. This condition imposes some restrictions in the supercritical region if $\varphi\nu_0$ is close to zero, and φ is close to one, but it is always satisfied in the subcritical region which is the primary object of our interest. Hence, after some rearrangements and with $(\nu_0 - 1)$ substituted from eq 11, the CPC eq 8 can be transcribed for $K = 1$ as

$$\sigma\Lambda(\sigma) = \gamma^2 \mathrm{M}(\gamma) \tag{14a}$$

where

$$\Lambda(\sigma) \equiv \frac{\sum_{i=2}^{\infty} [(i-1)/(i+1)]\sigma^i \mu_i/i!}{\sum_{i=1}^{\infty} \sigma^i \mu_i/i!} \tag{14b}$$

For any pair of φ and σ values satisfying the CPC equation, the parameter χ is then calculated from

$$2\chi\varphi(\nu_0 - 1) = K\sigma + \ln[(1-\varphi)/(1-\varphi\nu_0)] \tag{15}$$

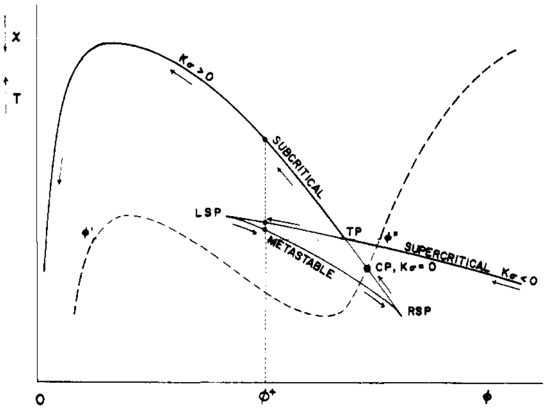

Figure 1. Scheme of a typical CPC (—) and shadow curve (- - -) for a system exhibiting three-phase equilibrium. Stable parts of both curves are drawn in bold lines. The left and right singular points (LSP and RSP) divide the CPC into three branches: subcritical, metastable, and supercritical. (Since the critical point may be either stable or metastable (but not thermodynamically unstable),[8] we use the latter word also for the CPC branch located entirely in the region which is not stable. By doing so, we do not wish to imply that all parts of CPC which are not stable are necessarily metastable in the strict thermodynamic sense of that word.) Depending on $w(x)$, the critical point (CP) may be located on any of these branches, and it may be thermodynamically stable or metastable (as in this particular case). At the triple point TP (point of intersection of sub- and supercritical branches) the system contains two incipient phases of different compositions φ' and φ''. Parameter $K\sigma$ monotonously increases along the CPC from negative values to zero (at CP) to positive values as indicated by arrows. The vertical dashed line indicates three solutions of CPC equation for a system with polymer concentration φ^+.

CPC for Polymers with Logarithmic-Normal Distribution

Analytical Form. Each point of a CPC is characterized by values of φ, χ, and $K\sigma$ which are interrelated by equations given in the preceding section. Since out of these three parameters only $K\sigma$ changes monotonously along the CPC under all conditions (see Figure 1), it is particularly suitable for discussing the CPC phenomena. Hence, we shall start inspecting the CPC equation for high positive $K\sigma$ (which correspond to the region of very low polymer concentrations) and proceed gradually to negative $K\sigma$.

The above-mentioned divergence of the terms of the CPC eq 8 for $K\sigma > 0$ is immediately recognized; indeed, from the very definition of "diverging" distributions, eq 1, it follows that in such case all ν_k of eq 9 grow to infinity which makes eq 8 useless for numerical computations. The rearranged expanded form, eq 14, however, does not pose any problems; although the individual terms of the series in the numerator and denominator again diverge with $i \to \infty$, the value of the ratio Λ asymptotically approaches unity since with $i \to \infty$, the most significant terms of both series become identical. Thus the lhs of (14a) equals simply σ, i.e., it is finite and positive, and consequently also the γ of the rhs of (14a) has to be finite.

Since it is known from the above that $(\nu_0 - 1)$ approaches infinity and, on the other hand, γ is required to be finite, it is obvious from the definition of γ, eq 13b, that φ has to simultaneously approach zero, $\varphi \to 0$. Positive nonzero $K\sigma$ thus can occur only in the region of zero concentrations φ. The quantity γ then becomes identical with the polymer concentration φ_i in the incipient phase (i.e., it specifies a point of the shadow curve[1])

$$\lim_{\substack{\nu_0 \to \infty \\ \varphi \to 0}} \gamma = \lim_{\substack{\nu_0 \to \infty \\ \varphi \to 0}} [\varphi(\nu_0 - 1)/(1 - \varphi)] = \varphi\nu_0 \equiv \varphi_i \tag{16}$$

With this interpretation of γ, it is now apparent that the expansion of the logarithmic term in eq 13a was permitted, and the σ corresponding to a point φ_i of the shadow curve becomes simply

$$\sigma = \varphi_i^{\,2}M(\varphi_i) \tag{17}$$

Finally, the interaction parameter χ specifying the shadow curve is obtained from eq 15

$$\lim_{\substack{\nu_0 \to \infty \\ \varphi \to 0}} (2\chi) = \varphi_i M(\varphi_i) - \varphi_i^{-1} \ln (1 - \varphi_i) \tag{18a}$$

At higher values of φ_i, it is more convenient to use the closed form of $M(\varphi_i)$ given by [cf. eq 13b]

$$\varphi_i^{\,3}M(\varphi_i) = (\varphi_i - 2) \ln (1 - \varphi_i) - 2\varphi_i \tag{18b}$$

Since the validity of eq 16–18a is restricted to the zero range of φ, the CPC here degenerates into a vertical line at zero polymer concentration, extending up to $\chi = \frac{1}{2}$. The shadow curve is given by eq 18a and it meets the CPC at the point $\varphi = 0$, $\chi = \frac{1}{2}$. This is unusual since normally, i.e., for polymers with "converging" distributions, the shadow curve intersects the CPC only at the critical point. The infinitely large ν_0 is now well understandable since ν_0 is equal to the ratio φ_i/φ in which the denominator approaches zero. It can be seen from eq 11 that also all the average chain lengths of the polymer in the incipient phase, $(x_n)_i$, $(x_w)_i$, $(x_z)_i$, etc., approach infinity in this region.

