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Dependence of Polymer Chain Entanglements on the Solution Concentration

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NOTE

DEPENDENCE OF POLYMER CHAIN ENTANGLEMENTS ON THE SOLUTION CONCENTRATION

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INTRODUCTION

For the viscometric determination of molecular weights of polymers, sufficiently dilute solutions have to be used so that entanglements of the polymer chain are absent. The concentration of the polymer should be such that the relative viscosity (η_r) lies in the range 1.1-1.5 [1]. Similarly, for molecular weight determination by light scattering, the suggested concentration for polymer with weight-average molecular weight (\bar{M}_w) $> 10^5$ is 0.5 wt%; for those with $\bar{M}_w < 10^5$, up to 1% may be used [2].

The limits of polymer concentration for such measurements are not clearly known. On dissolution, the polymer molecules adopt a more or less extended configuration whose shape depends on the structure and molecular weight of the polymer, the properties of the solvent, and the temperature [3]. The molecules of flexible linear polymers acquire a coiled configuration due to free rotation about the C—C bonds. When a dilute solution satisfies theta conditions, the polymer molecules are free from all kinds of interaction and move freely. Then their solution properties could possibly be related to their end-to-end distance. Based on this concept, our attempt to establish the permissible limits of polymer concentration for dilute solutions of several polymers of different molecular weights is reported here.

THEORETICAL BASIS

If C g of a polymer of molecular weight \bar{M}_n is dissolved in unit volume of solvent, and if each of these molecules is assumed to occupy the volume of a close-packed cuboid of side d , the following expression holds:

$$d^3 = \bar{M}_n / C N_0 \quad (1)$$

where N_0 is Avogadro's number. At low concentration, the distance d is a measure of the molecular dimensions of the polymer and is related to hydrodynamic parameters, such as the root-mean-square end-to-end distance, $\sqrt{\bar{r}^2}$, of the polymer molecule. This is related to the intrinsic viscosity $[\eta]$ and \bar{M}_n by the expression [4]

$$[\eta] = \phi (\sqrt{\bar{r}^2})^3 / \bar{M}_n, \quad (2)$$

where ϕ , barring a few exceptions [5, 6], is a constant and, as a good approximation, may be taken as 2.71×10^{21} [3].

In an unperturbed state, the end-to-end distance, $\sqrt{\bar{r}_0^2}$, obeys the expression $\sqrt{\bar{r}^2} = \alpha \sqrt{\bar{r}_0^2}$, where α is the expansion factor. Under theta conditions, $\alpha = 1$, and in Eq. (2), $[\eta]$ becomes $[\eta]_\theta$ and $\sqrt{\bar{r}_0^2}$ replaces $\sqrt{\bar{r}^2}$.

At constant \bar{M}_n , d decreases with increasing C (Eq. 1) and $\sqrt{\bar{r}_0^2}$ increases with $[\eta]/\alpha$ for nontheta solvents and with $[\eta]_\theta$ for theta solvents. It may therefore be deduced that, at constant \bar{M}_n , the entanglements will occur when C reaches such a value that $d \leq \sqrt{\bar{r}_0^2}$ or $d \leq \alpha \sqrt{\bar{r}_0^2}$ under the theta or nontheta conditions, respectively. Under these conditions, C is denoted as $C_{e\theta}$ or C_e (e = entanglement) expressed in g/mL. In the theta solvent we get, from Eqs. (1) and (2),

$$\left[\frac{\bar{M}_n}{C_{e\theta} N_0} \right]^{1/3} = \left[\frac{[\eta]_\theta \bar{M}_n}{\phi} \right]^{1/3} \quad (3)$$

Substituting the numerical values for ϕ and N_0 and replacing $[\eta]_\theta$ by $K_\theta \bar{M}_n^{0.5}$ [1] in Eq. (3), we arrive at

$$C_{e\theta} = 0.4499 / K_\theta \bar{M}_n^{0.5} \quad (4)$$

Thus, at constant \bar{M}_n , $C_{e\theta}$ is inversely proportional to K_θ , which is related to the molecular properties of the polymer in dilute solution.

