

Effects of Polydispersity on Critical Concentration of Polymer Solutions

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Synopsis

A semiempirical equation is developed to compute the unperturbed parameter from the critical concentration of polymer solutions derived from the viscometric and kinetic data. This equation gives satisfactory results for various vinyl polymers including poly(vinyl chloride), polystyrene and poly(methyl methacrylate) among others that follow the Schulz molecular weight distribution function. It is found that the segments of a Gaussian polymer chain are associated with an equal number of foreign segments near its center of mass, when the polymer solution has attained a uniform segment density at the critical concentration. The effect of molecular weight distribution on the present studies is significantly large that it merits an empirical treatment. Defects of the model is also discussed.

INTRODUCTION

The zero shear viscosity η_0 of moderately concentrated polymer solutions, specifically with relative viscosity less than 10^6 , increases appreciably with increasing polymer concentration C .¹ This η_0 - C relationship may be divided into two distinct regions at the critical concentration C_0 , beyond which the η_0 is directly proportional to C^n , where the power law constant n is usually not less than 5. Various methods have been devised to assess the C_0 ,²⁻⁵ which in most cases is higher than 0.05 g/ml. In this concentration region, the excluded-volume effect vanishes and the macromolecules assume the unperturbed dimensions.⁶ This would provide a theoretical basis for the present analyses.

Efforts have been made by Onogi et al.² and Cornet³ to correlate the mean-square unperturbed end-to-end distance \bar{r}_0^2 with C_0 . The former authors consider the randomly coiled polymers as rigid spheres distributed in a close-pack array, while the latter worker recognizes the long-chain molecules as penetrable Gaussian coils with their centers of mass arranged in a regular lattice. Both theories make no allowance for the influence of polydispersity. This article reports an alternative semiempirical approach to the problem. The reality of the present ideas is best tested by the experimental data of vinyl polymers.

THEORY

We first consider that a polymer solution consists of a series of polymer species with molecular weights M_1, M_2, \dots, M_i , and their respective concentrations (in g/ml) are C_1, C_2, \dots, C_i , where the subscript i is associated with the i th species hereafter. It is well known that the segment density of an isolated vinyl polymer of molecular weight M_i in the unperturbed state, $\rho_i(r)$, is a Gaussian function of distance r from its center of mass⁷ irrespective of direction, given as

$$\rho_i(r) = \frac{2M_i}{M_0} \left(\frac{a_i}{\pi} \right)^{3/2} \exp(-a_i r^2) \quad (1)$$

where M_0 is the molecular weight of the monomer unit and the parameter $a_i = 9/r_{0i}^2$. The volume of a spherical shell element of thickness dr situated at a distance r from the above-mentioned center of mass is, of course, $4\pi r^2 dr$. It follows that the number of i -mers lying in this volume is equal to the product $4\pi r^2 dr \times n_i(r)$, where $n_i(r)$ is the corresponding number concentration (in molecules/ml) of i -mers. At sufficiently high concentrations, the polymer takes on the unperturbed dimensions, and the quantity $n_i(r)$ is so large that the fluctuating number concentrations in the volume element are insignificant. Moreover, chain entanglements may also diminish the translational diffusion of the polymer substantially herein.⁸ This would tend to localize the motion of the chains and reduce the concentration fluctuation. Hence, under this particular situation the parameter $n_i(r)$ may be represented by the macroscopic density $C_i N_0/M_i$, which is independent of the position r , where N_0 is Avogadro's number. Following Cornet's approach,³ the total segment density of the polymer species M_i near the center of mass of the foregoing molecule is then given by

$$D_i(0) = \int_0^\infty 4\pi r^2 \frac{C_i N_0}{M_i} \rho_i(r) dr \quad (2)$$

Integration of eq. (2) results in

$$D_i(0) = \frac{2N_0 C_i}{M_0} \quad (3)$$

Equation (3) shows that the above argument agrees with the uniform segment density assumption^{3,9} that would produce intuitively the same expression for the total segment density of the i th species in the bulk solution. It is interesting to note that the presence of other polymer species has no effect whatsoever on this derivation, as the excluded volume effect is ignored in eq. (1). Consequently, the present treatment is relatively simple, in spite of the complexity of this polydisperse system.

