

## On the Relationship Between $K$ and $a$ and Between $K_\theta$ and the Molecular Weight Per Chain Atom

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### Synopsis

It is shown that in  $[\eta] = KM^a$  there exists a relationship between  $K$  and  $a$  of the form  $\log K = C - Ba$ . The parameters  $C$  and  $B$  are typical of each polymer and, under  $\theta$  conditions, define a characteristic  $K_\theta$  for the polymer. When plotted against  $m_0/z$ , the molecular weight per backbone atom, the values of  $\log K_\theta$  cluster along three distinct lines. In a fashion similar to the observed dependence of number of atoms between chain entanglements on  $m_0/z$ , the lines are associated with highly flexible polymers, intermediate flexibility polymers, and stiff chain polymers. Deviations from the intermediate flexibility line are explained on the basis of changes in the distribution of mass in the plane perpendicular to the overall direction of the backbone chain.

### INTRODUCTION

For a given combination of linear polymer, solvent, and temperature, the intrinsic viscosity  $[\eta]$  appears to be a unique function of the molecular weight  $M$ . This function,

$$[\eta] = KM^a \quad (1)$$

is known as the Mark-Houwink equation. In it,  $K$  and  $a$  are two empirical constants,  $K$  has the dimension of reciprocal concentration, and  $a$  is dimensionless. Despite the apparent uniqueness of eq. (1), different values for  $K$  and  $a$  were found by different investigators for the same polymer-solvent-temperature systems, leading to a considerable scatter of data. Nevertheless, when many values of  $K$  are plotted against  $a$ , it became obvious that a distinct relationship exists between the two: the higher is  $a$ , the lower is the value of  $K$ .<sup>1,2,3</sup>

Two teams of researchers found that the data points cluster about a line represented by the equation

$$\log K = C - Ba \quad C < 0, B > 0 \quad (2)$$

VanKrevelen and Hoftyzer,<sup>1</sup> treating a relatively large number of points belonging to flexible polymers, and working in the range of  $0.5 \leq a \leq 1.0$ , determined that  $C = -1.42$  and  $-B = -3.00$ . Millich, Hellmuth and Huang,<sup>2,3</sup> treating data mostly of rigid rod molecules in the  $0.53 \leq a \leq 1.8$  range, found that  $C = -0.55$  and  $-B = -4.63$ . Both these teams used dl/g as the units of  $K$ . When  $K$  is expressed in units of ml/g, as will be the case throughout this paper,  $C$  increases by two whole units and, because of the magnitudes involved, eq. (2) transforms into

$$\log K = C - Ba \quad C > 0, B > 0 \quad (3)$$

Because each of the investigating teams above treated different bodies of data, one may expect that the constants  $B$  and  $C$  obtained by the two groups would be different. It must be emphasized that the parameters obtained by Millich et al.<sup>2</sup> pertain to relatively rigid polymers with very good fit of the data points to the calculated curve. The data of van Krevelen and Hoftyzer<sup>1</sup> pertain to many different flexible polymers and result in a broad scatter of points, making the derived constants unacceptable or just barely acceptable.

Under  $\theta$  conditions, i.e., a solvent-temperature combination that leaves the polymeric chain in its unperturbed configuration and dimension,

$$[\eta] = K_{\theta}M^{1/2} \quad (4)$$

where the coefficient  $K_{\theta}$  can be regarded as a characteristic parameter of any given polymer.<sup>1,4</sup>

### K-a RELATIONSHIP

About 600 data points, each representing one  $K$ - $a$  pair, were plotted to generate the  $K$ - $a$  relationships. Figures 1, 2, and 3 are typical. (Each of the eight lines in them stands, however, for only one entry in Table I.) From the intercept and slope of the lines, the parameters  $C$  and  $B$  were obtained. All polymers, except for polyelectrolytes, followed the linear  $\log K$ - $a$  relationship. In the case of polyelectrolytes, changes in the concentration of the solvent ions lead to different values of  $K$  for a given value of  $a$ .<sup>5</sup> Most of the information was extracted from Kurata et al.<sup>6</sup> Whenever sufficient data for a particular polymer were available, only the narrower molecular weight distributions, classified by Kurata et al.<sup>6</sup> under A, B, or R, were used. Otherwise, broader molecular weight distributions, classes C or D of Kurata et al.,<sup>6</sup> were employed. Similar considerations controlled the choice of data obtained under extreme temperature conditions. The widths of the molecular weight distribution and some extreme temperature results undoubtedly increase the scatter of the data points. Additional important data sources were Kurata and Stockmayer<sup>7</sup> and van Krevelen.<sup>8</sup>

