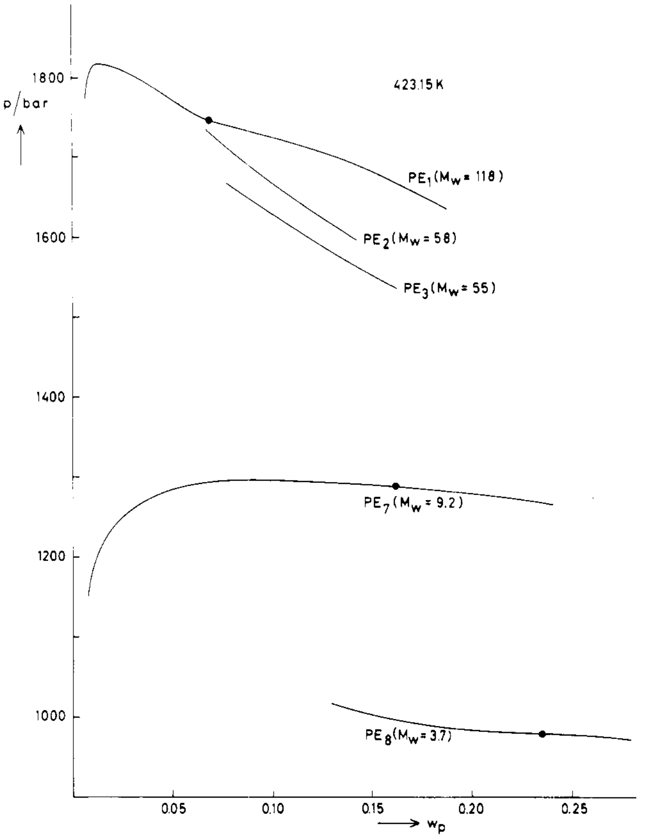

Figure 15. Cloud point curves of a number of $[w_p^{PE} + (1 - w_p)^{PE}]$ systems at $T = 423.15$ K showing the effect of the molecular weight of polyethylene (see Table I). (●) Critical point.

for putting the polyethylene samples at our disposal and to Dr. R. N. Lichtenthaler for constructive comments on the manuscript.

Registry No. Polyethylene, 9002-88-4; ethylene, 74-85-1.

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Fluid Phase Equilibria in the System Polyethylene + Ethylene. 2. Calculation of Cloud Point Curves for Systems of Linear Polyethylene + Ethylene

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ABSTRACT: The Flory–Huggins polymer solution theory as extended by Koningsveld and Kleintjens is used to calculate cloud point curves in systems of linear polyethylene + ethylene. To describe the effect of pressure we introduce an empirical pressure dependence in the interaction parameter. The adjustable parameters in this model are calculated from experimental critical loci, presented in the preceding paper. Attention is given to the effect of molecular weight distribution and to the algorithm for calculating the results. Calculated cloud point curves agree well with experimental cloud point curves, which were presented in the preceding paper for a number of linear polyethylene + ethylene systems.

Introduction

In a preceding paper[1] we reported experimentally determined cloud point curves and critical curves of a number of systems of linear polyethylene + ethylene. In this paper we show how the Flory–Huggins polymer solution theory[2,3] as extended by Koningsveld and Kleintjens[4] can be used to represent the cloud point curves of these systems. In these calculations the polydispersity of the polymer has to be taken into account. The adjustable parameters in the theory were obtained by fitting the experimentally determined critical curves. Due to the assumptions (e.g., rigid lattice model) made in deriving the Flory–Huggins theory, this theory and also its extension

0024-9297/83/2216-0117$01.50/0

by Koningsveld and Kleintjens cannot be used to describe the effect of pressure on solution properties. To circumvent this shortcoming we introduce an empirical pressure dependence in the interaction parameter.

The multicomponent version of the Flory equation-of-state theory[5] was used by Bonner et al.[6,7] and by Bogdanovič et al.[8-10] to calculate fluid phase behavior in model systems of polyethylene + ethylene. Comparison of their calculated results with real systems was not possible because the molecular weight distributions of the polyethylenes used in the experimental work were not known. We tried to apply this theory to the systems investigated by us but the results obtained are not very promising. Details will be given in a following paper.