For nontheta solvents, Eq. (4) becomes

$$C_e [\eta] = 0.4499. \quad (5)$$

Here $[\eta]$ is dependent on the structure of the polymer as well as the nature of the solvent and is, therefore, difficult to assign any specific value of C_e . On the other hand, in theta solvents, the state being unperturbed, $C_{e\theta}$ could be related to the structure of the polymer alone and, since K_θ values are available in the literature, it became possible to evaluate the system for theta solvents.

EVALUATION OF RESULTS

The K_θ values of polyolefins and vinyl, acrylic, and diene homopolymers were taken from the literature (Table 1). For polypropylene (PP), poly(1-butene), poly(vinyl acetate) (PVAC), polystyrene (PS), and poly(methyl methacrylate) (PMMA), the K_θ values are the average of those reported by different authors. The values of d for different molecular weights from 1×10^5 to 6×10^5 at constant C , e.g., 2.5, 5.0, 10, and 15 mg/mL, were calculated. Substitution of these data into Eq. (1) reveals that, at constant \bar{M}_n , d gradually decreases with increasing C . Substituting $K_\theta \bar{M}_n^{0.5}$ for $[\eta]_\theta$ in Eq. (2), for theta conditions, $\sqrt{\bar{F}_0^2}$ was calculated for the four groups of polymers by taking the K_θ values from Table 1. The results are for PP, poly(1-butene), and poly(isobutene) (PIB) shown in Fig. 1; similar plots for other polymers are not included here.

The dependence of $\sqrt{\bar{F}_0^2}$ on K_θ is shown in Fig. 2. It is interesting to note that, for $\bar{M}_n = 1.0 \times 10^5$, the plot is linear, while at higher \bar{M}_n it is no longer linear.

The $C_{e\theta}$ values for different polymers calculated from K_θ and \bar{M}_n following Eq. (4) are given in Table 2. Figure 3 illustrates the variation of $C_{e\theta}$ with \bar{M}_n for four different homopolymers.

DISCUSSION

In Fig. 1 the curves of d intersect those of $\sqrt{\bar{F}_0^2}$ for PP (1), poly(1-butene) (2), and PIB (3). Table 3 gives the values of C and \bar{M}_n corresponding to the intersecting point. The $C_{e\theta}$ values corresponding to the \bar{M}_n of the intersecting points (in parentheses in Table 3) are found to be in good agreement with

TABLE 1. Polymers and Their K_θ Values [6]

Polymers	$K_\theta \times 10^5$
1. Polyolefins:	
Polypropylene	174.2 (average of 182, 172, 168.5)
Poly(1-butene)	115.0 (average of 123, 107)
Poly(isobutene)	91.0
2. Vinyl polymers:	
Poly(vinyl chloride)	156.0
Poly(vinyl acetate)	85.0 (average of 90, 82, 78, 82, 92.9, 101)
Polystyrene	77.0 (average of 82, 70, 76)
Poly(vinyl benzoate)	62.0
3. Acrylic polymers:	
Poly(acrylic acid)	76.0
Poly(methacrylic acid)	66.0
Poly(methyl methacrylate)	59.3 (average of 50.5, 57.5, 63.1, 59.0, 58.0, 67.9)
4. Diene polymers:	
Polyisoprene (gutta percha)	232
Polybutadiene (1,3)	185
Polyisoprene (atactic)	119

the C values of the intersecting points. This confirms the validity of the above deductions. Thus, the data in Table 2 and 3 can be taken as guides for the upper concentration limits for determination of molecular weights under theta conditions.

