

# Correlation Between Unperturbed Parameter and Critical Molecular Weight of Flexible Polymers

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A unique feature of amorphous polymers is the presence of entanglements that plays a prominent role in the understanding of the rheological properties of polymer.<sup>1</sup> The onset of this peculiar phenomenon in polymer melts may be associated with the critical molecular weight, hereafter designated as  $M_c$ , which is obtainable from the break point of a double logarithmic plot of the zero-shear viscosity ( $\eta_0$ ) and the molecular weight of polymer ( $M$ ).<sup>2</sup> It has been shown that  $M_c$  or, more precisely, the corresponding number of backbone chain atoms can be related to various chain parameters such as chain thickness,<sup>3</sup> cross-sectional area per polymer chain, and chain stiffness parameter,<sup>4</sup> as well as characteristic ratio and other.<sup>5,6</sup> Although these relationships are useful from a predictive point of view, they are yet to be justified theoretically.

Another important parameter that may be derived from the viscometric studies of the polymer solutions is the unperturbed parameter, hereafter denoted by  $K_\theta$ . This quantity measures the unperturbed dimension of a polymer by means of the Flory-Fox relation<sup>7</sup> and is easily accessible.<sup>8</sup> Aharoni has observed that  $\log K_\theta$  is a linear function of the ratio of molecular weight per repeat unit and number of backbone chain atoms per repeat unit.<sup>9</sup> However, no theory was proposed to explain the result. In this note, we present a molecular interpretation for a correlation between  $K_\theta$  and  $M_c$  of flexible polymers.

According to the close-packing<sup>10</sup> and lattice models<sup>11</sup> of semidilute polymer solutions, the  $K_\theta$  is inversely proportional to the critical concentration of polymer ( $C_0$ ) and the square root of polymer molecular weight, i.e.,

$$K_\theta = p / (C_0 \sqrt{M}) \quad (1)$$

where  $p$  is the proportionality constant. Recently, we have extended eq. (1) to deal with the influence of polydispersity of  $K_\theta$  based on the assumptions of uniform polymer concentration and Gaussian distribution of chain segments.<sup>12</sup> This semiempirical approach results in

$$p = \left( \frac{9}{\pi} \right)^{3/2} \left( \frac{\phi}{\alpha N_0} \right) \quad (2)$$

where  $\phi$  is the Flory's universal constant and  $N_0$  is the Avogadro's number.

Here,  $\alpha$  is a characteristic constant of the model defined by

$$\alpha = \rho_0/D_0 \quad (3)$$

where  $D_0$  is the overall segment density of all the polymer molecules near the center of mass of a particular component whose segment density is  $\rho_0$  in the vicinity of the same site.<sup>12</sup> This indicates that the reciprocal of  $\alpha$  is basically a factor monitoring the degree of polymer chain packing at the critical concentration  $C_0$ . Previous investigations have revealed  $1/\alpha = 2$ .<sup>12</sup>

It has been suggested empirically that the  $\eta_0$  of a polymer solution is directly proportional to a structural factor  $F$ , which is sensitive to  $M$  as well as the polymer concentration  $C$  at a constant temperature.<sup>13</sup> These  $F$ - $M$ - $C$  relationships are usually accessible by two main routes. The first approach involves plotting of  $\ln \eta_0$  vs.  $\ln C$  or other relevant graphical presentations.<sup>14</sup> An abrupt change in the dependent variable or a discontinuity of the curve would signify the  $C_0$ . If the molecular weight of polymer is relatively high (i.e.,  $M > M_c$ ), the  $C_0$  is probably in the semidilute regime, where the extent of coil overlap controls the flow properties.<sup>15,16</sup> Hence,  $C_0$  is physically regarded as an overlap concentration that corresponds to a critical degree of chain packing specifically with  $1/\alpha = 2$ , in the present context. Alternatively, one may collect the isothermal  $\eta_0$  data over a wide range of molecular weights of polymer whose concentration is fixed. For highly concentrated systems, the intersection of the conventional bilinear plot of  $\ln \eta_0$  vs.  $\ln M$  defines the critical molecular weight,  $M_s$ , which is independent of temperature but increases with dilution according to (1):

$$M_s = \rho M_c / C_* \quad (4)$$

where  $\rho$  is the density of bulk polymer and  $C_*$  is the concentration of the polymer in this particular study. The origin of eq. (4) is attributed principally to the importance of physical segment-segment contacts or chain entanglement.