A new parameter, α_i , is now defined mathematically for the species M_i as

$$\alpha_i = \frac{\rho_i(0)}{D_i(0)} \quad (4)$$

Physically, it represents the ratio of the segment density of a reference polymer molecule of M_i to that of all the polymer molecules of the same species in the system; both quantities refer to the center of mass of the reference molecule. The numerator of eq. (4) can be derived from eq. (1) by setting $r = 0$. The result is then combined with eqs. (3) and (4) to get

$$N_0^{2/3} \bar{r}_{0i}^2 (\alpha_i C_i)^{2/3} = 9 \frac{M_i^{2/3}}{\pi} \quad (5)$$

For high polymer species of molecular weight M_i , the unperturbed parameter K_θ is related to \bar{r}_{0i}^2 by the Flory-Fox equation¹⁰:

$$K_\theta = \phi \left(\frac{\bar{r}_{0i}^2}{M_i} \right)^{3/2} \quad (6)$$

where the universal constant $\phi = 2.87 \times 10^{23}$ if the concentration is expressed in g/ml.¹² Both sides of eq. (5) are multiplied by the concentration C_i and summed over all the i species. Equation (6) is then introduced to replace \bar{r}_{0i}^2 with K_θ . The resulting equation is finally divided through by $\sum_{\text{all } i} C_i$ to yield,

$$\left(\frac{K_\theta N_0}{\phi}\right)^{2/3} \overline{(\alpha_i C_i)_z^{2/3}} = 9 \frac{\overline{M}_v^{2/3}}{\pi \overline{M}_w} \quad (7)$$

where \overline{M}_w is the weight-average molecular weight; and \overline{M}_v and $\overline{(\alpha_i C_i)_z^{2/3}}$ are a viscosity-average molecular weight and a z -average parameter defined respectively by

$$\overline{M}_v = \left(\frac{\sum^{\text{all } i} C_i M_i^{2/3}}{\sum^{\text{all } i} C_i} \right)^{3/2} \quad (8)$$

$$\overline{(\alpha_i C_i)_z^{2/3}} = \frac{\sum^{\text{all } i} M_i C_i (\alpha_i C_i)^{2/3}}{\sum^{\text{all } i} M_i C_i} \quad (9)$$

It is noted that eq. (7) is in the general form that holds for concentrated polymer solutions. However, at the critical concentration C_0 , the system is proposed to be characterized by

$$\overline{(\alpha_i C_i)_z^{2/3}} = \alpha^{2/3} C_0^{2/3} \quad (10)$$

where $C_0 = \sum^{\text{all } i} C_i$ and α is an empirical constant to be determined. Introduction of eq. (10) into eq. (7) obtains

$$K_\theta = \left(\frac{9}{\pi}\right)^{3/2} \left(\frac{\phi}{\alpha N_0}\right) \left(\frac{\overline{M}_v}{C_0 \overline{M}_w^{3/2}}\right) \quad (11)$$

For polymer that follows the Schulz molecular weight distribution function,¹² we have

$$\frac{\overline{M}_v}{\overline{M}_n} = 0.15 + 0.85\Delta \quad 1.0 \leq \Delta \leq 3.0 \quad (12)$$

where $\Delta = \overline{M}_w/\overline{M}_n$, \overline{M}_n being the number-average molecular weight. Combination of eqs. (11) and (12) leads to

$$K_\theta = 4.85 \frac{0.15 + 0.85\Delta}{g C_0 \Delta^{3/2} \overline{M}_n^{1/2}} \quad (13)$$

where

$$g = \frac{\alpha N_0}{\phi} \quad (14)$$

The factor g is a decreasing function of polydispersity index Δ , and it may be effectively described by the following empirical equations as suggested by the experimental data that will be presented in the next section of this article:

$$\ln g = 3.378 - 4.78 \ln (\Delta + \Delta^{-1}) \quad 1.0 \leq \Delta \leq 1.5 \quad (15a)$$

$$\ln g = -0.908 + 2.48 \ln (1 + \Delta^{-2\Delta}) \quad 1.5 < \Delta \leq 2.5 \quad (15b)$$

Equation (15a) demonstrates a value of $g = 1.067$ for ideally monodisperse system with $\Delta = 1.0$. It follows from eq. (13) that

$$K_\theta = \frac{4.55}{C_0 \overline{M}^{1/2}} \quad (16)$$

Referring to eq. (4), it physically implies that each polymer molecule forms an entanglement network with approximately an equal number of foreign segments in the vicinity of its center of mass at the C_0 if the sample is perfectly monodisperse, as $\alpha = 1/2$ under this particular condition. Comparing with the close-packing theory, the present model predicts a value of packing factor equal to 0.79, which is close to that indicated by Turner.⁴ Incidentally, the numerical value appearing in eq. (16) is between 4.27 obtained from the close-packing model⁴ and 6.57 derived from the crystalline lattice theory³ with a weighting toward the former figure.