At nonzero polymer concentrations, $\varphi > 0$, ν_0 necessarily has to be finite since its product with φ (indicating the polymer concentration in the incipient phase, $\varphi_i \equiv \varphi\nu_0$) has to be smaller than unity. Hence, σ in eq 11 has to approach zero to counterbalance the effect of the moments μ_{k+i} growing faster than the factorial $(i!)$. Furthermore, none of the series terms in the numerator of eq 14b is greater than the corresponding term in the denominator; i.e., the ratio Λ can never be higher than unity, and hence, its product with σ approaches zero too. This implies that also γ on the rhs of eq 14a has to go to zero. Since we presently consider the region of nonzero concentrations, however, this can be true only if ν_0 approaches unity. The zero range of the parameter σ thus spreads from the point $\varphi = 0$, $\chi = \frac{1}{2}$, to the critical point where $\sigma = 0$ by definition, and the shadow curve in this whole region is superimposed onto the CPC, as predicted earlier.[1] The CPC in this region then takes the form [cf. eq 15]

$$2\chi\varphi = \lim_{\substack{\sigma \to 0 \\ \nu_0 \to 1}} \frac{\sigma + \ln [(1 - \varphi)/(1 - \varphi\nu_0)]}{\nu_0 - 1} = Y + \varphi(1 - \varphi)^{-1} \tag{19a}$$

Our problem has thus been reduced to two tasks: (i) calculating the indeterminate expression

$$Y \equiv \lim_{\substack{\sigma \to 0 \\ \nu_0 \to 1}} \sigma(\nu_0 - 1)^{-1} \tag{19b}$$

whose value may vary as σ approaches zero, and (ii) specifying the correspondence between σ and the polymer concentration φ from eq 14a which now $(\gamma \to 0)$ can be simplified as

$$6Y\Lambda/(\nu_0 - 1) = \varphi^2/(1 - \varphi)^2 \tag{20}$$

It should be reminded that so far we did not have to make any specific assumptions about the type of distribution (except for its "divergence") and thus our conclusions were quite general. However, in order to deal with the indeterminate expressions occurring in (19) and (20), it is illustrative (though not necessary) to choose a specific type of "diverging" distribution, to retreat in our discussion back to the corresponding quasi-distribution with a finite $x_{\max}$, and only after having reached some concrete results to let the upper limit $x_{\max}$ grow to infinity.

If the integration in eq 2 is performed only up to $x_{\max}$ (which is assumed to be very large but still finite), eq 4 for statistical moments of the LN distribution is modified to

$$\mu_{k,\mathrm{Q}} = x_0^{\,k} \exp(k^2\beta^2/4)[1 + \mathrm{erf}(y_{\max} - \tfrac{1}{2}k\beta)]/2 \tag{21a}$$

where

$$y_{\max} = \beta^{-1} \ln (x_{\max}/x_0) \tag{21b}$$

Equation 21a offers some insight into the special character of quasi-LN distributions. For $k \ll 2y_{\max}/\beta$, the moments $\mu_{k,\mathrm{Q}}$ of (21) are almost identical with the moments $\mu_{k,\mathrm{LN}}$ of the corresponding "diverging" distribution [eq 4] since

$$1 + \mathrm{erf}(y_{\max} - \tfrac{1}{2}k\beta) \approx 2 \qquad \text{if } k \ll 2\,y_{\max}/\beta,\ y_{\max} \gg 1 \tag{22}$$

In this region, $\mu_{k,\mathrm{Q}}$ grows extremely fast with k (note the square of k in the exponent of eq 4). On the other hand, for $k \gg 2y_{\max}/\beta$, we have[9]

$$1 + \mathrm{erf}(y_{\max} - \tfrac{1}{2}k\beta) \approx \frac{\exp[-(y_{\max} - \frac{1}{2}k\beta)^2]}{\pi^{1/2}(\frac{1}{2}k\beta - y_{\max})} \qquad \text{if } k \gg 2y_{\max}/\beta \tag{23}$$

which gives with eq 21a

$$\mu_{k,\mathrm{Q}} \approx \frac{\exp(-y_{\max}{}^2)}{2\pi^{1/2}(\frac{1}{2}k\beta - y_{\max})} \approx x_{\max}{}^k \qquad \text{if } k \gg 2y_{\max}/\beta \tag{24}$$

Here the moments $\mu_{k,\mathrm{Q}}$ grow much slower (in fact, they would grow no faster than the moments for a monodisperse polymer of chain length $x_{\max}$), and in series 11, they are eventually overcome by the factorial term (which constitutes the convergence of this "quasi-diverging" distribution). It is this profound change in the growth pattern of the moments $\mu_{k,\mathrm{Q}}$ in a relatively narrow interval of k which is typical for "quasi-diverging" distributions, and responsible for the extreme sensitivity of their CPC's to the chosen value of $x_{\max}$ (as will be shown below).

We will now inspect the behavior of individual terms

$$v_i = \frac{\sigma^i\mu_{i,\mathrm{Q}}}{i!} = \frac{(\sigma x_0)^i}{2i!} [1 + \mathrm{erf}(y_{\max} - \tfrac{1}{2}\beta i)] \exp(\beta^2 i^2/4) \tag{25}$$

Table I
Limiting Values for $x_{\max} \to \infty$ of Different Parameters of Phase Separation at the Cloud Point for a Polymer with True LN Distribution, in Dependence on ϵ of eq 31

	ν_0	Λ	Y	$Y/(\nu_0 - 1)$	$\Lambda/(\nu_0 - 1)$	φ
$\epsilon > 0$	∞	1	0	0	0	0
$-\frac{1}{2} < \epsilon < 0$	1	1	0	0	∞	0
$-1 < \epsilon < -\frac{1}{2}$	1	1	0	∞	∞	1
$-2 < \epsilon < -1$	1	0	x_w^{-1}	∞	∞	1
$-y_{\max}/\beta < \epsilon < -2$	1	0	x_w^{-1}	∞	${}^1/_6 x_z x_w^{-1}$	$(1 + x_w x_z^{-1/2})^{-1}$

which are needed for both $(\nu_0 - 1)$ and Λ of eq 19b and 20. At first sight, it is apparent that in the region of our interest, i.e., for $(\sigma x_0) \ll 1$ and $y_{\max} \gg 1$, the very first term v_1 of the series will dominate above its not too remote neighbors; for instance, we have

$$v_2/v_1 \approx \tfrac{1}{2}\sigma x_z \ll 1 \tag{26}$$

Far more important for our conclusions, however, is the appearance of a second maximum at high values of i which is brought up by the special character of the moments $\mu_{k,Q}$ discussed above. Its contribution Δ_0 to the sum Σv_i is evaluated in the Appendix as

$$\Delta_0 \approx (\pi^{1/2}\beta\sigma x_{\max})^{-1} \exp(\sigma x_{\max} - y_{\max}^2 + \tfrac{3}{2}) \tag{27}$$

A crucial feature of these two contributions, v_1 and Δ_0, is that with $x_{\max}$ growing, their importance increases, until in the limit for $x_{\max} \to \infty$ (and $\sigma \to 0$) they represent the only potentially significant terms. For instance, this is obvious from eq 26 indicating that in such case, indeed $v_2/v_1 \to 0$. Consequently, we can write

$$(\nu_0 - 1) = \sum_{i=1}^{\infty} v_i \approx v_1 + \Delta_0 \approx \sigma x_w + \Delta_0 \tag{28}$$

and from eq 14b and 19b also

$$\Lambda \approx \frac{6^{-1}\sigma^2 x_w x_z + \Delta_0(1 - 2i^{*\,-1})}{\sigma x_w + \Delta_0} \tag{29}$$

$$Y \approx [x_w + (\Delta_0/\sigma)]^{-1} \tag{30}$$

where i^* is the subscript of the maximum term v_{i^*}.