Recently, Liu and Prausnitz[11] applied the perturbed hard chain theory to phase equilibrium calculations in the system polyethylene + ethylene, while Kleintjens[12] used a lattice–gas theory, but in both cases comparison with experiment is very limited.

Theory

The Flory–Huggins expression for the free enthalpy of mixing per mole of lattice sites, $\Delta\bar{G}$, is given by[13]

$$\Delta\bar{G}/RT = \phi_0 \ln \phi_0 + \textstyle\sum \phi_i r_i^{-1} \ln \phi_i + g\phi\phi_0 \qquad (1)$$

where ϕ is the overall polymer volume fraction, ϕ_i is the volume fraction of polymer species i ($\sum\phi_i = \phi$), ϕ_0 is the volume fraction of solvent, and r_i (a measure for the chain length) is the number of lattice sites occupied by a macromolecule i. The pair interaction parameter g was found to depend on the composition and the temperature of the mixture.

The more refined lattice theory developed by Koningsveld and Kleintjens[4] gives the following expression for g as a function of the overall polymer volume fraction:

$$g = \alpha + (z - 2 + 2/r_n)(\Delta u_{op}/RT)/(1 - \gamma\phi) \qquad (2a)$$

where

$$\gamma = 2(1 - 1/r_n)/z \qquad (2b)$$

The quantity Δu_{op} stands for the difference between the interaction-free enthalpy of unlike neighbors and the arithmetic mean of the values for identical neighbors, z is the coordination number of the lattice, r_n is the number-average chain length, and α is an empirical parameter, which leads to an entropy correction term. Neglecting terms in $1/r_n$ and abandoning the physical significance of the different parameters, we can write

$$g = \alpha + \beta/(1 - \gamma\phi) \qquad (3)$$

Following Koningsveld and Kleintjens, we assume that the temperature dependence of g is confined to the interaction parameter β.

Although the Flory–Huggins theory is based on a rigid lattice model and as a consequence is unable to describe volume-of-mixing effects, pressure effects can be incorporated formally by making g pressure dependent. We assume that the pressure dependence is restricted to the parameter β. Such a pressure-dependent β was proposed by Koningsveld et al.[14] in order to fit Swelheims phase equilibrium data of the system polyethylene + ethylene.[15]

From eq 1 and 3, expressions for the chemical potential can be derived. We find for the solvent

$$\mu_0/RT = \mu_0^*/RT + \ln \phi_0 + (1 - 1/r_n)\phi + [\alpha + \beta(1 - \gamma)/(1 - \gamma\phi)^2]\phi^2 \qquad (4)$$

and for polymer species i

$$\mu_i/RT = \mu_i^*/RT + \ln \phi_i + 1 - r_i(\phi/r_n + \phi_0) + [\alpha + \beta/(1 - \gamma\phi)^2]r_i\phi_0^2 \qquad (5)$$

μ_0^* and μ_i^* are the chemical potentials of the pure solvent and pure polymer species i, respectively.

Koningsveld and Kleintjens derived the expressions

$$1/(\phi r_w) + 1/(1 - \phi) = 2[\alpha + \beta(1 - \gamma)/(1 - \gamma\phi)^3] = 2X \qquad (6)$$

for the spinodal and

$$-r_z/(r_w^2\phi_c^2) + 1/(1 - \phi_c)^2 = 6\beta\gamma(1 - \gamma)/(1 - \gamma\phi_c)^4 = 6Y \qquad (7)$$

for the critical state. For a critical point both equations must hold. The left-hand side of these equations contains only the critical concentration ϕ_c and the z- and weight-average chain length r_z and r_w, quantities that can be determined experimentally. Combination of eq 6 and 7 gives

$$X + \phi_c Y = \alpha + Y/\gamma \qquad (8)$$

This equation can be used to calculate α and γ from a set of experimentally determined critical points. β as a function of pressure and temperature follows from eq 6.