Thus, under the theta conditions, the entanglement concentration is a combined function of the molecular weight and the structure of the molecules. The values of $C_{e\theta}$ are different for different polymers of the same \bar{M}_n . This is

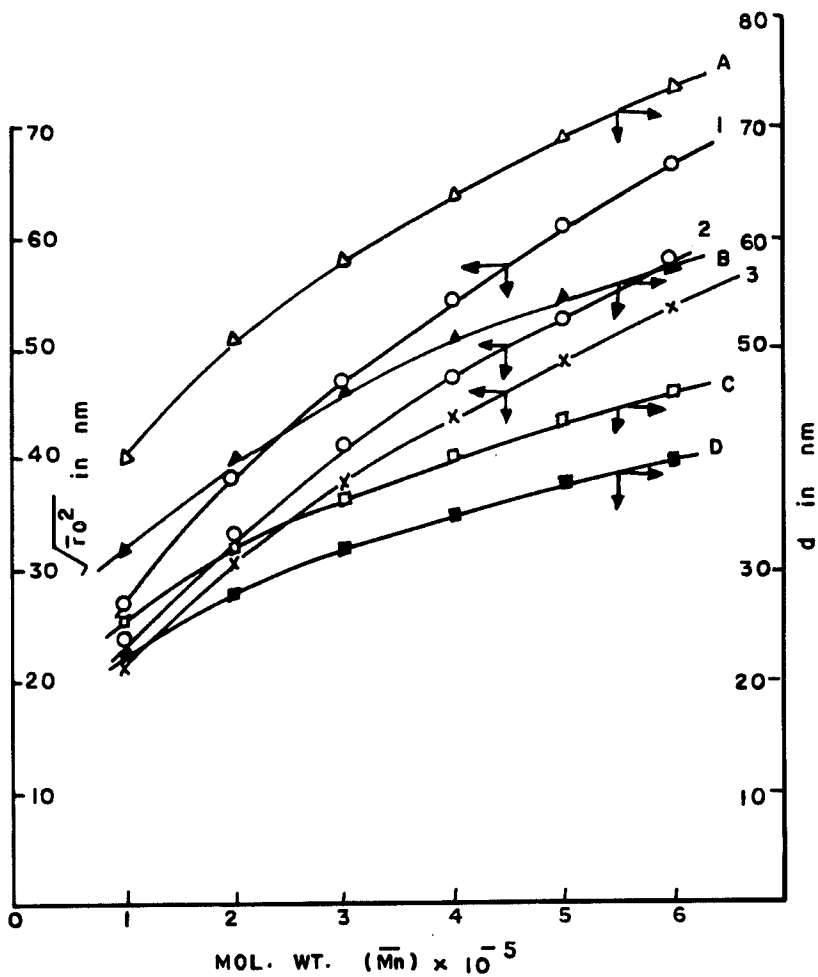


FIG. 1. Plot of $\sqrt{\bar{r}_0^2}$ vs \bar{M}_n for different polyolefins and plot of d (in nm) vs \bar{M}_n at different concentrations, C , in g/mL. Curves 1 to 3 are, respectively, for PP, poly(1-butene), and PIB, whereas Curves A to D are at C of 2.5, 5.0, 10, and 15 mg/mL.