Now we are in a position to proceed with the discussion of the CPC. Since our greatest concern is to examine the CPC for a polymer with a true LN distribution, i.e., for $x_{\max} \to \infty$, the interpretation of eq 27–30 together with eq 19 and 20 offered in the following paragraphs will be restricted to this limiting case. However, the same equations can also serve as the first-order approximations for polymers with quasi-LN distributions as shown in the paragraph on precipitation threshold.

It turns out that all important effects occur in a relatively narrow range of σ around $\sigma = y_{\max}^2/x_{\max}$; therefore, it is convenient to discuss the CPC in terms of ϵ which is defined by the relation

$$\sigma x_{\max} = y_{\max}(y_{\max} + \epsilon\beta) \tag{31}$$

It is apparent that in the limit for $x_{\max} \to \infty$, this indeed represents the zero range for σ as suggested above, since $\lim_{x_{\max}\to\infty} (y_{\max}^2/x_{\max}) = 0$ [cf. eq 21b]. The results of the following discussion are summarized in Table I and Figure 2.

(i) If $\sigma \gg y_{\max}^2/x_{\max}$, i.e., if ϵ of eq 31 is positive, then the contribution of the second maximum Δ_0 of eq. 27 diverges, and so does of course $(\nu_0 - 1)$ from eq 28. Λ here approaches unity, Y of eq 30 goes to zero, and eq 20 indicates also that φ has to approach zero. All this only confirms the results obtained above for positive nonzero σ by a different method. The CPC degenerates into a vertical line at $\varphi = 0$; the shadow curve (upper dashed line in Figure 2) is given by eq 18a.

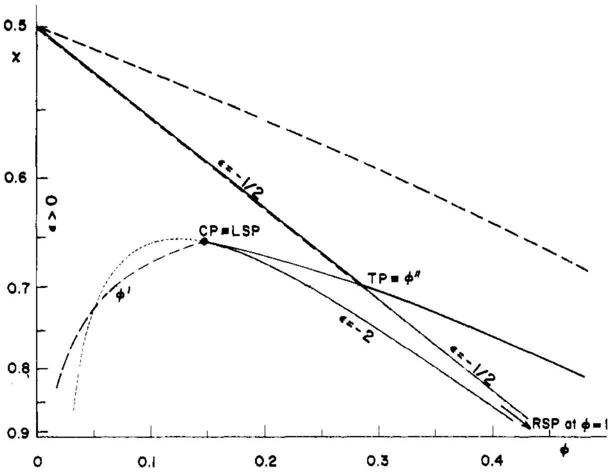

Figure 2. CPC (—) and shadow curve (- - -) for a polymer with true LN distribution (x_n = 33.3, x_w = 50). The upper dashed line gives the shadow curve corresponding to the vertical zero-concentration portion of CPC. For the rest of the subcritical branch as well as for the metastable branch of CPC, the shadow curve becomes identical with the CPC; i.e., the polymer concentrations in both equilibrium phases are the same. The spinodal (· · ·) coincides with the metastable branch of CPC at concentrations higher than the critical one.

(ii) In the range $-\frac{1}{2} < \epsilon < 0$, Δ_0 of eq 27 does not diverge any longer but rather approaches zero. However, it is still infinitely higher than σ itself; therefore, it still makes the only significant contribution to $(\nu_0 - 1)$ in (28) as well as to both the numerator and the denominator of Λ in (29). This means that both $(\nu_0 - 1)$ and Y approach zero whereas Λ stays at one. Since $Y/(\nu_0 - 1)$ stays at zero also, we are still at zero polymer concentration [cf. eq 20]. Physically this range corresponds to the region of the precipitation threshold at $\chi = \frac{1}{2}$, $\varphi = 0$, where the zero concentration branch of the CPC meets the shadow curve of eq 18a. The number-average chain length of the polymer in the incipient phase here approaches its value in the original polymer, $(x_n)_i \approx x_n$, while the higher averages still diverge.

(iii) If $-1 < \epsilon < -\frac{1}{2}$, the term Δ_0 is still the most significant term in eq 28 and 29, i.e., we still have $\Lambda = 1$. It is large enough to keep the value of Y at zero as before; however, it is not high enough to ensure that also $Y/(\nu_0 - 1)$ be zero. The value of this ratio rather grows here to infinity, which implies from (20) that the concentration range for this region has to approach unity, $\varphi \to 1$. We can thus conclude that the subcritical branch of the CPC extending from $\chi = \frac{1}{2}$, $\varphi = 0$, up to $\varphi = 1$, is characterized by the value $\epsilon = -\frac{1}{2}$. Fortunately there is no need to investigate more closely the neighborhood of the point $\epsilon = -\frac{1}{2}$ since for the whole region $-1 < \epsilon < 0$, we have found both Y and $(\nu_0 - 1)$ approaching zero. The CPC is, therefore, given simply by [cf. eq 19a]

$$2\chi = (1 - \varphi)^{-1} \tag{32a}$$

and the shadow curve is superimposed onto it. Both curves are independent of common characteristics of the polymer like x_w, x_z, etc., since they are totally due to infinitesimally small but significant amounts of material with $x \to \infty$. The average chain lengths of the polymer in the incipient phase remain the same as in case (ii). It is interesting to compare this result with the CPC expected for a monodisperse polymer of infinite molecular weight. Since the critical point of such a polymer is at zero concentration and there is no triple point present, its CPC equation for nonzero concentrations can be written from eq 8 by putting $K = -1$ and $\nu_0 = \nu_{-1} = \mu_{-1} = 0$. From eq 15 we then get

$$\chi = -\varphi^{-2}\ln(1-\varphi) - \varphi^{-1} \tag{32b}$$

which turns out to be the same function as in eq 18a. The supercritical branch of CPC of a monodisperse polymer with $x \to \infty$ thus happens to be identical with the upper part of the shadow curve (upper dashed line in Figure 2) for a polymer with true LN distribution.

(iv) In the region $-2 < \epsilon < -1$ the contribution Δ_0 finally becomes negligible as compared to υ_1 of eq 28; however, it still dominates the σ^2 term in the numerator of Λ, eq 29. Hence, Λ approaches zero, and Y becomes equal to the reciprocal weight average chain length, $Y = x_w^{-1}$. The ratio $\Lambda/(\nu_0 - 1)$, however, still approaches infinity; therefore, this region of ϵ still corresponds to the concentration $\varphi \to 1$.