Calculation of the Parameters

Equation 8 suggests that a plot of $X + \phi_c Y$ vs. Y should yield a straight line with a slope γ^{-1} and an intercept α at the $X + \phi_c Y$ axis. The experimentally determined critical points of systems of linear polyethylene + ethylene reported in the preceding paper thus can be used to calculate X and Y. The results are given in Figure 1. A straight line is found indeed. The r_w and r_z values used in the calculations were obtained from experimental M_w and M_z values found from light scattering measurements and from ultracentrifuge measurements, respectively. Since these data were not available for all the polyethylene samples investigated, we also used M_w and M_z values found from gel permeation chromatography. As the concentration variable we used the weight fraction, which is in the case of the system polyethylene + ethylene identical with the segment mole fraction. From linear regression we find $\alpha = 0.1715$ and $\gamma = 0.4623$. The correlation coefficient is 0.996.

If we use the volume fraction instead, we find $\alpha = 0.1840$, $\gamma = 0.4236$, and a correlation coefficient of 0.975. The volume fraction ϕ is now calculated from

$$\phi = v_p^0 w/[v_0^0(1 - w) + v_p^0 w] \qquad (9)$$

where w is the weight fraction of the polymer. We used for the ratio between the so-called specific hard-core volume of a polymer segment (v_p^0) and a solvent molecule (v_0^0), $v_p^0/v_0^0 = 0.7930$. v_0^0 and v_p^0 are obtained by applying the Flory equation of state to p–V–T data of pure ethylene and pure polyethylene.[16] Comparison of the correlation coefficients obtained for the two different concentration variables shows that the weight fraction gives a better straight-line fit. Similar results were found by Koningsveld and Kleintjens[4] for the system polystyrene + cyclohexane. For this reason we use the weight fraction in the following exclusively.

Since for each polyethylene + ethylene system investigated by us the critical concentration is found to be nearly constant within the temperature range considered, eq 7 indicates that β is constant along the critical curve of each polyethylene + ethylene system considered. The pressure dependence of β at a given temperature can be determined as a function of the critical pressure by plotting

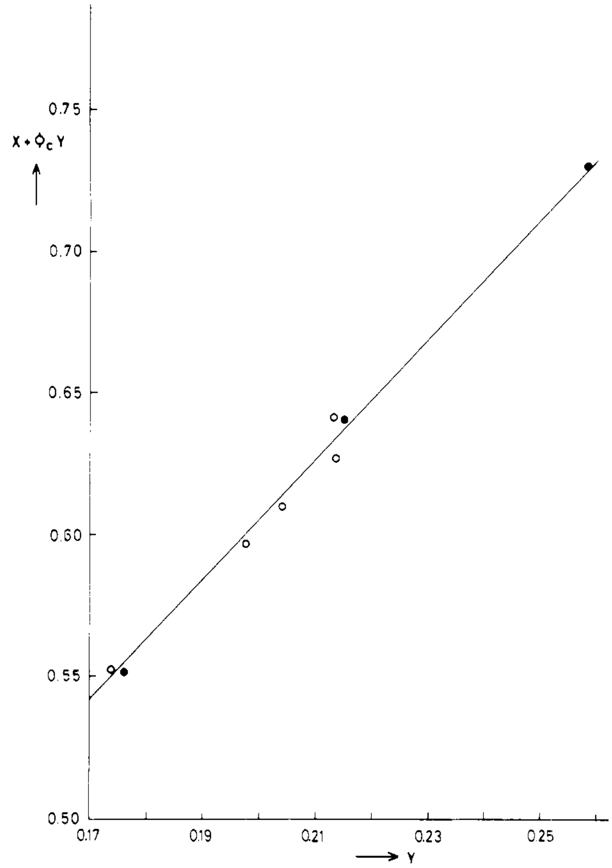

Figure 1. Systems of linear polyethylene + ethylene. Determination of the parameters α and γ from experimental critical points according to eq 8: (●) from absolute average molecular weights; (○) from average molecular weights found from gel permeation chromatography.