The present analysis is based on a useful assumption that connects the two distinct critical concentrations by

$$C_0 = k\sqrt{C_*} \quad (5)$$

where  $k$  is a proportionality constant and both  $C_0$  and  $C_*$  refer to the same  $M$ . Manipulation of eqs. (1), (2), (4), and (5) by setting  $M = M_s$  yields

$$K_\theta = (9/\pi)^{3/2} (\phi / (\alpha N_0 k \rho^{1/2} M_c^{1/2})) \quad (6)$$

Equation (6) illustrates that a plot of  $\ln K_\theta$  vs.  $\ln(\rho M_c)$  should yield a straight line whose intercept and gradient are equal to  $\ln[(9/\pi)^{3/2}(\phi/\alpha N_0 k)]$  and  $-0.5$ , respectively.

A total of 35 representative flexible polymers including some semiflexible polymers is collected in Table I. The values of  $M_c$ ,  $K_\theta$ , and  $\rho$  are acquired respectively from references 17-19, unless otherwise specified. These data are plotted in Figure 1 with  $\ln K_\theta$  vs.  $\ln(\rho M_c)$ . The intercept and gradient of the

TABLE I  
Characteristic Parameters for Various Flexible Polymers

No.	Polymer	$M_c \times 10^{-4}$	$K_\theta$ (mL/g)	$\rho$ (g/mL) <sup>a</sup>
1	Polyacrylonitrile	0.133	0.250	1.18
2	Poly(tetramethylene oxide)	0.253	0.231	0.98
3	Poly(ethylene terephthalate)	0.327	0.210	1.34
4	Poly(2,6-dimethyl-1,4-phenyl oxide)	0.336	0.171	1.07
5	Polyethylene	0.350 <sup>b</sup>	0.225	0.85
6	Poly(ethylene oxide)	0.441	0.170	1.13
7	Poly(decamethylene adipate)	0.450 <sup>b</sup>	0.198 <sup>b</sup>	1.02 <sup>c</sup>
8	Poly(phenyl-silsequioxane)	0.452	0.220	1.20 <sup>c</sup>
9	Poly(decamethylene succinate)	0.470	0.196 <sup>b</sup>	1.06 <sup>c</sup>
10	Poly(hexamethylene adipamide)	0.470	0.196	1.07
11	Poly(carbonate of bisphenol A)	0.490	0.210	1.24
12	Poly(decamethylene sebacate)	0.490	0.220	1.00
13	Poly( $\epsilon$ -caprolactam)	0.500	0.208	1.08
14	Polyoxyundecanoyl	0.500	0.185	0.98 <sup>c</sup>
15	Cis-polybutadiene	0.590	0.205	0.89
16	Poly(tetramethylene adipate)	0.600 <sup>b</sup>	0.190 <sup>b</sup>	1.02
17	Poly(vinyl chloride)	0.630	0.156	1.39
18	Polypropylene(isotactic)	0.690	0.152	0.85
19	Cis-polyisoprene	0.77	0.129	0.91
20	Poly(propylene oxide)	0.78	0.116	1.00
21	Poly(2-vinylnaphthalate)	1.47	0.065	1.19
22	Polyisobutene	1.60	0.107	0.84
23	Poly(propylene sulfide) (isotactic)	2.00	0.060	1.04 <sup>c</sup>
24	Poly(methyl acrylate)	2.41	0.068	1.22
25	Poly(dimethyl siloxane)	2.45	0.077	0.98
26	Poly(vinyl acetate)	2.45	0.082	1.19
27	Poly( <i>N</i> -vinyl carbozole)	2.71	0.076	1.19 <sup>c</sup>
28	Polystyrene	3.50	0.084	1.05
29	Poly(methyl methacrylate)	3.63 <sup>d</sup>	0.059 <sup>b</sup>	1.17
30	Poly( $\alpha$ -methyl styrene)	4.08	0.076	1.07
31	Poly( <i>p</i> -methyl styrene)	5.01	0.069	1.04
32	Poly( <i>n</i> -butyl methacrylate)	6.04	0.038	1.06
33	Poly( <i>n</i> -hexyl methacrylate)	9.19	0.043	1.01
34	Poly( <i>n</i> -octyl methacrylate)	11.40	0.030	0.97
35	Poly( <i>n</i> -dodecyl methacrylate)	18.64	0.035	0.93

<sup>a</sup>For polymers in amorphous state at 25° C.