Other data sources used in obtaining the  $\log K$  versus  $a$  plots are referenced in Table I. The standard deviation of  $\log K$ , as calculated from the differences between the experimental points and the corresponding curve, such as the eight curves in Figures 1, 2, and 3, together with the number of data points weighted in each statistic, are also given in the table. Except for the case of PVC, the scatter of data points is remarkably narrow, lending credence to each polymer being associated with its own curve.

The figures make it abundantly clear that for each polymer there exists a characteristic relationship between  $K$  and  $a$ . As was previously noted by Millich et al.,<sup>2</sup> this relationship is remarkably independent of solvent and, within a relatively broad interval, of temperature, too. It is of interest to note here that our  $C$  and  $B$  constants for "poly( $\gamma$ -benzyl L-glutamate) and others,"  $C = 1.60$  and  $B = 4.81$ , are in excellent agreement with the constants of Millich et al. When their constants are calculated in units of ml/g instead of dl/g, one obtains  $C = 1.45$  and  $B = 4.63$ .

Rearrangement of eq. (3) yields

$$a = (C/B) - (\log K)/B \quad (5)$$

TABLE I  
Characteristic Constants

Polymer	Constants for eq. (3)		Standard deviation of log $K$	No. of points in statistics	Source references
	$C$	$B$			
Polyethylene	1.29	3.56	0.075	16	6,7,8
Polypropylene	0.96	3.66	0.14	26	6,7,8
Polybutadiene	1.17	3.74	0.17	18	6,7,8
Polyisobutene	1.19	4.28	0.20	22	6,7,8
Polyisoprene	1.55	4.61	0.13	11	6,7,8
Poly(ethylene oxide)	1.35	4.36	0.15	20	6,7,8
Poly(vinyl acetate)	0.90	3.80	0.10	44	6,7,8
Poly(vinyl chloride)	1.87	4.76	0.36	18	6,7,8
Poly(methyl acrylate)	1.07	4.41	0.11	21	6,7,8
Poly(methyl methacrylate)	1.09	4.41	0.13	91	6,7,8
Sodium salt of poly(acrylic acid)	0.38	2.51	0.065	15	6
Polystyrene	0.86	3.97	0.070	125	6,7,8,9,10,11
Nylon 6	0.91	3.05	0.11	16	6,7,8
Poly(ethylene terephthalate)	1.82	4.37	0.21	22	6,7,8
Polyacrylonitrile	1.20	3.62	0.072	23	6,7,8
Polycarbonate of bisphenol A	1.36	3.95	0.049	10	6,8
Poly(phenylsilsequioxane)	2.08	5.65	0.17	8	6
Cellulose trinitrate	1.96	4.41	0.12	21	6
Poly( $\gamma$ -benzyl L-glutamate) and others	1.60	4.81	0.22	30	2,6,7,12,13
Poly(phenylquinoxaline) and others	1.18	3.82	0.030	6	6,7,14,15
Poly( $n$ -hexyl isocyanate)	1.40	3.89	0.024	12	16
Poly(vinylferrocene)	0.78	4.10	0.014	3	17

and

$$[\eta] = KM^{(C/B) - (\log K)/B} \quad (6)$$

relating  $[\eta]$  to  $M$  through three parameters,  $B$ ,  $C$ , and  $K$ , instead of through the two variables  $K$  and  $a$ .

Under  $\theta$  conditions,

$$\log K_\theta = C - (B/2) \quad (7)$$

indicating that  $K_\theta$  is indeed a characteristic quantity of each polymer. Hence, one can obtain the value of  $K_\theta$  through extrapolation of the  $\log K$  versus  $a$  plots even in cases where  $a \gg 0.5$ .