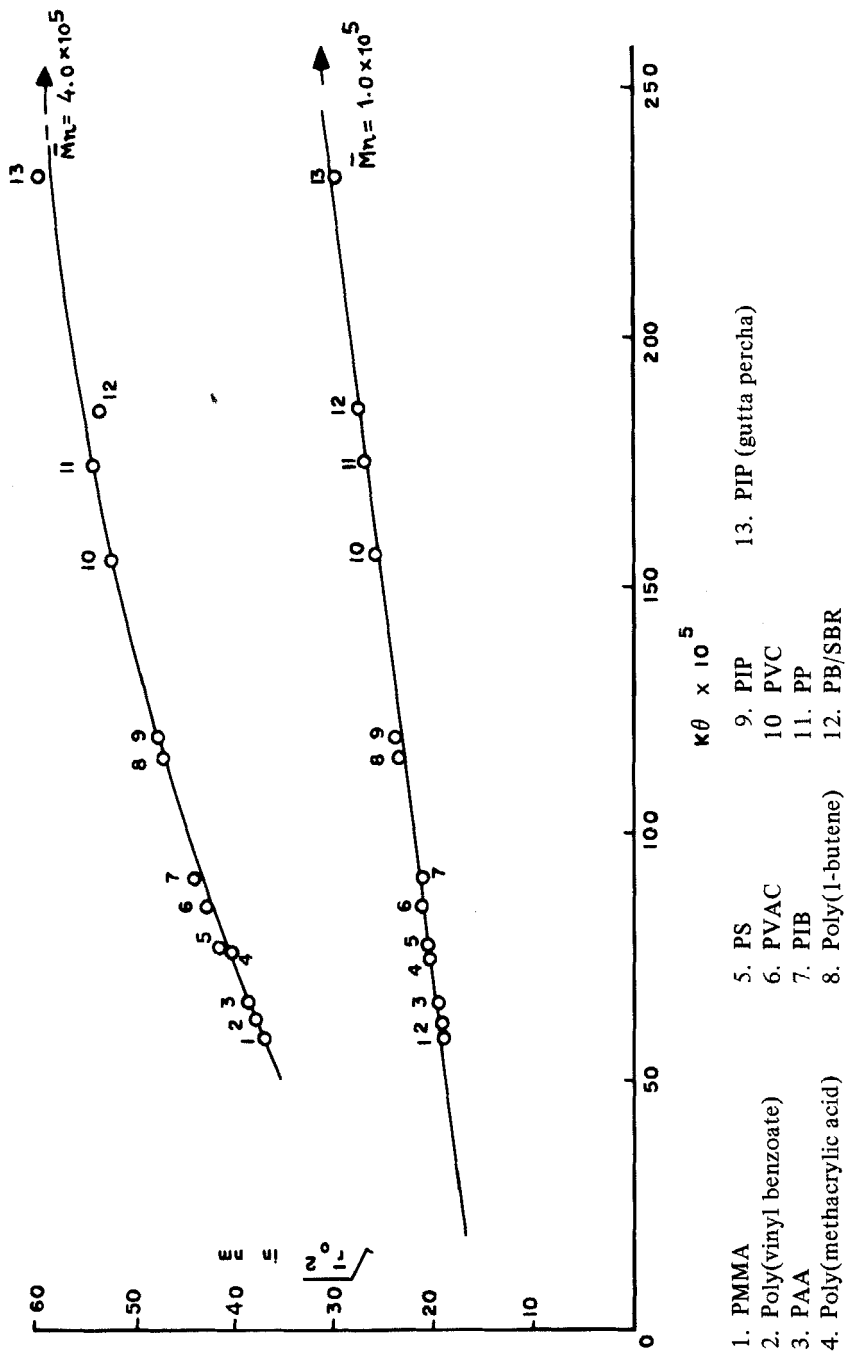


FIG. 2. Plot of $\sqrt{\eta_0}^2$ vs $K\theta$ for different polymers at \bar{M}_n of 4.0×10^5 and 1.0×10^5 .

TABLE 2. Calculated Values of $C_{e\theta}$ for Homopolymers^a

$\bar{M}_n \times 10^{-5}$	Polyolefins			Vinyl polymers		
	PP	Poly(1-butene)	PIB	PVC	PVAc	PS
0.5	1.143	1.750	2.196	1.2969	2.370	2.595
1.0	0.806	1.237	1.549	0.917	1.766	1.834
2.0	0.570	1.875	1.096	0.648	1.185	1.297
3.0	0.465	0.714	0.895	0.529	0.968	1.059
4.0	0.403	0.618	0.773	0.838	0.838	0.917
5.0	0.360	0.353	0.693	0.410	0.749	0.820
6.0	0.329	0.636	0.374	0.684	0.748	1.942