the different β values vs. the corresponding critical pressures at that temperature found from the critical curves of the different polyethylene + ethylene systems. This is shown in Figure 2 for three different temperatures. We found that the pressure and temperature dependence of β can be described with reasonable accuracy by the equation

$$\beta = \beta_{00} + \beta_{01}/T + (\beta_{10} + \beta_{11}/T)p + (\beta_{20} + \beta_{21}/T)p^2 \tag{10}$$

as shown in Figure 2. The coefficients of this equation are $\beta_{00} = 0.82785$, $\beta_{01} = -41.110$ K, $\beta_{10} = -0.29252 \times 10^{-3}$ bar^{-1}, $\beta_{11} = 84.864 \times 10^{-3}$ bar^{-1} K, $\beta_{20} = 65.687 \times 10^{-9}$ bar^{-2}, and $\beta_{21} = -20.856 \times 10^{-6}$ bar^{-2} K.

Calculation of the Cloud Point Curves

For the calculation of the cloud point curves we use a modification of the method described by Šolc.[17] This method is based on the equality of the chemical potentials of all components in the two phases (indicated by single and double primes) and the mass balance for the distribution of polymer species i over the two phases. At a cloud point we have an infinitely small amount of the second phase (indicated by double prime) and then the mass balance leads to

$$\phi' = \phi \tag{11}$$

and

$$\phi_i' = \phi\phi_i^0 \tag{12}$$

where ϕ is again the overall polymer concentration in the

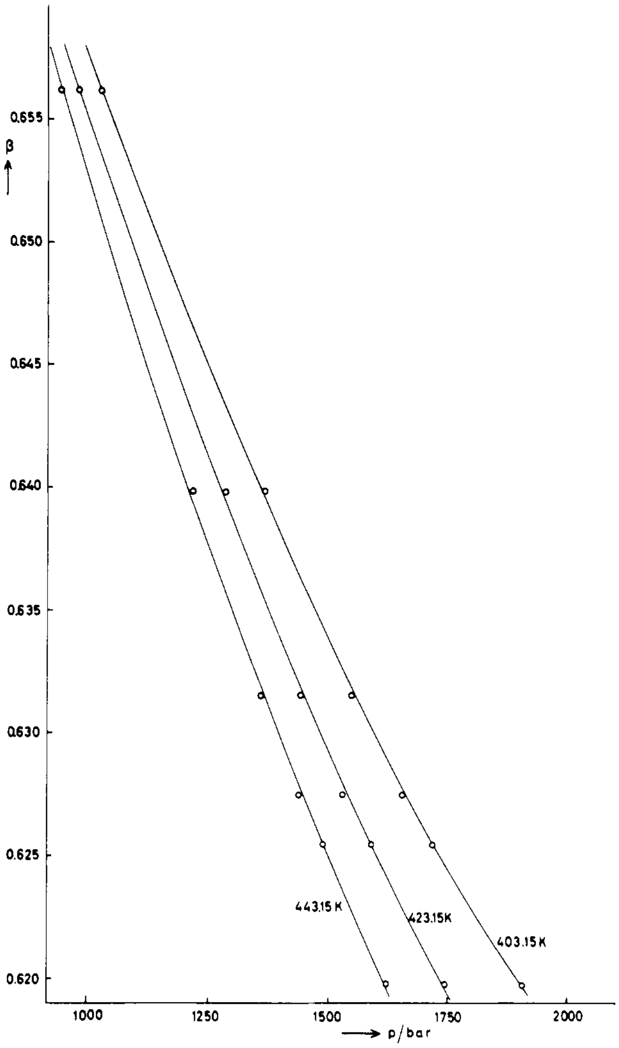

Figure 2. Systems of linear polyethylene + ethylene. Pressure dependence of the interaction parameter β at constant temperature: (○) from eq 6 and experimental critical pressures; (—) from eq 10.