Theoretically, the value of  $a$  for macromolecules behaving as hydrodynamic solid spheres is  $a = 0$ ; and for macromolecules behaving as rigid rods,  $a = 2.0$ .<sup>18</sup>

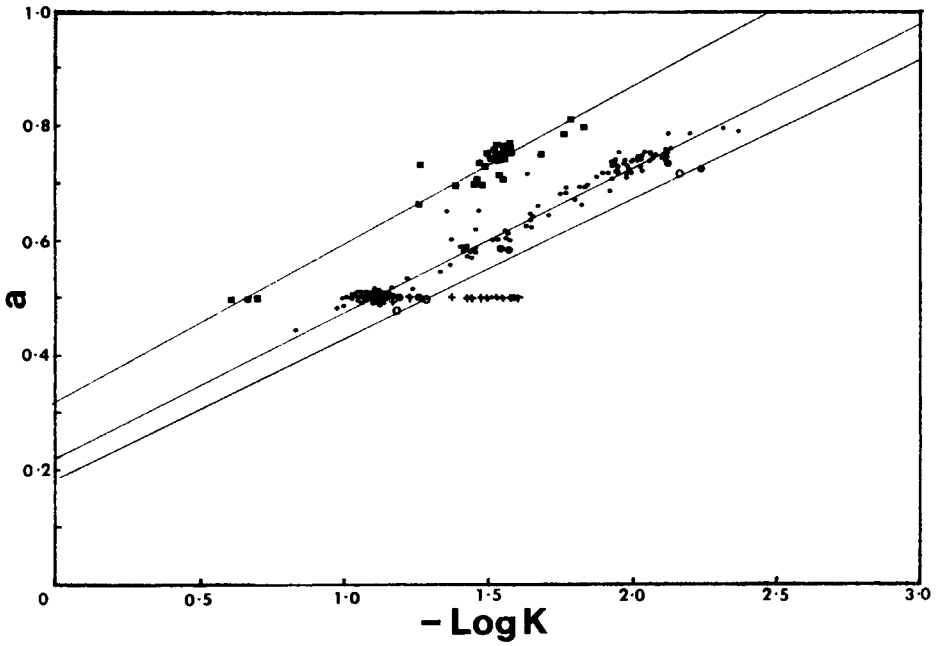


Fig. 1. Log  $K$ -vs.- $\alpha$  relationship for atactic polystyrene ( $\cdot$ ), star-shaped polystyrene ( $\bullet$ ), comb-shaped polystyrene ( $+$ ), polyacrylonitrile ( $\blacksquare$ ), and poly(vinylferrocene) ( $\circ$ ).

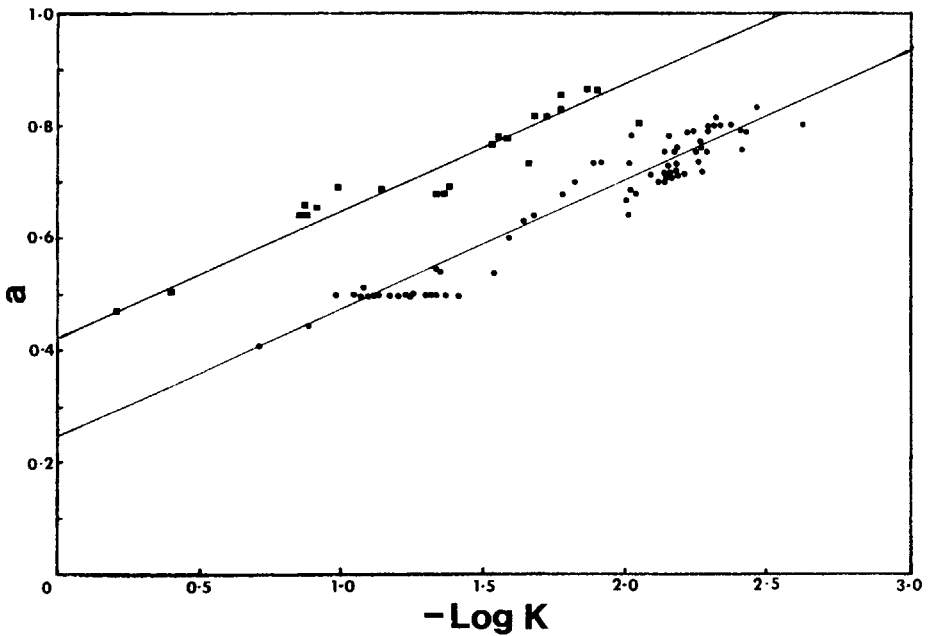


Fig. 2. Log  $K$ -vs.- $\alpha$  relationship for atactic and isotactic poly(methyl methacrylate) ( $\bullet$ ) and poly(ethyleneterephthalate) ( $\blacksquare$ ).