The effects of polydispersity on C_0 are indeed noticeably large even for moderate molecular weight distribution. This contradicts the works reported previously.

RESULTS AND DISCUSSION

Table I reports the results of four different types of polymers computed by eqs. (13) and (15a). Though the viscosity data of these polymer fractions are available in the literature, the exact values of Δ are not provided. However, it is not unreasonable to consider $\Delta = 1.20$ as the practical value for the present analyses, as it is generally believed that the actual deviation from this optimum figure is minor in that it will not affect the final conclusion herein. The values of critical concentration are obtained from the $\log \eta_0$ - $\log C$ plots and a new graphic method proposed by us recently.⁵ Flow properties of five poly(vinyl chloride) fractions in cyclohexanone have been studied by Asai¹³ and Pezzin et

TABLE I
Critical Concentrations and Unperturbed Parameter of Various Polymer Fractions

Polymer No.	$\bar{M}_w \times 10^{-4}$	C_0 , g/ml	K_θ , ml/g	
			Calculated	Literature
Poly(vinyl Chloride) in Cyclohexanone at 30°C				
1	10.32	0.0954	0.157	
2	7.82	0.1095	0.157	
3	6.06	0.1243	0.157	0.150 (Ref. 5)
4	4.63	0.1422	0.157	
5	10.00	0.112	<u>0.136</u>	
			ave. 0.153 \pm 0.008 ^a	
Polystyrene in Toluene at 40°C				
1	123.0	0.046	0.094	
2	58.7	0.0685	0.091	
3	28.2	0.1022	0.088	0.088 (Ref. 25)
4	15.7	0.1325	<u>0.091</u>	
			ave. 0.091 \pm 0.002 ^a	
Poly(vinyl Alcohol) in Water at 40°C				
1	9.68	0.078	0.198	
2	8.80	0.0825	0.196	
3	7.04	0.093	0.195	0.205 (Ref. 21)
4	4.84	0.1083	0.201	
5	2.82	0.1476	<u>0.194</u>	
			ave. 0.197 \pm 0.002 ^a	
Poly(α -methylstyrene) in Toluene				
1	38.0	0.125	0.062	0.067 (Ref. 26)

^a Standard deviation from the mean.

al.¹⁴ The predicted average value of K_θ is 0.153 ± 0.008 ml/g, which coincides remarkably well with the literature figure of 0.150 ml/g. Other systems contained in the table are polystyrene in toluene,² poly(vinyl alcohol) in water,² and poly(α -methylstyrene) in toluene.³ They all demonstrated results compatible with the documented values. It is noted that the deviation between predicted and measured K_θ values is within $\pm 10\%$ if polymer fractions are employed in any case.

Ferry and co-workers¹⁵ have provided data on zero shear viscosities of an unfractionated poly(vinyl acetate) of $\bar{M}_n = 1.4 \times 10^5$ in three different solvents over a wide range of concentrations. These data are used to produce the critical concentrations listed in Table II.⁵ The intrinsic viscosity $[\eta]$ of the sample in butanone at 25°C is found to be 96 ml/g, which gives a viscosity-average molecular weight of 2.68×10^5 using the Mark-Houwink constants derived by Chinai and Guzzi.¹⁶ Assuming the polymer conforms to the Schulz distribution function, the parameter Δ is estimated to be 2.08 from eq. (12). Finally, eqs. (13) and (15) report an average K_θ value comparable with a measured datum as displayed in the table. It is well known that vinyl acetate has a large monomer chain transfer constant¹⁷ which may cause noticeable branching and eventually enhance the polydispersity of the polymer. We believe that the present Δ value is underestimated and the actual computed value of K_θ would be somewhat higher than that shown herein.

It has been proposed recently⁴ that the onset of autoacceleration in the rate of free radical polymerization of vinyl monomers occurs at the critical concentration. As such, the parameter C_0 is obtainable by reference to the departure point from the constant initial rate of polymerization. One of the most exten-

TABLE II
Critical Concentrations and Unperturbed Parameter of Various Whole Polymers