mixture and ϕ_i^0 is the concentration of polymer species i in the pure polymer, which is given by the molecular weight distribution. Introduction of Flory's distribution coefficient parameter σ[13] defined by

$$\phi_i''/\phi_i' = \exp(\sigma r_i) \tag{13}$$

gives with eq 4, 5, 11, and 12

$$\phi_i'' = \phi\sum_{i=1}^{m}\phi_i^0 \exp(\sigma r_i) \tag{14}$$

$$\beta = \{\ln[(1-\phi)/(1-\phi'')] - (\phi''-\phi) + \phi\sum_{i=1}^{m}(\phi_i/r_i)[\exp(\sigma r_i - 1)] + \alpha(\phi^2 - \phi''^2)\}/[(1-\gamma)\phi''^2/(1-\gamma\phi'')^2 - (1-\gamma)\phi^2/(1-\gamma\phi)^2] \tag{15}$$

and

$$\sigma = \ln[(1-\phi'')/(1-\phi)] + 2\alpha(\phi''-\phi) + \beta[(1-2\phi+\gamma\phi^2)/(1-\gamma\phi)^2 - (1-2\phi''+\gamma\phi''^2)/(1-\gamma\phi'')^2] \tag{16}$$

The molecular weight distribution is introduced in the form of a set of m (~25) delta functions (w_i^0, M_i), which can be chosen by means of the gel permeation chromatograms available.[1]

The calculation of the cloud point for a given temper-

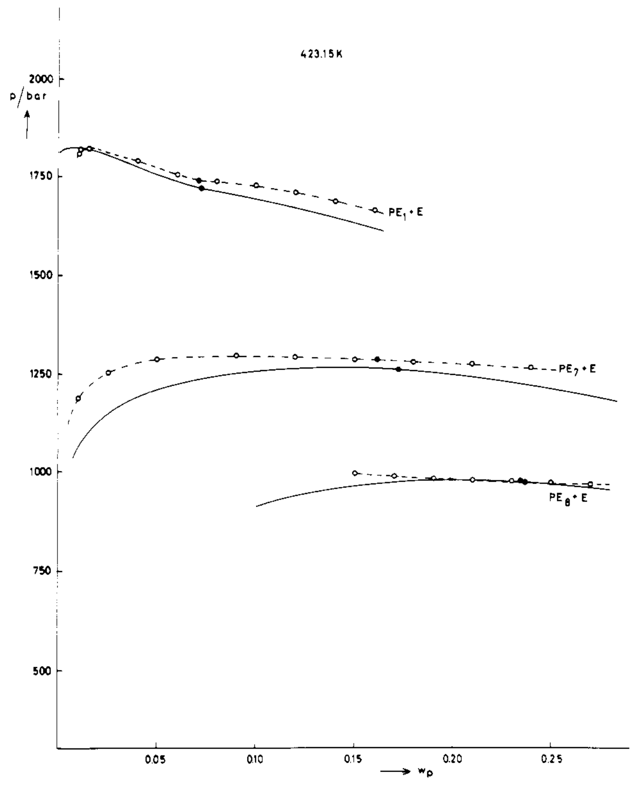

Figure 3. Cloud point curves for three systems of linear polyethylene + ethylene at 423.15 K: (○) measured; (—) calculated; (●) critical points. PE1: M_w = 118 000; PE7: M_w = 9200; PE8, M_w = 3700.

