

A Correlation between Critical End-to-End Distance for Entanglements and Molecular Chain Diameter of Polymers

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SYNOPSIS

The critical molecular weight M_c of 36 flexible and semirigid polymers has been studied. A unique correlation between the critical end-to-end distance $\langle R_c \rangle$ for entanglements and the average polymer chain diameter D is found. This correlation is discussed in the light of the reptation concept.

INTRODUCTION

The onset of entanglement behavior with increasing molecular weight appears universally in polymer melts and concentrated solutions.^{1,2} An example of this is the critical molecular weight M_c , which separates the dependence of zero-shear viscosity η_0 on molecular weight M into two regions: $\eta_0 \propto M$ and $\eta_0 \propto M^{3.4}$. In order to understand the molecular nature of entanglements, many attempts have been made to correlate M_c (or the critical number of main-chain bonds N_c) with some structural parameters of polymers.³⁻¹¹ A comparison of these different correlations reveals that the critical molecular weight M_c , or N_c , depends especially on the rigidity and cross-sectional area S of polymer chains. On the other hand, it has been recently recognized that entanglements can be modeled as a tube constraint on the diffusion of molecules (reptation models).^{12,13} According to the reptation models, the parameter controlling the degree of chain entanglement is the tube diameter, which is taken to be equal to the end-to-end distance between entanglements. However, no relationship between the tube diameter and the properties of polymer chains has been given. In the present work, the critical molecular weight for entanglements has been studied using the framework of the reptation models. Without linking directly M_c (or N_c) with structural parameters of polymers,

the critical end-to-end distance of a macromolecular chain for entanglements, $\langle R_c \rangle$ (corresponding to M_c), has been correlated with the average diameter D of the polymer chains.

DATA ANALYSIS

The critical end-to-end distance for entanglements, $\langle R_c \rangle$, has been calculated from the critical molecular weight M_c through the following relation¹⁴:

$$\langle R_c \rangle = \langle R_c^2 \rangle^{1/2} = M_c^{1/2} (\langle R^2 \rangle_0 / M)^{1/2} \quad (1)$$

where $\langle R^2 \rangle_0$ is the mean-square end-to-end distance for a polymer of molecular weight M in a theta solvent, which is approximately identical with that in amorphous or molten polymers.¹⁵

The use of eq. (1) implies the assumption that M_c is large enough so that the polymer chain is Gaussian.

The average polymer chain diameter D is estimated from the cross-sectional area of the polymer S using the approximate relation⁶

$$D = S^{1/2} \quad (2)$$

where the values of S are generally obtained from crystallographic data.¹⁷

Table I summarizes the values (taken from the literature) of $M_c (\langle R^2 \rangle_0 / M)^{1/2}$ and S together with the characteristic ratio C_∞ ($C_\infty = \langle R^2 \rangle_0 / Nl_0^2$, with N and l_0 being, respectively, the number and the

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Table I Critical Molecular Weight M_c and Characteristic Parameters of Polymers