(v) Finally, if $-y_{\max}/\beta \le \epsilon < -2$, the contribution of Δ_0 becomes so small that it can be neglected both in eq 28 and in the numerator and denominator of eq 29. The quantities Y, Λ, and $Y/(\nu_0 - 1)$ remain unaltered; the ratio $\Lambda/(\nu_0 - 1)$, however, becomes finite, $\Lambda/(\nu_0 - 1) = x_z/(6x_w)$, with the concentration given by $\varphi/(1-\varphi) = x_z^{1/2}/x_w$ which is indicative of critical region. Again, without further analysis, we can conclude that the branch of CPC extending from the region $\varphi \to 1$ back to the critical point corresponds to $\epsilon = -2$, and it is given by

$$2\chi = (\varphi x_w)^{-1} + (1-\varphi)^{-1} \tag{33}$$

This branch coincides with the spinodal[10] and as such it passes through the critical point. It is also coincident with the shadow curve, it is never thermodynamically stable, and along its entire length both the number and weight average in the incipient phase, $(x_n)_i$ and $(x_w)_i$, are equal to the respective values in the original polymer.

Let us now examine the position of the critical point relative to the left singular point (LSP) of the CPC. It has been shown quite generally for any type of distribution[1,5] that the critical point is located on the metastable branch of the CPC if the parameter $S \equiv -x_{z+1} + 3x_z + 2x_z^{1/2}$ is negative, whereas in the opposite case ($S > 0$) it is found either on the subcritical or on the supercritical branch. The latter ambiguity then disappears if the discussion is restricted to LN distributions; as follows from paragraphs (iii)–(v), the critical point cannot be located on the subcritical branch under any circumstances. This leaves us with the supercritical branch as containing the critical point if $S > 0$, as suggested earlier.[1] In order to estimate now the distance between the critical point and the left singular point, we return for a while to the quasi-LN distribution with a finite $x_{\max}$ for which one can use general arguments valid for "converging" distributions.

The detailed scheme of the left singular point and its neighborhood is drawn in Figure 3. Both branches of the CPC meeting there have to have identical slopes since $(\mathrm{d}\chi/\mathrm{d}\varphi)_{\mathrm{CPC}}$ (given in eq 8 of ref 5) is an analytical function of both σ and φ. Since the parameter $K\sigma$, however, changes monotonously along the CPC, its derivative with respect to the concentration, $[\mathrm{d}(K\sigma)/\mathrm{d}\varphi]_{\mathrm{CPC}}$, has to diverge and change its sign at the singular points. This will indeed happen if [cf. eq 7, ref 5]

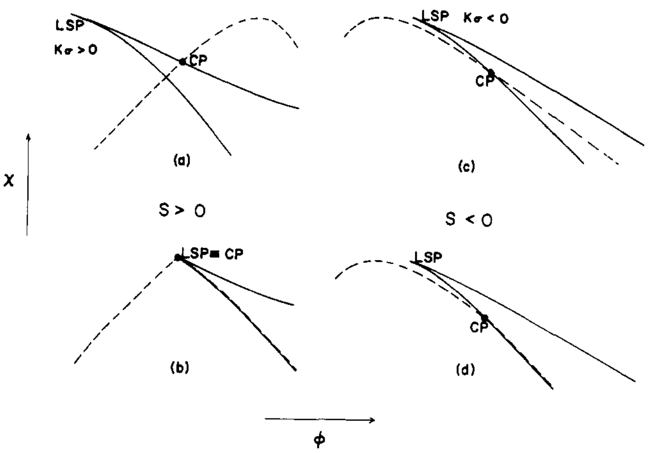

Figure 3. Neighborhood of the left singular point (LSP) of CPC for four types of polymers: (—) CPC, (- - -) shadow curve; a and c, polymers with quasi-LN distributions; b and d, polymers with true LN distributions (i.e., $x_{\max} \to \infty$); a and b, $x_{z+1} < 3x_z + 2x_z^{1/2}$; c and d, $x_{z+1} > 3x_z + 2x_z^{1/2}$.

$$2\chi\nu_1\varphi - \nu_1\varphi(1-\varphi\nu_0)^{-1} - 1 = 0 \tag{34a}$$

or, with χ substituted from eq 15

$$\frac{K\sigma}{\nu_0 - 1} + \frac{1}{\nu_0 - 1}\ln\frac{1-\varphi}{1-\varphi\nu_0} - \frac{\varphi}{1-\varphi\nu_0} - \frac{1}{\nu_1} = 0 \tag{34b}$$

Equation 34 together with the CPC eq 8 or 14a thus specifies the singular points on the CPC provided there are any. If the CPC is smooth with no triple point and singular points, these equations are not simultaneously satisfied for any value of $K\sigma$.

Let us first examine a polymer with quasi-LN distribution such that $x_{z+1} < 3x_z + 2x_z^{1/2}$, i.e., $S > 0$. Since the critical point is located on the supercritical branch (see Figure 3a) the left singular point (LSP) is characterized by positive $K\sigma$ and hence the above given formulas and conclusions [in particular those of paragraph (v)] relate also to LSP. After expanding the logarithmic term and rearranging, eq 34b can be written in the form

$$\Psi^2[\tfrac{1}{2} + \tfrac{2}{3}\Psi(\nu_0 - 1) + \ldots] = \sigma(\nu_0 - 1)^{-2} - \nu_1^{-1}(\nu_0 - 1)^{-1} \tag{35}$$

where Ψ serves as the abbreviation for $[\varphi/(1-\varphi)]$ at LSP. The ν_0 and ν_1 can then be expanded in series according to eq 11 and approximated by formulas analogous to eq 28

$$\begin{aligned} \nu_0 - 1 &\approx \sigma\mu_1 + \tfrac{1}{2}\sigma^2\mu_2 + \Delta_0 \\ \nu_1 &\approx \mu_1 + \sigma\mu_2 + \Delta_1 \end{aligned} \tag{36}$$

The beginning of the series for $\nu_0 - 1$ has to be considered up to the second-order term σ^2 since the first-order terms cancel out in eq 35; Δ_0 of eq 36 is identical with that of eq 28, and Δ_1 can be shown to be

$$\Delta_1 \approx x_{\max}\Delta_0 \tag{37}$$

Substitution of eq 36 into 35 then gives Ψ in the form

$$\Psi = \mu_2^{1/2}\mu_1^{-3/2} + O\left(\frac{\Delta_0}{\sigma}\right) + O\left(\frac{\Delta_0}{\sigma^2}\right) + O\left(\frac{\Delta_1}{\sigma}\right) + O(\sigma) \tag{38}$$

This equation indicates that the difference in $\varphi/(1-\varphi)$ between LSP and the critical point is of the order given by the last four terms in (38). Since at LSP, however, the parameter ϵ equals -2, the largest of these terms, Δ_1/σ, will be only of the order $y_{\max}^{-4}$; i.e., with $x_{\max}$ increasing, the difference between the two points will become smaller. Hence, in the case of a polymer with a true LN distribution (Figure 3b) the LSP becomes identical with the critical point.