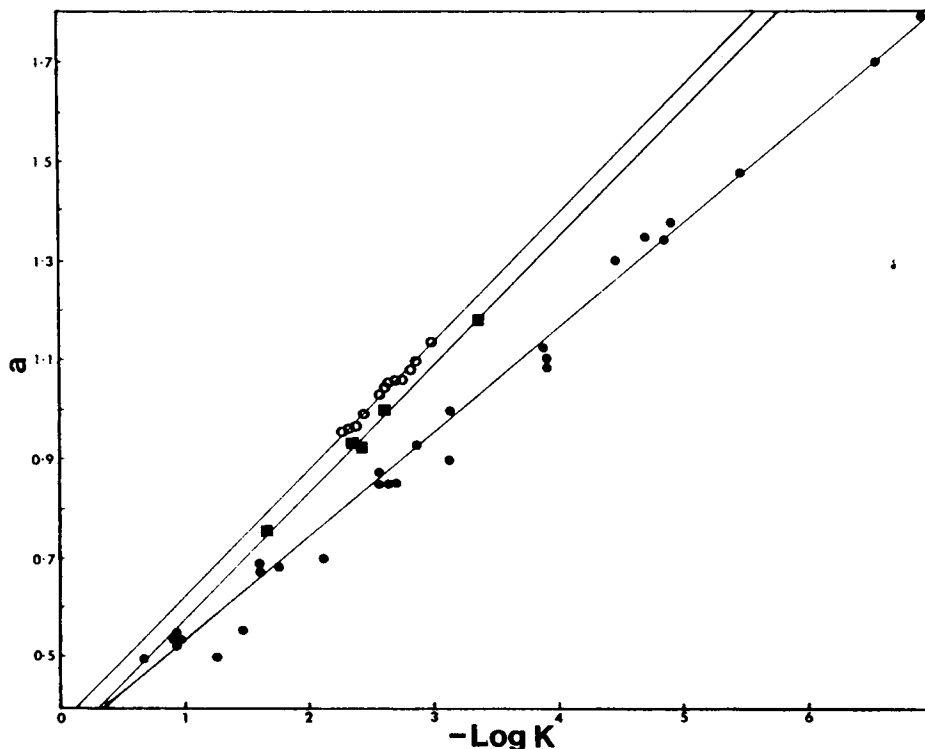


Fig. 3. Log  $K$ -vs.- $a$  relationship for poly( $\gamma$ -benzyl L-glutamate), polyaminoacids, poly(phenylsilsesquioxane), polyamides, and polyisocyanides (●); poly(phenylenebisphenylquinoxaline), poly( $n$ -butyl isocyanate), isotactic polypropylene, and poly(vinyl chloride) (■); and poly( $n$ -hexyl isocyanate) (○).

In this work, experimental data spanning the range of  $0.22 \leq a \leq 1.8$  and eight decades of  $K$  are covered. (The value of  $a = 0.22$  belongs to nylon 6 oligomers<sup>6</sup> and  $a = 1.8$ , to collagen.<sup>2</sup>) The linear relationship between  $\log K$  and  $a$  holds throughout the covered range.

Several data points of branched polystyrene, shown in Figure 1, indicate that branching causes some diminution in  $K_\theta$  and  $C$  values. The small number of points for branched nylon 6 are too scattered to show any trend.

The dependence of  $a$  on the hydrodynamic shape of the molecule, and the relationship between  $K$  and  $a$  described in eq. (3), define a dependence of  $K$  on the macromolecular shape. Accordingly, when the macromolecule behaves as a hydrodynamic solid sphere, the magnitude of  $K$  is the same as  $[\eta]$  since  $a = 0$  and  $M^0 = 1$ . When the macromolecule behaves as a rigid rod, the magnitude of  $K$  can easily be in the range of  $10^{-7}$  to  $10^{-10}$  ml/g. The diminution of  $K$  is, hence, associated with the uncoiling and straightening out of the macromolecular chain. One may speculate that the magnitude of  $K$  is dependent on the ability of the macromolecular chain to retain solvent. When the chain behaves as a collapsed coil, a large portion of its pervaded volume is filled with a nondraining solvent. At this point,  $K$  is large. On the other extreme,  $K$  becomes very small when the macromolecule is a rigid rod and the solvent around it drains practically completely.