No.	Polymer	M_c	C_∞	$(\langle R^2 \rangle_0/M)^{1/2}$ (Å)	S (Å ²)	$\langle R_c \rangle/D$
1	Polyethylene	3800 ^{8,18}	7.0	1.08 ¹⁶	18.3 ¹¹	15.6
2	Polypropylene	7000 ⁸	6.2	0.83 ¹⁶	34.3 ¹¹	11.9
3	Polystyrene	35,000 ^{8,18}	10.3	0.67 ¹⁶	69.8 ¹¹	15.1
4	Poly(vinyl chloride)	6250 ^{10,18}	7.7	0.82 ¹⁶	27.2 ¹¹	12.4
5	Poly(vinyl acetate)	24,500 ^{8,18}	9.0	0.70 ¹⁶	59.3 ¹¹	14.2
6	Poly(vinyl alcohol)	5300 ¹⁸	8.3	0.95 ¹⁶	21.4 ¹⁷	13.6
7	Polyacrylamide	9100 ¹⁰	14.8	1.00 ¹⁶	45.2 ¹¹	14.2
8	Poly(α -methyl styrene)	40,800 ^{5,10}	10.5	0.65 ¹⁶	100.0 ¹¹	13.1
9	Polyisobutylene	15,200 ⁸	6.2	0.74 ¹⁶	41.2 ¹¹	14.2
10	Poly(methyl acrylate)	24,100 ^{10,a}	8.0	0.68 ¹⁶	59.3 ¹¹	13.7
11	Poly(ethyl acrylate)	31,300 ^{10,a}	8.8	0.72 ¹⁶	73.0 ¹¹	14.9
12	Poly(methyl methacrylate)	31,000 ^{8,10}	8.7	0.62 ¹⁶	63.8 ¹¹	13.7
13	Poly(<i>n</i> -butyl methacrylate)	60,400 ^{10,a}	8.0	0.52 ¹⁶	93.6 ¹¹	13.2
14	Poly(<i>n</i> -hexyl methacrylate)	91,900 ^{10,a}	10.3	0.54 ¹⁶	114.2 ¹¹	15.3
15	Poly(<i>n</i> -octyl methacrylate)	114,000 ^{10,a}	10.0	0.50 ¹⁶	135.1 ¹¹	14.5
16	Poly(2-ethylbutyl methacrylate)	42,800 ^{10,a}	9.1	0.51 ¹⁶	100.0 ¹¹	10.6
17	Poly(dimethyl siloxane)	24,500 ^{8,10}	5.2	0.66 ¹⁶	63.8 ¹¹	15.6
18	Poly(ethylene oxide)	4400 ^{7,10}	4.2	0.81 ¹⁶	21.5 ¹¹	11.6
19	Poly(propylene oxide)	7700 ^{10,18}	5.1	0.77 ¹⁶	24.5 ¹¹	13.7
20	Poly(tetramethylene oxide)	2500 ¹⁰	6.1	0.93 ¹⁶	17.6 ¹⁷	11.2
21	<i>Cis</i> -polyisoprene	7700 ¹⁰	5.0	0.84 ¹⁶	28.0 ¹¹	13.9
22	Hydrogenated polyisoprene	4000 ^{10,a}	6.8 ⁸	0.92 ^b	28.5 ¹¹	11.4
23	<i>Cis, trans</i> , vinyl-polybutadiene	4500 ^{8,10}	5.4	1.01 ¹⁶	19.3 ¹¹	15.4
24	<i>Cis</i> -polybutadiene	5900 ¹⁰	4.9	0.88 ¹⁶	20.7 ¹¹	14.9
25	1,2-Polybutadiene	12,700 ^{19,a}	6.6 ⁸	0.76 ^b	49.9 ¹¹	13.7
26	Hydrogenated 1,2-polybutadiene	26,700 ^{19,a}	5.5 ¹⁹	0.68 ^b	49.9 ^c	15.8
27	Poly(ϵ -caprolactam) nylon 6	5000 ¹⁰	5.3	0.94 ¹⁶	17.9 ¹¹	15.7
28	Poly(hexamethylene adipamide) nylon 66	4700 ¹⁰	6.1	0.94 ¹⁶	17.6 ¹¹	15.4
29	Poly(decamethylene succinate)	4600 ^{10,18}	5.5 ^d	0.87 ²⁰	18.5 ^e	13.7
30	Poly(decamethylene adipate)	4400 ^{10,18}	4.8 ^d	0.83 ²⁰	18.5 ⁷	12.8
31	Poly(decamethylene sebacate)	4500 ^{10,18}	6.0 ^d	0.94 ²⁰	18.5 ⁷	14.7
32	Poly(diethylene adipate)	4800 ¹⁸	4.7 ^d	0.79 ²⁰	18.1 ¹⁷	12.9
33	Poly(ethylene terephthalate)	3300 ¹⁰		0.98 ^{16,21}	20.0 ¹¹	12.6
34	Poly(carbonate of bisphenol A)	4900 ¹⁰		0.93 ¹⁶	30.9 ¹¹	11.7
35	Poly(ester carbonate of 1- bisphenol A and 2- terephthalic acid)	4800 ¹⁰		0.95 ^f	30.9 ¹¹	11.8
36	Poly(ester of bisphenol A and diphenyl sulfone)	7100 ¹⁰		0.80 ²²	30.9 ¹¹	12.1
	Average value					13.6
	Standard deviation					0.11

^a Estimated as $M_c = 2M_e$.^b Calculated from C_∞ .^c Estimated from 1,2-polybutadiene.^d Calculated from $(\langle R^2 \rangle_0/M)$.^e Estimated from poly(decamethylene adipate) and poly(decamethylene sebacate).^f Estimated between poly(ethylene terephthalate) and poly(carbonate of bisphenol A).

average length of main-chain bonds¹⁴) for 36 polymers.

Figure 1 shows the critical end-to-end distance for entanglements $\langle R_c \rangle$ plotted as a function of D

for all of the polymers listed in Table I. Despite some scatter, $\langle R_c \rangle$ is clearly a linear function of polymer chain diameter D , given by

$$\langle R_c \rangle = 13.6D \quad (3)$$

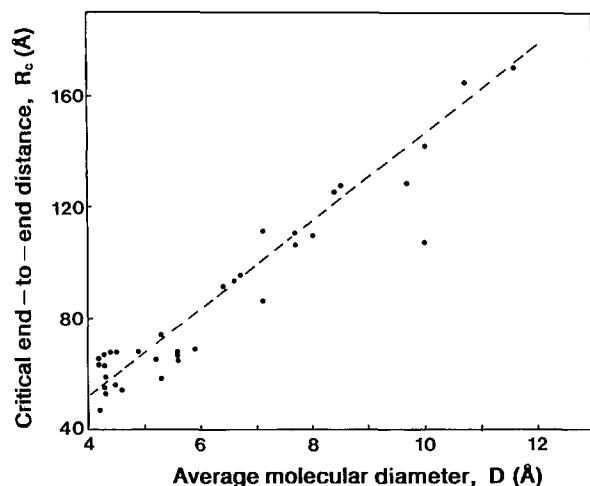


Figure 1 Critical end-to-end distance $\langle R_c \rangle$ vs. average molecular diameter D of polymer chains.