$\bar{M}_n \times 10^{-5}$	Acrylic polymers				Diene polymers		
	Poly(vinyl benzoate)	PAA	PMAA	PMMA	PIP	PB (1,3)	PIP (atactic)
0.5	3.265	2.638	3.041	3.399	0.849	1.073	1.699
1.0	2.308	1.866	2.150	2.403	0.601	0.759	1.202
2.0	1.632	1.319	1.521	1.699	0.425	0.537	0.849
3.0	1.333	1.077	1.242	1.388	0.347	0.438	0.694
4.0	1.154	0.933	0.075	1.207	0.300	0.399	0.601
5.0	1.032	0.834	0.962	1.075	0.268	0.339	0.537
6.0	0.762	0.878	0.981	0.245	0.245	0.309	0.497

^a $C_{e\theta} \times 10^2$ in g/mL.

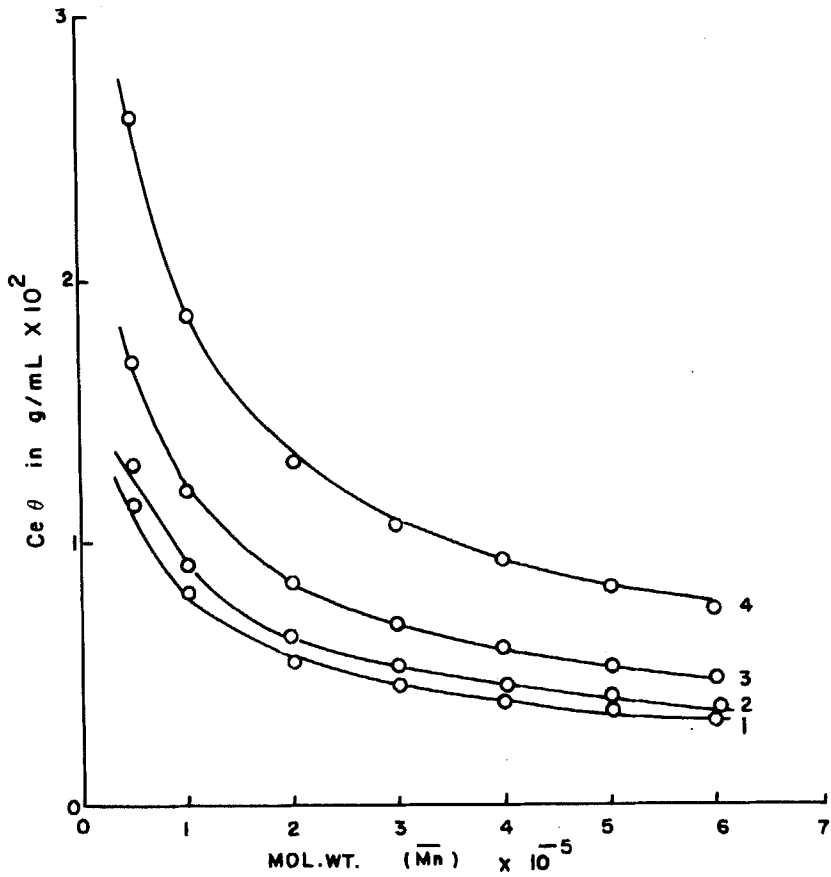


FIG. 3. Plot of $C_{c\theta}$ vs \bar{M}_n for four different homopolymers: (1) PP, (2) PVC, (3) PIP, and (4) PAA.