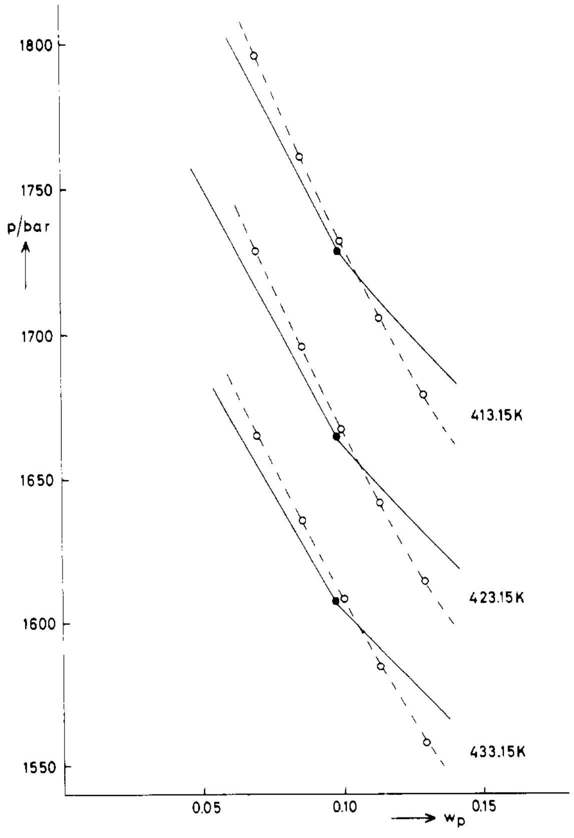

Figure 4. Cloud point curves of the system PE2 + ethylene at three constant temperatures: (○) measured; (—) calculated; (●) calculated critical points. M_w = 58 000.

ature and weight fraction polymer then is possible in the following way: (a) input: α, γ, w, T, and w_i^0 and M_i for $i = 1, 2, ..., m$; (b) $\phi = w$; $\phi_i^0 = w_i^0$; $r_i = M_i/28.05$; (c) calculate ϕ_c and β_c from eq 6 and 7; (d) choose a trial value for σ: σ_a ($\sigma_a > 0$ for $\phi < \phi_c$, $\sigma_a < 0$ for $\phi > \phi_c$); (e) calculate ϕ'' from eq 14; (f) calculate β from eq 15; (g) calculate σ from eq 16: σ_b; (h) with the aid of a suitable optimalization method, σ_a is changed and steps e–h are repeated until $|(\sigma_a - \sigma_b)/\sigma_b| < 10^{-8}$; (i) calculate the cloud point pressure from eq 10. This direct calculation method of the cloud point avoids the inaccuracies caused by the extrapolation of calculated phase equilibria to the phase boundaries, which is customary in other methods.[12,18] An extra advantage of our calculation method is the great reduction in computer time.

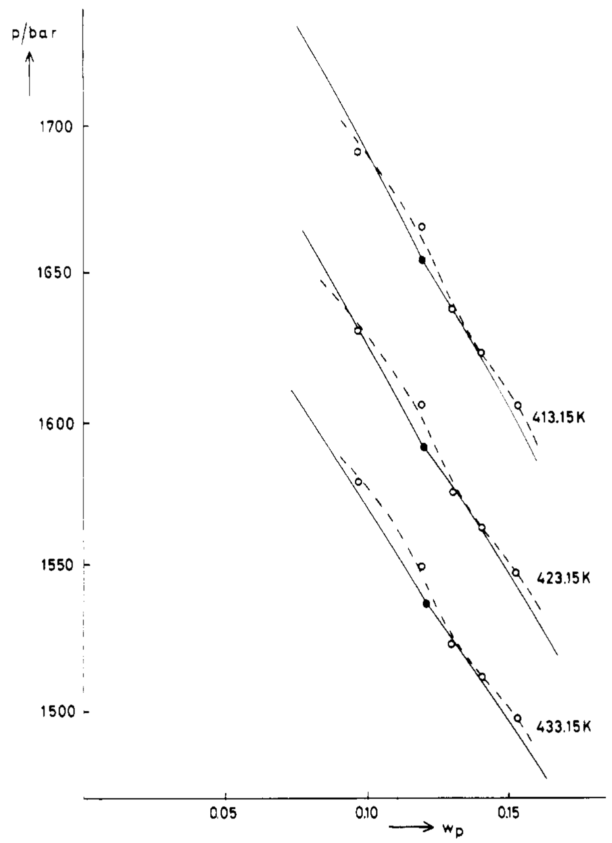

Figure 5. Cloud point curves of the system PE3 + ethylene at three constant temperatures: (○) measured; (—) calculated; (●) calculated critical points. M_w = 55 000.

Results

For a number of polyethylene + ethylene systems we calculated the cloud point pressures at constant temperature for different values of polymer concentration. The results are shown in Figures 3–5. In Figure 3 the calculated cloud point curves at 423.15 K for three systems are compared with those determined experimentally. The critical points of these three systems were used in the calculation of α, γ, and $\beta(p,T)$. From Figure 3 it can be seen that the experimental and calculated cloud point curves agree quite well. At 403.15 and 423.15 K we find similar results.