DISCUSSION AND CONCLUSION

Equation (3) provides a new correlation for entanglements relating the critical end-to-end distance to polymer chain diameter. As already mentioned in the Introduction, many other empirical correlations³⁻¹¹ have been developed before. Some similarities can be found between the proposed correlation and the literature ones: Using the relation $\langle R_c^2 \rangle = C_\infty N_c l_0^2$, the critical number of main-chain bonds N_c can be calculated from eq. (3):

$$N_c = (185/l_0^2)(D/C_\infty^{1/2})^2 \quad (4)$$

Equation (4) is similar to the Privalko-Lipatov relation,⁶ $N_c = 240 (D/\sigma)^{2.5}$, where σ is the chain stiffness factor. Moreover, Boyer and Miller⁷ pointed out that the exponent of the Privalko-Lipatov correlation should be between 2 and 2.2 instead of 2.5, thus supporting the proposed correlation.

Equation (4) predicts that for polymers with similar characteristic ratios C_∞ , like polyalkyl methacrylates, N_c should depend only on the polymer chain diameter D , or cross-sectional area S , as suggested by Boyer and Miller⁷ earlier. On the other hand, for polymers having similar average molecular diameters, N_c should decrease with increasing rigidity of the chains. This was indeed observed by Prevorsek and De Bona,²³ who reported that replacing a fraction of the flexible carbonate moiety in polycarbonates with a more rigid group (such as terephthalate) reduces the average molecular weight between entanglements.

The proposed correlation [eq. (3)] can also be reduced to a form which is similar to the Graessley-Edwards⁸ and Fox-Allen³ correlations for N_c . These authors found⁸

$$N_c \rho (\langle R^2 \rangle_0 / M) = 2.3 \times 10^{-14} \text{ cm}^{-1} \quad (5)$$

where ρ is the density of the polymer.

Using the relation proposed by Vincent,²⁴ $S = m_0 / (N_a \rho l_0)$ (m_0 is the average molecular weight per main-chain bond, and N_a Avogadro's number), one obtains, by combining eqs. (1), (2), and (3),

$$N_c \rho (\langle R^2 \rangle_0 / M) = 185 / (N_a l_0) \quad (6)$$

Taking a typical value, $l_0 = 1.5 \times 10^{-8}$ cm, the value on the right side of eq. (6) is $2.1 \times 10^{-14} \text{ cm}^{-1}$, showing a good agreement with eq. (5).

On the other hand, the proposed correlation [eq. (3)] has the following main advantages compared with the literature correlations:

- (1) Most of the literature correlations provide a purely empirical relation between N_c (or M_c) with some structural parameters of the polymer chains. As they are not dimensionally consistent, the connection between the molecular nature of entanglements and the critical molecular weight is unclear. In contrast, the proposed correlation [eq. (3)] is very simple, and is dimensionally consistent. It is also clearly related to the well-known reptation ("tube") models.^{12,13} The reptation models state that polymer chains entangle when their end-to-end distance becomes larger than the "diameter" of the tube. Equation (3) suggests that molecules move freely in any direction if their end-to-end distance is shorter than $13.6D$, whereas entanglement behavior occurs when the end-to-end distance of polymer chains becomes larger than $13.6D$. Moreover, the proposed correlation indicates that the diameter of the tube, which has been taken as an adjustable variable in the reptation models,¹³ is a well-defined parameter, determined by the diameter of the polymer chains.
- (2) The literature correlations generally fit one kind of polymer (flexible, rigid, or semirigid) and fail for the others.⁹⁻¹¹ The proposed correlation holds true not only for flexible chains (this was found by other authors³⁻⁹), but also for semirigid chains such as for polymers with high characteristic ratio C_∞ (polysty-

rene and polyacrylamide) and for polymers containing para-aromatic rings (polycarbonate and polysulfone). This also suggests that the entanglements in polymers may arise from a common effect of interaction between end-to-end distance and diameter of polymer chains.

- (3) The proposed correlation has a relatively small standard deviation being equal to 0.11 for thirty six polymers. This is much better than the correlations available so far.

In summary, we propose a correlation relating the critical end-to-end distance for entanglements $\langle R_c \rangle$ to the polymer chain diameter D . This correlation is consistent with the reptation concept. Moreover, the proposed correlation holds true not only for flexible polymer chains, but also for semi-rigid chains. This suggests that the entanglements in polymers may arise for a common effect of topological interactions between the end-to-end distance and polymer chain diameter. This correlation also provides a simple method to predict the critical molecular weight M_c from polymer chain rigidity and cross-sectional area. For example, it predicts that poly(2-ethylbutyl methacrylate) would have a somewhat larger critical molecular weight than that found in the literature. Further experimental assessments of this correlation will be necessary to understand the universal entanglement behavior of polymers.

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