The situation is quite different if the polymer has a very wide and asymmetric distribution so that $x_{z+1} > 3x_z + 2x_z^{1/2}$ ($S < 0$). Here the critical point is located on the metastable branch of the CPC (Figure 3c) and therefore, $K\sigma$ at the LSP has to be negative. With negative $K\sigma$, however, there is no need to be concerned about the high molecular end of the distribution since the effect of high species on ν_k in eq 9 is screened off by the exponential term. A similar argument can be extended to the expanded form of (11); although the absolute value of the series terms still shows a second maximum (which was so physically significant for positive $K\sigma$), the contribution made by those terms tends to zero because of the alternating sign of $(K\sigma)^i$. Hence, there is no reason for the LSP being shifted toward the critical point with $x_{\max} \to \infty$; the LSP will rather approach some limiting value consistent with eq 34b, which, however, will be different from the critical point (see Figure 3d). The same type of argument suggests that the entire supercritical branch of CPC will be little sensitive to $x_{\max}$.

It is apparent that the above conclusions are by no means restricted to the LN distributions; they are valid for any distribution of the "diverging" type. The common denominator to all such distributions is the appearance of the second maximum in υ_i of eq 25, resulting then in relations of the type of eq 28–30. Although the particular values of σ may be different for different distributions, in all cases the parameters of interest will show the same development upon decrease in σ, as given in Table I. Hence, the CPC eq 32a and 33 as well as the shadow curve eq 18a are generally valid for any "diverging" distribution. The differences will appear only in the supercritical region (or, more accurately, for $K\sigma < 0$). In a way, polymers with "diverging" distributions thus represent the simplest rather than the most difficult case since at least a part of their CPC's is given by a simple closed formula requiring no iteration procedures.

Another interesting problem is the position of the precipitation threshold for a polymer with a "quasi-diverging" type of distribution. Since the maximum of the CPC is in the region of very low φ as well as γ of eq 13b, the threshold equation, eq 10 of ref 5, can be expanded into

$$\sigma(1-\varphi)/\gamma = \varphi + \gamma M(\gamma) + \varphi \sum_{n=1}^{\infty} \gamma^n/(n+1) \qquad (39)$$

On the other hand, the CPC eq 14a can be written as

$$\sigma/\gamma \approx \gamma M(\gamma)[1 + 2i^{*-1}] \qquad (40)$$

since in this region $\Lambda \approx 1 - 2i^{*-1}$. In the first-order approximation, the two equations are simultaneously satisfied if

$$\varphi \approx \gamma/(3i^*) \qquad (41)$$

Equation 41 then yields the condition for the threshold

$$(\nu_0 - 1)_{\text{th}} \approx \Delta_{0,\text{th}} \approx 3i^* \qquad (42)$$

and, together with eq 40, the relation for φ_{th}

$$\varphi_{\text{th}} \approx (2\sigma_{\text{th}}/3)^{1/2}(i^*)^{-1}(1 - (\text{i}^*)^{-1}) \qquad (43)$$

Similarly, the first-order approximation for χ_{th} is obtained by expanding eq 15 and using eq 42 and 43

$$2\chi_{\text{th}} \approx 1 + \sigma_{\text{th}}^{1/2}(6^{-1/2} + 3^{1/2}/2^{1/2}) \approx 1 + 1.633\sigma_{\text{th}}^{1/2} \qquad (44)$$

Specifically, for a polymer with quasi-LN distribution the subscript of the maximum term υ_{i*} is $i^* \approx \sigma x_{\max}$, and the contribution Δ_0 of the second maximum is given by eq 27; hence, σ_{th} can be determined from (42) as the root of equation

$$(\sigma x_{\max})^{-2} \exp(\sigma x_{\max}) = 3\pi^{1/2}\beta \exp(y_{\max}^2 - 3/2) \qquad (45)$$

and the threshold coordinates then calculated from eq 43 and 44. Not surprisingly, in this case, i.e., for finite $x_{\max}$ and $y_{\max}$, the precipitation threshold depends on the distribution parameters x_0 and β. This dependence, however, fades out with $x_{\max}$ growing to infinity as the threshold moves to $\sigma_{\text{th}} = 0$, $\varphi_{\text{th}} = 0$, $\chi_{\text{th}} = 1/2$.

In the next section the above results will be supported by data on numerically computed CPC's for a series of hypothetical polymers with quasi-LN distribution with gradually increasing upper limit $x_{\max}$.

Numerical Solution. In our preceding paper[1] the CPC equation was approached in a traditional way; for the given polymer distribution $w(x)$ and a chosen polymer concentration φ, we examined the dependence of $F(\varphi,\sigma)$ on σ, i.e., $F_\varphi(\sigma)$. This function, however, sometimes exhibits quite a complex behavior; it can show three nontrivial extremes and possess three nontrivial (i.e., other than zero) roots σ. This is illustrated in Figure 1 where the vertical dashed line of constant polymer concentration φ^+ displays three points of intersection with the CPC (only one of which is thermodynamically stable). Such a situation brings little comfort to the computer programmer who has to ensure that all roots of the function $F_\varphi(\sigma)$ be found under all conditions (not knowing how many of them to expect for any particular case). It turns out to be more convenient to utilize the fact that along the CPC in the direction indicated by arrows in Figure 1, the product $K\sigma$ always monotonically increases. This means that for a chosen value of parameter $K\sigma$, there is only one value of the polymer concentration φ satisfying the CPC equation. Hence, the φ dependence of $F(\varphi,\sigma)$ at fixed σ, i.e., $F_\sigma(\varphi)$, has only one single root which is easy to numerically determine. Another time-saving factor is that in this case, the numerical integrations needed for ν_0 and ν_{-1}, eq 9, have to be carried out just once for each point of the CPC. This modification simplifies and speeds up considerably the numerical calculation of CPC's.

Since we wish to study the quasi-LN distributions for upper limits $x_{\max}$ exceeding the weight average x_w by several orders of magnitude, it is convenient to transform the distribution function (eq 3) into a Gaussian function of y by substitution

$$x = x_0 \exp(\beta y) \qquad (46)$$

The statistical moments of this distribution are then calculated by numerical integration as

$$\mu_{k,\text{Q}} = \pi^{-1/2} x_0^k \int_{y_{\min}}^{y_{\max}} \exp(-y^2 + k\beta y)\,\mathrm{d}y \qquad (47\text{a})$$

Similarly, the statistical moments characterizing the polymer in the incipient phase can be computed for a chosen value of $K\sigma$ as

$$\nu_{k,\text{Q}} = \pi^{-1/2} x_0^k \int_{y_{\min}}^{y_{\max}} \exp(-y^2 + k\beta y + K\sigma x)\,\mathrm{d}y \qquad (47\text{b})$$

or from the precalculated moments $\mu_{k,\text{Q}}$ in the form of series 11. The polymer concentration φ corresponding to the chosen value of σ is then found from the CPC eq 8 or its expanded form eq 14 as its single root.