Polymer No.	C_0 g/ml	Δ	$\bar{M}_n \times 10^{-5}$	K_θ (mL/g)		Remarks
				Calculated	Literature	
Poly(vinyl Acetate) in Various Solvents at 25°C						
1	0.242	2.08	1.40	0.076		in butanone; [η] = 96 ml/g
2	0.246	2.08	1.40	0.074	0.078 (ref. 27)	in 4-methyl-2-pentanone; [η] = 68 ml/g
3	0.253	2.08	1.40	<u>0.072</u>		in 1,2,3-trichloropropane; [ν] = 10 ml/g
ave. 0.074 ± 0.001^a						
Poly(methyl Methacrylate) ^b in Methyl Methacrylate at Various Temperatures						
1	0.396	1.90	0.65	0.065	0.058 (Ref. 23)	<u>Temp., °C</u> 90
2	0.298	2.10	1.35	0.063		70 ^c
3	0.182	2.20	4.50	0.057		50
4	0.188	2.30	3.80	0.059		50 ^c
5	0.406	2.00	0.50	<u>0.075</u>		90
ave. 0.061 ± 0.003^a						

^a Standard deviation from the mean.

^b The polymerization reactions were initiated by different amounts of azobisisobutyronitrile, and the average molecular weight data were determined by GPC.

^c Average values of C_0 and \bar{M}_n are used.

sively investigated monomers in this connection perhaps is the methyl methacrylate. Some works of Bulke and Hamielec¹⁸ are cited in Table II. Comparisons between the estimated and experimental figures are reasonably good, except for sample 5, which has the lowest \bar{M}_n . This is not unexpected, as the Flory-Fox equation from which eq. (13) is derived does not hold for low-molecular-weight species.¹⁹

Detailed studies of the autoacceleration of methyl methacrylate were performed by Turner et al. recently.²⁰ Their results are faithfully reproduced in Table III. Equations (13) and (15) result in a broad range of K_θ values. However, on close examination, it reveals that most of these data are scattered within $\pm 10\%$ from either a recommended value¹⁷ of 0.048 ml/g or a measured value of 0.058 ml/g. The inconsistent data of runs 4 and 6-8 may be attributed to the poor estimates of various quantities, particularly \bar{M}_n and Δ .

Limitations of eq. (13) are encountered in the present investigations when the degree of polymerization is less than 600. In addition, this analysis by no means warrants the model in producing acceptable K_θ values for polymer samples of very broad molecular weight distribution, presumably with a polydispersity index exceeding 3.0.

The present findings imply that under all circumstances the difference between the theoretical and experimental K_θ values is confined to within $\pm 12\%$ of the latter value. This figure of discrepancy is as good as those values obtained by the other approaches.^{3,20-27} Hence, we have established a reliable method by which only a polymer sample of moderate polydispersity ($\Delta < 2.50$) is required to determine the unperturbed parameter satisfactorily.

TABLE III
Critical Concentrations and Unperturbed Parameter of Poly(methyl Methacrylate) Based on Ref. 20

Polymer no.	Initiator	wt %	Temp., °C	C_0 , g/mL	$\bar{M}_n \times 10^{-5}$ ^a	Δ	K_θ , mL/g
1	AZBN ^b	0.3	50	0.152	5.62	1.59	0.047
2	AZBN	0.4	50	0.152	4.86	1.50	0.049
3	AZBN	0.5	50	0.152	4.37	1.44	0.049
4	AZBN	0.3	70	0.178	1.91	1.55	0.067
5	AZBN	0.5	70	0.219	1.55	1.53	0.059
6	AZBN	0.3	90	0.256	0.743	1.76	0.088
7	AZBN	0.5	90	0.298	0.590	1.69	0.081
8	Bz ₂ O ₂ ^c	2.0	30	0.145	8.47	1.26	0.033
9	Bz ₂ O ₂	0.25	50	0.103	9.07	1.67	0.059
10	Bz ₂ O ₂	1.0	50	0.133	4.98	1.55	0.055
11	Bz ₂ O ₂	2.0	50	0.152	3.64	1.08	0.048
12	Bz ₂ O ₂	4.0	50	0.172	2.46	1.13	0.051
13	Bz ₂ O ₂	7.0	50	0.203	2.10	1.11	0.047
14	Bz ₂ O ₂	10.0	50	0.213	1.76	1.05	0.050
15	Bz ₂ O ₂	15.0	50	0.225	1.45	1.05	0.052
16	Bz ₂ O ₂	2.0	70	0.219	1.21	1.27	0.059
17	Bz ₂ O ₂	4.0	70	0.250	0.85	1.34	0.063
18	Bz ₂ O ₂	7.0	70	0.280	0.67	1.31	0.063

^a Values of \bar{M}_n are estimated from the initial rates of polymerization.

^b Azobisisobutyronitrile.

^c Benzoyl peroxide.

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