TABLE 3. Intersecting Point of $\sqrt{F_0^2}$ and d Against \bar{M}_n (plot of Eqs. 1 and 2 for theta conditions)^a

Concentration X 10 ² g/mL	Polymers with levels of \bar{M}_n at intersecting point						
	PP	Poly(1-butene)	PIB	PVC	PVAc	PS	
0.25	—	—	—	—	—	—	—
0.50	250 000 (0.0050)	600 000	—	360 000 (0.0050)	—	—	—
1.00	75 000 (0.0096)	190 000	250 000	85 000 (0.01)	180 000	325 000	—
1.50	—	75 000	—	—	120 000	165 000	—

Concentration X 10 ² g/mL	Polymers with levels of \bar{M}_n at intersecting point						
	Poly(vinyl benzoate)	PAA	PMAA	PMMA	PIP	PB (1,3)	PIP (atactic)
0.25	—	—	—	—	285 000	—	—
0.50	—	—	—	—	140 000	245 000	590 000 (0.0048)
1.00	580 000 (0.0102)	340 000	420 000	550 000	—	—	103 000 (0.0106)
1.50	260 000	150 000	190 000	270 000	—	—	—

^aValues in parentheses calculated for C_e corresponding to the \bar{M}_n of the intersection point of curves of $C_{e\theta}$ vs \bar{M}_n (Fig. 2).