As mentioned earlier,[1] for small values of σ the original form of (8) becomes practically useless since it contains small differences of large terms and is thus sensitive to the round-off errors in the computer. This is particularly true of polymers with quasi-diverging distribution where this failure occurs in a broad interval of polymer concentra-

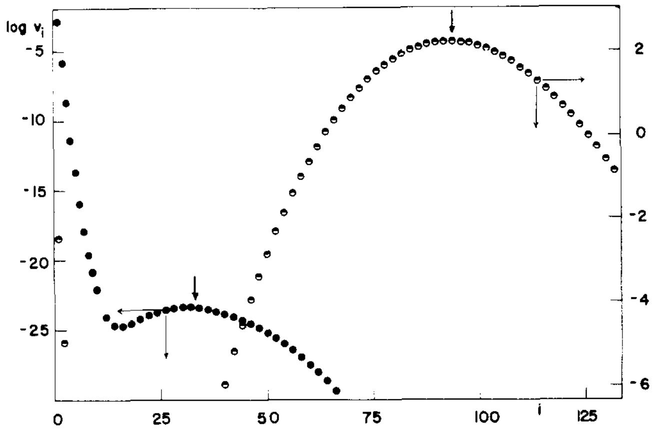

Figure 4. Semilogarithmic plot of series terms v_i (eq 25) against the subscript i for a polymer with quasi-LN distribution ($x_n = 120$, $x_w = 240$, $x_{max} = 7 \times 10^6$) for two values of $K\sigma$: (●) $K\sigma = 4.81 \times 10^{-6}$, (⊖) $K\sigma = 1.35 \times 10^{-5}$. Bold arrows indicate the positions of maxima estimated from $i^* \approx \sigma x_{max}$.

tions. Consequently, in the region of small σ we used exclusively the expanded forms (11) and (14). For actual computation the terms occurring in these series still have to be modified; otherwise, with increasing subscript i, the terms μ_i would soon overflow whereas the powers σ^i would cause underflow (although their product might be a significant number). This difficulty can be easily overcome by working with reduced quantities μ_i' and σ' defined as

$$\mu_i' = \frac{1}{i!} \int w(x) \left(\frac{x}{C}\right)^i \mathrm{d}x = \mu_i/i!C^i \qquad (48)$$
$$\sigma' = \sigma C$$

where C is a suitable constant;[1] then, e.g., $\mu_i \sigma^i/i! = \mu_i'(\sigma')^i$, etc. As the first approximation we used the constant $C = (x_0 x_{max})^{1/2}\beta/y_{max}$. If the moments μ_i' obtained in this way were inappropriately high or low (i.e., close to the maximum or minimum real positive number which could be represented in the computer), the constant C was slightly modified until the moments were satisfactory. For instance, in a specific case of $x_n = 120$, $x_w = 240$, and $x_{max} = 7 \times 10^6$, we were ready to use up to 350 terms in the above series. If left unreduced, the moment μ_{350} would reach an unmanageable order of magnitude of $\sim 10^{2356}$. On the other hand, all of the moments μ_i' reduced with $C \approx 5.2 \times 10^4$ remain in the relatively narrow range from 10^{-33} up to 10^{19}.

For higher values of σ, the series forms are no longer convenient. This is in particular true if $K\sigma$ is negative; the series then contains many large terms with alternating signs which contribute to large round-off errors. In this range, the closed forms (8) and (9) were used. The intermediate range of σ was covered by both methods with results identical within the accuracy of the computer.

First we would like to numerically document the validity of the simplifying eq 28 underlying the whole treatment. Figure 4 shows the dependence of $v_i \equiv \sigma^i \mu_i/i!$ on the subscript i for a polymer with $x_n = 120$, $x_w = 240$, and $x_{max} = 7 \times 10^6$ for two values of σ. Both dependences exhibit a steep decrease in the region of low i (which justifies our replacing the sum of beginning terms of the series by its single first term v_1) and a broad maximum at higher i values. The approximate positions of maxima calculated from $i^* \approx \sigma x_{max}$, [cf. eq A6] and indicated by arrows in Figure 4, fit very well the true dependences, and on the semilogarithmic scale both maxima are indeed of parabolic shape, with their contribution given approximately by an integral of a Gaussian function, eq A8. It is also apparent that for $\sigma = 4.81 \times 10^{-6}$ corresponding to the case (v) above, the first term dominates the sum. On the other hand, for $\sigma = 1.35 \times 10^{-5}$ [which represents a point on the almost vertical "zero concentration" portion of CPC, case (i)], the first term can be neglected relative to the contribution Δ_0 of the maximum.

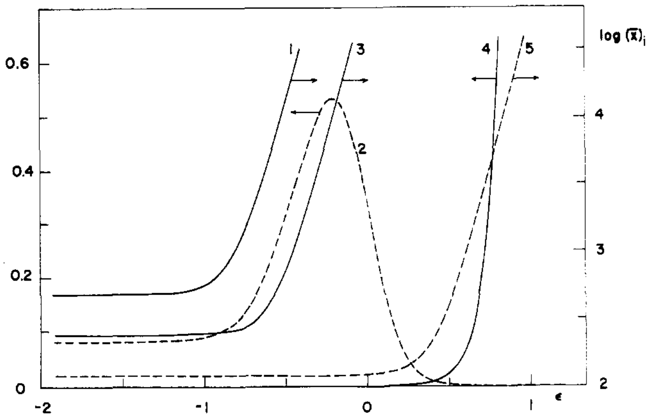

Figure 5. Plots of several parameters characterizing the equilibrium at the cloud point, against ϵ of eq 31 for the polymer of Figure 4: (1) $6\Lambda/\sigma$; (2) polymer concentration φ; (3 and 5), weight- and number-average chain lengths of the polymer in the incipient phase; (4) $(\nu_0 - 1) \times 10^{-2}$. Logarithmic ordinate scale for curves 1, 3, and 5 is on the right side, linear scale for curves 2 and 4 is on the left side.

Figure 5 contains plots of several variables as functions of ϵ of eq 31 for the same polymer. The critical point would be located at $\epsilon = -y_{max}/\beta \approx -7.67$; the region of $\epsilon < -2$, however, has been omitted from Figure 5 since all the dependences on the given scale yield practically horizontal lines, with ordinates close to the critical values $(6\Lambda/\sigma)_c = x_z = 480$, $\varphi_c = 0.0836$, $(\nu_0 - 1)_c = 0$, and the number- and weight-average chain lengths of the polymer in the incipient phase, $(x_n)_i$ and $(x_w)i$, are close to the original values of 120 and 240, respectively. The very shallow minimum on the φ function at $\epsilon \approx -2$ (corresponding to the left singular point of the CPC) is hardly recognizable. The first change to occur is a sharp increase in Λ/σ and φ, soon followed by an increase in $(x_w)_i$; this region corresponds to the metastable part of the CPC. At $\epsilon \approx -0.22$ the polymer concentration reaches a maximum (corresponding to the right singular point) and starts sharply dropping. Note that up to this point, the shadow curve is indistinguishable from the CPC ($\nu_0 - 1 \approx 0$), and $(x_n)_i$ of the precipitated polymer remains at 120 [although the weight average $(x_w)_i$ has increased to the order of 10^4]. It is only in the region of high σ and low concentrations that $\nu_0 - 1$ and $(x_n)_i$ start to deviate significantly from the original values. This development is in accord with predictions of Table I, with the exception of ϵ values at which the changes occur. This disagreement, however, is due to the finite upper limit x_{max}; it has been observed that with increasing x_{max} the whole set of curves shifts to the lower values of ϵ as predicted.