**$K_\theta$ - $m_0/z$  RELATIONSHIP**

It has been shown recently by this author<sup>19</sup> that linear relationships exist between  $N_c$  and  $m_0/z$ . The  $N_c$  is the critical number of backbone chain atoms for entanglement,  $m_0$  is the molecular weight per repeat unit, and  $z$  is the number of backbone atoms per repeat unit. Figure 4 is a plot of  $N_c$  against  $m_0/z$ . The numerical data are given in Appendix I. Several polymers that were not reported in reference 19 and new data on some of the previously reported polymers are included. From the figure, it is obvious that when plotted against  $m_0/z$ , the  $N_c$  data points fall on three separate lines. The highly flexible polymers fall on line A; polymers of intermediate flexibility, on line B; and the stiff backbone polymers fall on line C. The equations describing these lines are

$$\text{A:} \quad N_c = 275 + 10.5(m_0/z) \quad (8a)$$

$$\text{B:} \quad N_c = 125 + 10.2(m_0/z) \quad (8b)$$

$$\text{C:} \quad N_c = 0 + 5.35(m_0/z) \quad (8c)$$

When  $\log K_\theta$  values are plotted against  $m_0/z$ , one finds that they, too, fall on three distinctly different lines. Here again, the differentiation is according to the overall flexibility of the polymer chains. In Figure 5,  $\log K_\theta$  values of close to 100 polymers, belonging to many structural families, are plotted against  $m_0/z$ . The data in numerical form are given in Appendix II. Whenever they were in the literature several, yet relatively close,  $K_\theta$  values, they were averaged out before taking the logarithm. The equations describing the lines in Figure 5 are

$$\text{Line A:} \quad \log K_\theta = 6.75 - 0.500(m_0/z) \quad (9a)$$

$$\text{Line B:} \quad \log K_\theta = 0.63 - 0.009035(m_0/z) \quad (9b)$$

$$\text{Line C:} \quad \log K_\theta = 0.89 + 0.008625(m_0/z) \quad (9c)$$

Combination of eqs. (8) and (9), followed by rearrangement, leads to the following relationships between  $N_c$  and  $\log K_\theta$ :

$$\text{Line A:} \quad N_c = -21 \log K_\theta + 417 \quad (10a)$$

$$\text{Line B:} \quad N_c = -1129 \log K_\theta - 586 \quad (10b)$$

$$\text{Line C:} \quad N_c = 620 \log K_\theta + 552 \quad (10c)$$

Now, it is well known that

$$K_\theta = \Phi(\langle L^2 \rangle / M)^{3/2} \quad (11)$$

where  $\Phi$  is Flory's constant and  $\langle L^2 \rangle$  is the mean square end-to-end distance.  $\langle L^2 \rangle / M$  is, then, a measure of the polymer chain expansion per unit molecular weight. In light of eq. (9), one reaches the conclusion that, when chain expansion is considered as a function of  $m_0/z$ , polymers fall into three broad, yet distinct, categories. In the case of highly flexible chains, line A in Figure 5, a small increment in  $m_0/z$  causes very sharp diminution in  $\langle L^2 \rangle / M$ . The flexible chain rapidly becomes more compact. In the case of intermediate polymers, line B, increases in  $m_0/z$  are associated with only moderate decreases in  $\langle L^2 \rangle / M$ . In the case of the stiff polymers, line C, an increase in  $m_0/z$  causes a moderate increase in  $\langle L^2 \rangle / M$ ; that is, when the weight per chain atom of a stiff polymer chain is increased, the chain becomes less coiled, more similar to a rigid rod.