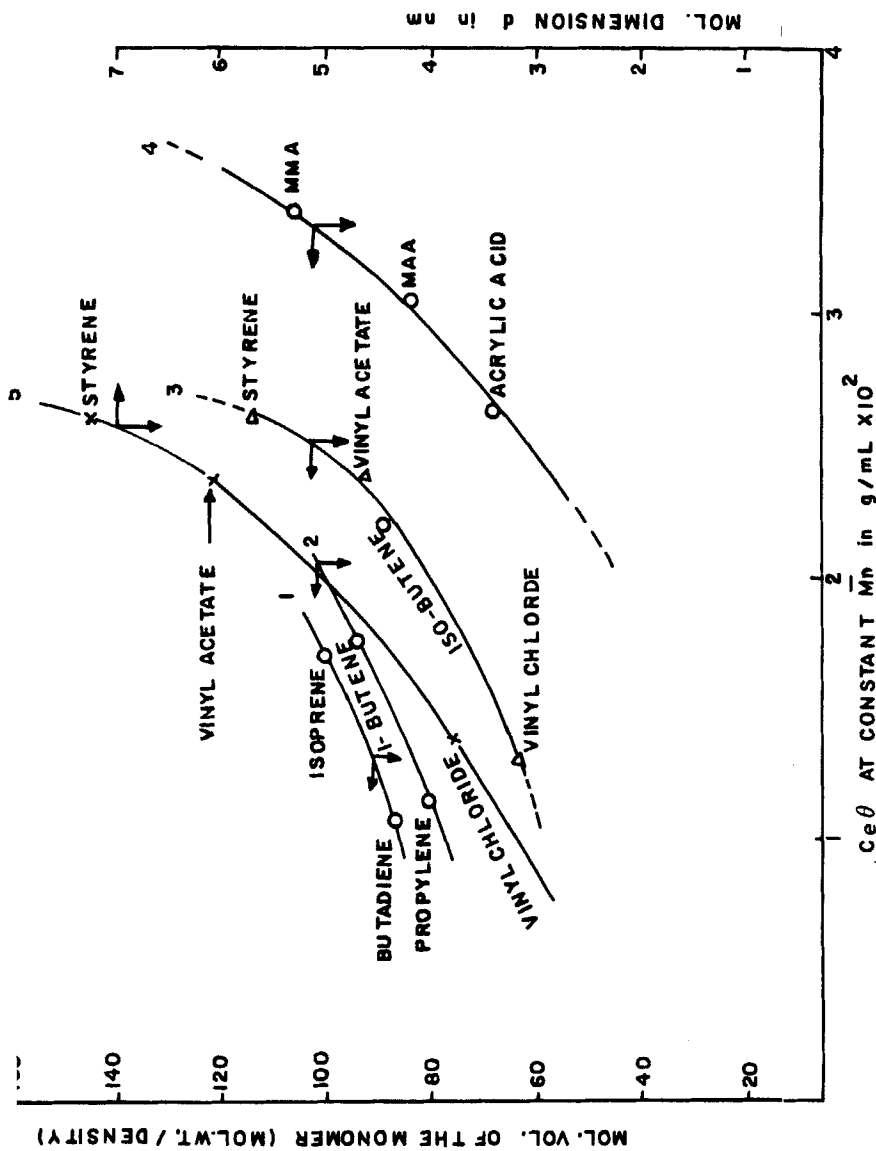


FIG. 4. Molecular volume of various monomers vs $C_{e\theta}$ of corresponding polymers at $\bar{M}_n = 50\,000$: (1) diene, (2) olefins, (3) vinyl, and (4) acrylic monomers. Curve (5) depicts d (in nm) (monomer molecular dimensions) vs $C_{e\theta}$ of vinyl polymers.

TABLE 4. Molecular Dimensions (molecular volume and end-to-end distance) of Monomers

Monomers	MW	Density ^a	Molecular volume, mL/mol	End-to-end distance, <i>d</i> , nm
Propylene	42.07	0.5139 ⁻²⁰	81.86	3.81 2.99
1-Butene	56.104	0.5951	94.28	3.81
Isobutene	56.100	0.6266 ^{-6.6}	89.52	—
Vinyl chloride	62.50	0.9918 ⁻¹⁵	63.02	3.67
Vinyl acetate	86.09	0.9338	92.19	6.09 5.32
Styrene	104.14	0.9090 0.9075	114.57 114.75	7.24 6.54
Vinyl benzoate	148.0	—	—	—
Acrylic acid	72.06	1.0472 1.0511	68.81 68.56	— —
Methacrylic acid	86.09	1.0313	84.79	—
Methyl methacrylate	100.11	0.936	106.96	5.81 6.81
Butadiene (1,3)	54.09	0.6211	87.09	5.48 4.96
Isoprene	68.11	0.6806	100.07	—
Vinyl butyrate	114.11	0.9022 0.8994	126.48 126.87	— —

^aAt 70°C, except where noted otherwise.

in agreement with Eq. (4), confirming the validity of its derivation. The data in Table 2 and Fig. 3 allow two inferences to be drawn: 1) for a particular polymer, $C_{e\theta}$ decreases with increasing \bar{M}_n ; and 2) at constant \bar{M}_n , $C_{e\theta}$ increases with decreasing K_θ . The import of 1) for practical use is that the higher the \bar{M}_n , the lower should be the concentration.

Inference 2) indicates that for different polymers of the same \bar{M}_n , $\sqrt{r_0^2}$ decreases with K_θ , resulting in higher $C_{e\theta}$ values. For rational correlation of these findings, the molecular volume and molecular dimension (end-to-end distance) of the monomers were calculated (Fig. 4 and Table 4). Though the curves in Fig. 4 are similar, their shape depends on the type of monomer. One unified curve relating $C_{e\theta}$ for all these monomer parameters does not seem to be possible. However, such plots at different \bar{M}_n values would enable us to determine the $C_{e\theta}$ values of the respective polymers.

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REFERENCES

- [1] F. W. Billmeyer, *Textbook of Polymer Science*, Wiley, New York, 1962, p. 81.
- [2] *Instruction Manual*, Phoenix Precision Co., Philadelphia, Pennsylvania, 1964, p. 22. A. Tayger, *Physical Chemistry of Polymers*, Mir, Moscow, 1972, p. 489.
- [3] D. A. Smith, *Addition Polymers (Formation and Characterization)*, Plenum, New York, 1968, p. 208.
- [4] P. J. Flory and T. G. Fox, *J. Am. Chem. Soc.*, **73**, 1904 (1951).
- [5] M. Kurata, W. H. Stockmayer, and A. Roig, *J. Chem. Phys.* **33**, 151 (1960).
- [6] M. Kurata, M. Iwawa, and K. Kamada, in *Polymer Handbook* (J. Brandrup and E. Immergut, eds.), Wiley-Interscience, New York, 1966, p. IV-1-72.

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