In Figures 4 and 5 the experimental and calculated cloud point curves for different temperatures are compared for two different polyethylene + ethylene systems from which no experimental data have been used in the evaluation of α, γ, and $\beta(p,T)$. Here again the agreement is good.

Conclusion

The Flory–Huggins theory of polymer solutions as ex-

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tended by Koningsveld and Kleintjens is suitable for calculating cloud point curves at high pressure if a pressure dependence is introduced in the interaction parameter. The particular pressure dependence for systems of linear polyethylene + ethylene has been evaluated and is given in an analytical form. Thus the calculation of the phase behavior of any system of linear polyethylene + ethylene is now possible if the molecular weight distribution of the linear polyethylene is known.

Experimental work on systems of branched polyethylene + ethylene indicates a strong effect of the degree of branching on the cloud point curves.[19] This effect cannot be described by the model in the present form. Proper modification of the model taking into account the degree of branching is in progress.

Acknowledgment. We are indebted to Dr. R. Koningsveld and Dr. L. A. Kleintjens (Central Laboratory, DSM) for stimulating discussions.

Registry No. Polyethylene, 9002-88-4; ethylene, 74-85-1.

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Equilibrium Polymer Size Distributions

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ABSTRACT: In this paper, we give general methods of determining the equilibrium distribution of polymer sizes. Our methods apply to any closed system, subject to the following conditions: (1) the structural units composing the polymers are identical, (2) the forward reaction rates of aggregation a_{ij} depend only on the sizes (and not the structures) of the reacting species, and (3) intramolecular reactions do not occur. In 1943, Stockmayer determined a particular equilibrium distribution of polymer sizes by maximizing statistical mechanical entropy. In our paper, we use another statistical mechanical quantity, our so-called polymer partition function Z. Using Z, we give general formulas for polymer size distributions and gelation conditions. These formulas admit numerical solution for any form of a_{ij}. On the other hand, when $a_{ij} = A + B(i + j) + Cij$, the polymer partition function Z is determined by an ordinary differential equation. By solving the differential equation and applying Lagrange's expansion to the resulting functional equation, we give explicit size distributions for Flory's f-functional random polycondensation (RA_f) model and for the ARB_{f-1} model, along with the size distributions in the limiting case as f tends to infinity. These distributions agree with classical results. We give explicit gelation conditions for the A_gRB_{f-g} model of polymerization. Donoghue and Gibbs gave asymptotic series (as the system size approaches infinity) for the distribution of polymer sizes in the RA_f model. In statistical mechanics, this is equivalent to applying Darwin and Fowler's method of mean distributions (steepest descents method) instead of the method of most probable distributions (Lagrange multipliers). Knowing this, we can state that our results will apply only if the system has not gelled. In addition, the discussion announces new results concerning the agreement between models of reversible and irreversible polymerization, while the Appendix gives some solutions for reversible polymerization in cases other than $a_{ij} = A + B(i + j) + Cij$.

I. Introduction

This paper concerns itself with the determination of equilibrium polymer size distributions, and its methods are quite general. Here is a list of sections in the paper, along with a resumé of each section:

Section II: The Different Models

We introduce some classical models for polymerization reactions. These models can be characterized by their forward reaction rates for aggregation (which we call the a_{ij}'s). In a crucial step, we relate these forward reaction rates to the number of polymeric isomers of size k (which we call w_k).

Section III: Polymer Partition Functions

In 1943, Stockmayer determined the equilibrium distribution of polymer sizes for one particular model of polymerization (Flory's RA_f model). He did this by maximizing the entropy of the size distribution, a quantity that involved the w_k's. Because his methods generalize, we summarize them. We then show that his results are simplified by the use of the exponential generating function of the w_k's, which we call the polymer partition function Z. Hence, *we reduce the calculation of polymer size distributions to the calculation of the polymer partition function Z.*

Section IV: Specific Polymer Partition Functions

In this section, we show how several classical models can be handled by our methods. When $a_{ij} = A + B(i + j) + Cij$, we can manipulate the relationship between the a_{ij}'s and w_k's (at the end of section II) into an ordinary dif-

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