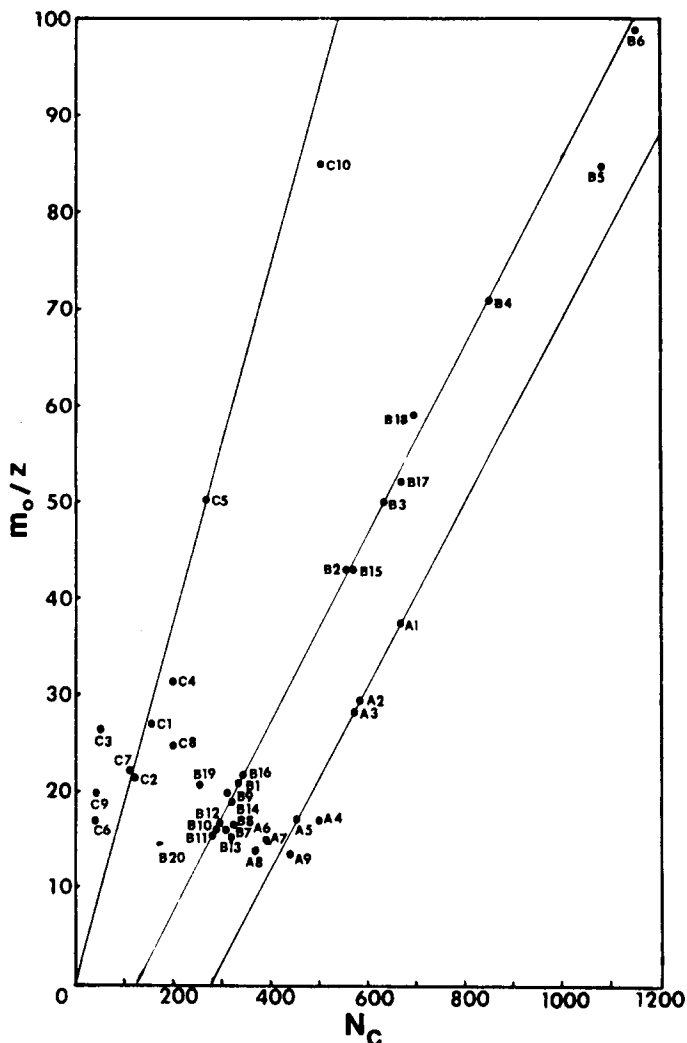


Fig. 4.  $N_c$ -vs.- $m_0/z$  relationship. Polymers listed in Appendix I.

A secondary factor controlling the behavior of polymer chains under  $\theta$  conditions, beyond the flexibility factor, is the distribution of mass in the plane perpendicular to the general direction of the backbone. In the highly flexible polymers, line A in Figure 5, the molecular mass  $m_0/z$  is not large and is practically all concentrated in the backbone atoms. In the stiff polymers backbone, rigidity effectively controls the polymer behavior. There are also not enough literature data to indicate whether the scatter of points about line C in the figure is indicative of any structural characteristic. The number of data points along line B, describing intermediate flexibility polymers, is sufficiently large to reveal that the scatter of points along this line is meaningful.

In general, a significant portion of  $m_0/z$  of the polymers conforming with line B is not right in the polymer backbone but in atoms pendent to it. This is the major difference in mass distribution between polymers described by lines A and