The CPC's and shadow curves of the same polymer ($x_n = 120$, $x_w = 240$) for four values of x_{max} are shown in Figures 6 and 7. If $x_{max} = 10^3$ (curve 1), both of these functions are smooth with no indication of a triple point and singular points; this is not surprising since the neglect of all species with $x > 10^3$ causes a serious misrepresentation of the LN distribution. The weight fraction of the neglected portion is high (1.61%), and, e.g., x_{z+1} of this quasi-LN distribution is only 507 instead of the ideal 960. Also, the critical concentration (0.0794) is distinctly different from the ideal one (0.0836). When x_{max} is increased to 10^4 (curve 2), the weight fraction of the neglected species becomes negligible ($<10^{-6}$) and the first average notably deviating from the

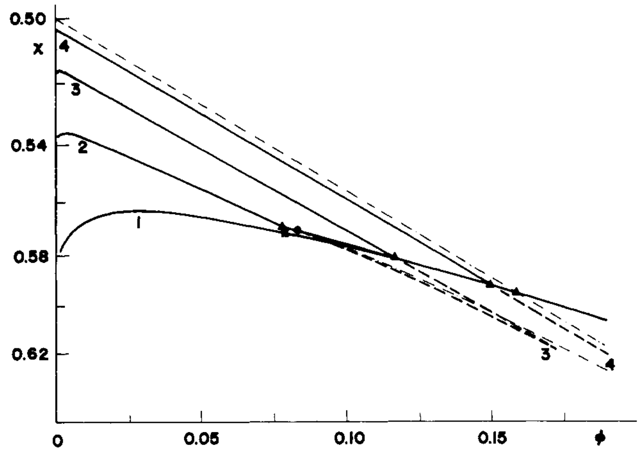

Figure 6. Cloud-point curves of four polymers with quasi-LN distributions ($x_n = 120$, $x_w = 240$) and various upper limits x_{max}: (1) $x_{max} = 10^3$, (2) $x_{max} = 10^4$, (3) $x_{max} = 10^5$, (4) $x_{max} = 7 \times 10^6$; (—) stable parts, (- - -) metastable parts, (- · -) analytical limit for $x_{max} \to \infty$. (■) Critical point for $x_{max} = 10^3$, (●) critical point for all other samples, (△) triple points.

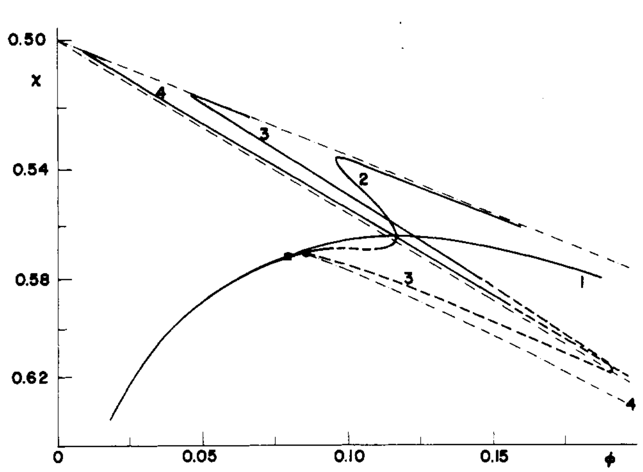

Figure 7. Shadow curves for polymers of Figure 6. All symbols identical with those of Figure 6.

Table II

Comparison of Numerical and Approximate Values of σ, φ, and χ at the Precipitation Threshold for Polymers with Quasi-LN Distribution ($x_n = 120$, $x_w = 240$) and Different Values of the Upper Limit x_{max}

x_{max}	$\sigma^a \times 10^4$	$\sigma^b \times 10^4$	$\varphi^a \times 10^4$	$\varphi^b \times 10^4$	χ^a	χ^b
10^4	18.1	18.6	18	~25	0.5348	0.5363
10^5	3.69	3.78	4.1	~4.5	0.5157	0.5161
10^6	0.630	0.640	1	~1	0.5065	0.5066
7×10^6	0.130	0.131	0.3	~0.3	0.5029	0.5030

[a] First-order approximation calculated from eq 43–45.
[b] Values obtained by numerical solution of CPC equation.

ideal value is x_z (479.7 instead of 480). The CPC shows a distinct triple point, the stable critical point lies on its supercritical branch, and the shadow curve exhibits already the characteristic backswing; the detailed structure of the metastable region, however, could easily escape ones attention if not looked for very carefully. The critical point as well as the portion with $K\sigma < 0$ of the supercritical branch of CPC have reached already their limiting forms within accuracy of displayed Figures 6 and 7; i.e., they also represent the subsequent polymers with higher x_{max}. For the polymer with $x_{max} = 10^5$ (curve 3), the typical triangle of the metastable region of CPC is already well developed. The critical point is here metastable and practically coincides with the left singular point, while the right singular point is located at $\varphi \approx 0.173$. Correspondingly, also the shadow curve exhibits a large metastable region (dashed line). The last of the investigated series of polymers has $x_{max} = 7 \times 10^6$ (curve 4). Its precipitation threshold is at $\chi \approx 0.5030$ and $\varphi \approx 3 \times 10^{-5}$, and the right singular point is at amazingly high concentration $\varphi \approx 0.53$ (outside the scope of Figures 6 and 7). The metastable branch of the CPC is so close to the predicted limit for $x_{max} \to \infty$ that it could not be plotted as a separate curve.

These four investigated samples clearly document an extreme sensitivity of the subcritical branch of CPC for polymers with quasi-LN distribution of molecular weight, to the upper limit x_{max} considered in the computation. It is also evident that their CPC's and shadow curves asymptotically approach the limiting forms derived analytically and indicated in Figures 6 and 7 by dash-dot lines. The critical point is rather insensitive to x_{max} since it is fixed by low-order averages x_w and x_z which attain their limiting values very soon. However, the triple point and the threshold, both of them belonging to the subcritical branch of CPC, are greatly dependent on the upper limit x_{max} (cf. Figure 6).