<sup>b</sup>Data obtained from Ref. 19.

<sup>c</sup>Estimated by the structural group additivity method outlined in Ref. 19.

<sup>d</sup>Obtained from Ref. 20.

linear least-squares regression line are respectively found to be 2.56 and  $-0.50$  with their respective standard deviations equal to 0.14 and 0.09. The linear correlation coefficient is  $-0.9573$  confirming the validity of eq. (6) statistically. The present analysis also concludes

$$K_\theta M_c^{1/2} \rho^{1/2} = 12.9 \pm 1.8 \text{ (mL/g)}^{1/2} \quad (7)$$

Incidentally, van Krevelen and Hoftyzer<sup>19</sup> have offered an empirical expres-

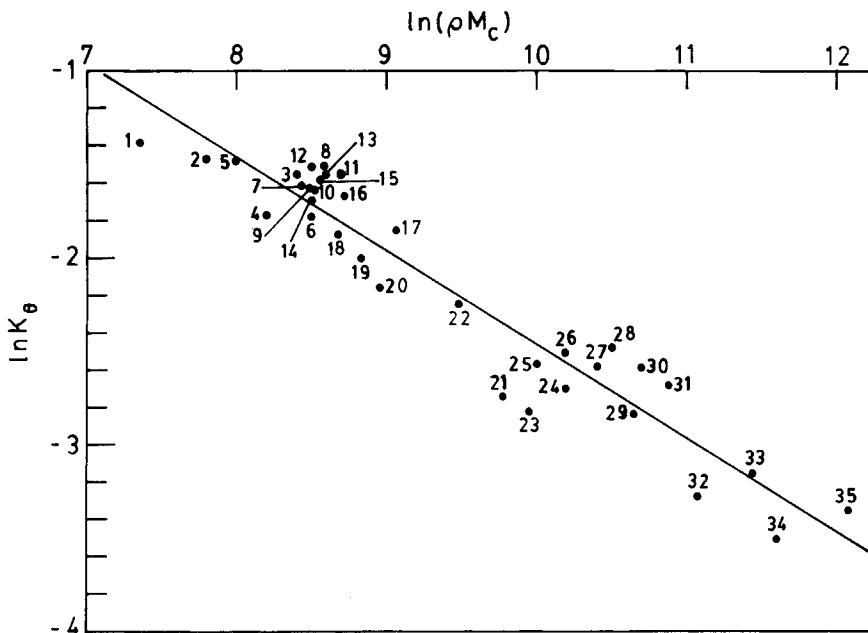


Fig. 1. Linear plot of  $\ln K_\theta$  vs.  $\ln(\rho M_c)$  for various flexible polymers. The data points are identified by the numerical codes of these polymers listed in Table I.

sion given as

$$K_\theta M_c^{1/2} = 13 \text{ (mL/g)} \quad (8)$$

Equations (7) and (8) are indeed comparable, since the values of  $\rho$  for most amorphous polymers are close to 1.0 g/mL.

The constant  $k$  is found to be 0.36. This means that the above critical value of  $1/\alpha$  is limited to  $C_0 < 0.36\sqrt{\rho}$  beyond which it is believed to exceed 2, since the polymer segments are more densely packed under this particular situation.<sup>21</sup> Apparently,  $k$  is independent of  $C_0$ , at least for a variety of flexible polymers analyzed herein. Hence, a reliable  $K_\theta$ - $M_c$  expression is established by assuming a simple correlation between the critical concentrations arising from the coil overlap and chain entanglement effects of polymeric systems.

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