The numerical results also confirm the predicted relation between the critical point and the left singular point. For the sample with $x_n = 120$, $x_w = 240$ ($S \approx 524 > 0$), the concentration difference $\Delta\varphi$ between these two points steadily decreases with growing x_{max} from $\Delta\varphi \approx 6 \times 10^{-3}$ for $x_{max} = 10^4$ to $\Delta\varphi \approx 9 \times 10^{-5}$ for $x_{max} = 7 \times 10^6$. On the other hand, for the sample with a negative parameter S ($x_n = 120$, $x_w = 600$, $S = -5890$) the difference is practically constant, $\Delta\varphi \approx 2.4 \times 10^{-3}$, in the interval of x_{max} from 10^6 to 10^8.

Finally, Table II indicates that the first-order approximation formulas for σ, φ, and χ at the threshold, eq 43–45, agree well with numerical results if x_{max} is high enough ($\geq 10^6$ for the polymer quoted in Table II).

Conclusions

Both the analytical and the numerical study presented in this paper confirm our earlier conclusions about the CPC of polymers with "diverging" distribution of molecular weight, in particular that (i) the subcritical branch of CPC is given by the simple formula in (32a) which is independent of any other parameters of the distribution than just its "divergence"; (ii) the shadow curve in this region is superimposed onto the CPC; (iii) the critical point of such polymers is never thermodynamically stable; (iv) the CPC always shows a triple point (i.e., a "depression"). Although this result might seem to be rather academic (since there are no real polymers with a true "diverging" distribution) there are some implications to it which may be of practical interest.

(1) Our results show that the low-concentration region of CPC's is extremely sensitive to the presence of minute amounts of polymer species with molecular weight substantially higher than the common averages M_w and M_z. Consequently, in CPC's with a profound "depression", the region left of the dip is little dependent of low-order averages M_w, M_z, etc. (in fact, for $x_{max} \to \infty$ it becomes totally independent of them), and is rather indicative of highest fractions present in the sample. This conclusion is supported by experimental data of Klein, Patat, and Wittenberger[12,13] indicating that the cloud point in very dilute solutions of mixtures of two polymers greatly differing in molecular weight is practically independent of the amount and the average molecular weight of the lower fraction.

(2) There are many experimental data on CPC's showing a "depression" on its right-hand branch (listed, e.g., in ref

3). It is perhaps not surprising that they have been fitted without exception (to our knowledge) by smooth curves since the common sense seems to reject the presence of any sharp discontinuities in a phase diagram of a quasi-binary system. It has been shown both experimentally[11] and theoretically,[1] however, that such systems may exhibit a three-phase region (due only to great differences in chain lengths of the polymer molecules) which may extend up to the CPC at the triple point. Therefore, there is no reason to force the interpolated line into a smooth function; the data should be rather fitted respectfully by two curves intersecting each other at the triple point.

(3) Because of divergence problems, the LN distribution has often been dismissed as unsuitable for representing the polymer sample in CPC experiments. As shown above, however, the divergence disappears if the equations are treated properly. Furthermore, the quasi-LN (or, more generally, "quasi-diverging") distributions seem to be the only monomodal continuous analytical distributions which are capable of generating CPC's with triple points and thus describing the experimental CPC's with "depression". For this reason their recognition may be enhanced in the future.

(4) Finally, we wish to emphasize that any attempt to generate the experimental curve by model calculations has to be done with utmost care. For instance, the indirect extrapolation method of calculating the CPC failed to recognize both the metastable region and the significant $x_{\max}$ dependence of CPC's for polymers with quasi-LN distribution of molecular weight; hence, it does not seem reliable enough for such purposes. It is also apparent that the computer-generated CPC's of polymers with a "quasi-diverging" distribution have to be specified as to the upper limit $x_{\max}$ employed in the computation.

Appendix

For high values of i, the factorial in eq 25 can be approximated by Stirling formula, yielding

$$\upsilon_i \approx \tfrac{1}{2}(2\pi i)^{-1/2}(\sigma x_0 e/i)^i \exp(\beta^2 i^2/4)(1 + \operatorname{erf} z) \quad \text{(A1)}$$

where $z \equiv y_{\max} - \tfrac{1}{2}\beta i$.

First, we ought to find the subscript i^* of the maximum term υ_{i^*}. The condition for extremum, $(\mathrm{d}\upsilon_i/\mathrm{d}i)_{i=i^*} = 0$, leads to the relation

$$\ln (x_0\sigma/i^*) + \tfrac{1}{2}\beta^2 i^* - 1/(2i^*) - \beta\pi^{-1/2}\Psi(z^*) = 0 \quad \text{(A2)}$$

where

$$\Psi(z^*) \equiv \exp(-z^{*2})/(1 + \operatorname{erf} z^*) \quad \text{(A3)}$$

while the condition for maximum ($\mathrm{d}^2\upsilon_i/\mathrm{d}i^2 < 0$) requires that

$$\tfrac{1}{2}\pi - \Psi^2(z^*) - \pi^{1/2}z^*\Psi(z^*) - (\pi/\beta^2 i^*) < 0 \quad \text{(A4)}$$

Closer inspection of (A4) shows that for large i^*, this condition can be met only if z^* is negative and its absolute value $|z^*|$ large. In this region, however, $\Psi(z)$ can be approximated as[9]

$$\Psi(z) \approx \frac{\pi^{1/2}|z|}{1 - \tfrac{1}{2}z^{-2} + \tfrac{3}{4}z^{-4} - \ldots} \quad \text{(A5)}$$

which, substituted into eq A2, gives a simple relation between the subscript i^* of the maximum term υ_{i^*}, and chosen values of σ and $x_{\max}$

$$\sigma x_{\max} = i^* \exp[(1/2i^*) - (\beta/2z^*)] \quad \text{(A6)}$$

Now we are in a position to examine the region around the maximum and to evaluate its contribution Δ_0 to the sum $\Sigma\upsilon_i$. By substituting σ from (A6) into (A1), using again the approximate $\Psi(z)$ of (A5), replacing the subscript i by a continuous variable, $i = i^* + i^{*\,1/2}\tau$, and finally using the series representation $1 + x = \exp(x - \tfrac{1}{2}x^2 + \ldots)$ which is valid for $|x| < 1$, it can be shown that in the neighborhood of i^*, the terms υ_i approximately follow a Gaussian function

$$\upsilon_i \approx (\pi 2^{1/2} i^{*\,3/2}\beta)^{-1} \exp(i^* - y_{\max}{}^2 + \tfrac{3}{2}) \exp(-\tau^2/2) \quad \text{(A7)}$$

It should be noted that this simple result holds only if $i^* = O(y_{\max}{}^2)$; however, this is indeed the interval of our interest as follows from eq A6 and 31. The contribution Δ_0 of the maximum region to the sum $\Sigma\upsilon_i$ is then obtained by integrating υ_i of eq A7

$$\Delta_0 \approx (\pi^{1/2}\beta i^*)^{-1} \exp(i^* - y_{\max}{}^2 + \tfrac{3}{2}) \approx (\pi^{1/2}\beta\sigma x_{\max})^{-1} \exp(\sigma x_{\max} - y_{\max}{}^2 + \tfrac{3}{2}) \quad \text{(A8)}$$

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