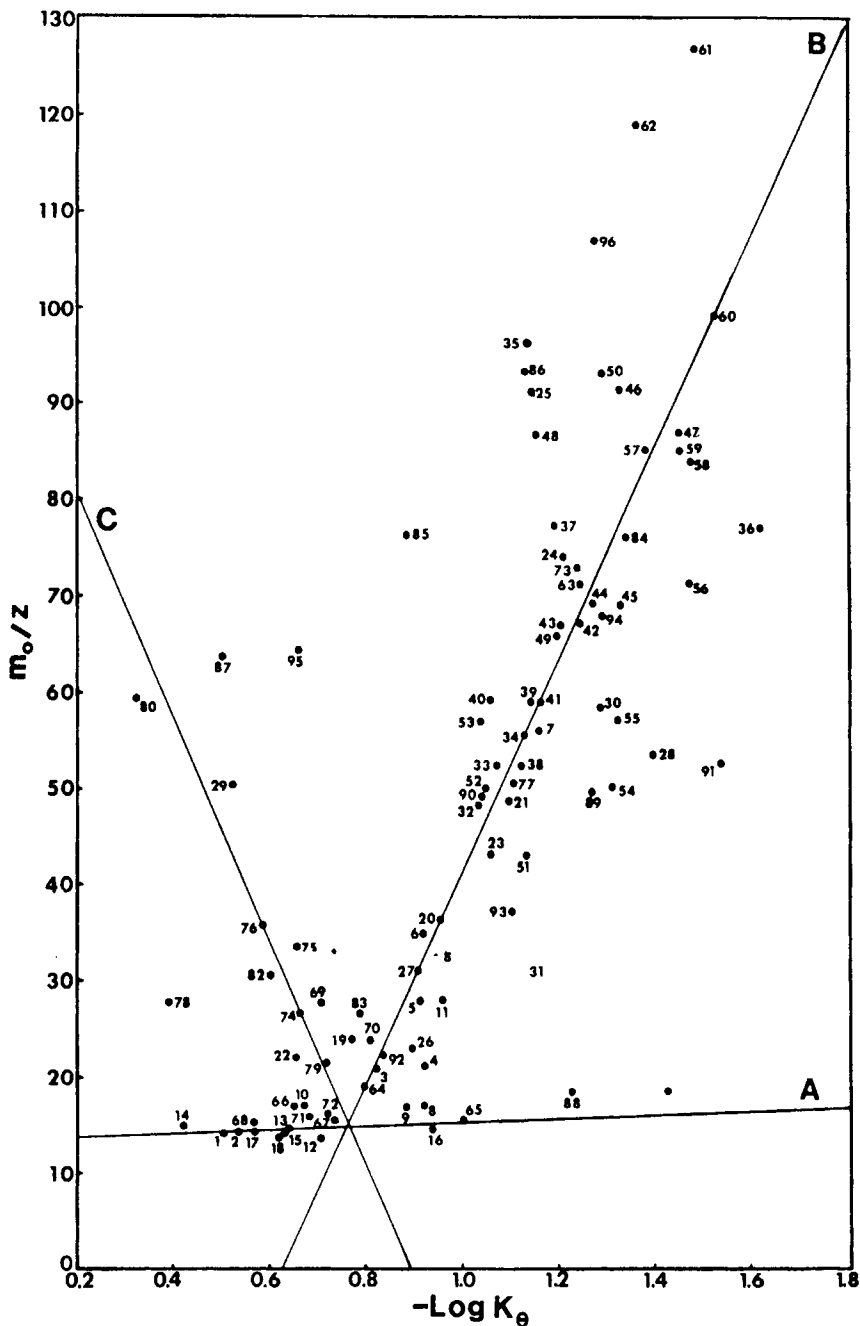


Fig. 5.  $\log N_{\theta}$ -vs.- $m_0/z$  relationship. Polymers listed in Appendix II.

B. The data points significantly away from line B are divisible into two groups. One group, to the right of line B, contains such polymers as poly(vinyl bromide) (28), poly(vinylidene fluoride) (31), poly(1-vinyl naphthalene) (36), poly(hexene-1 sulfone) (89), and poly(bicycloheptane sulfone) (91). These polymers are characterized by relatively high concentration of mass near to, but not exactly



in, the polymer backbone. They are all reasonably flexible; but due to their distribution of mass, their compactness about the chain backbone is enhanced. Surprisingly, three low homologs of the polymethacrylate family, methyl (54), ethyl (55), and *n*-butyl (56), also fall in this range. This behavior is yet unaccounted for. To the left of line B, there exists another group of polymers significantly deviating from the line. These polymers are poly(vinyl 4-chlorobenzoate) (25), poly(vinylcarbazole) (35), poly(3,4-dichlorostyrene) (48), poly(4-cyclohexylstyrene) (50), poly(dodecyl methacrylate) (61), poly(*p*-biphenyl methacrylate) (62), poly(isobutyldioxopyrrolidine) (85), poly(*p*-tolylidioxopyrrolidine) (86), and poly(vinylferrocene) (96). These polymers are all characterized by most of their  $m_0/z$  mass being a rather long distance from the backbone atoms. Because of the bulkiness of their pendent groups and their distance from the backbone, these polymers are typified by a compactness about their backbones which is significantly reduced relative to most other polymers that follow line B.

The points of cellulose trinitrate (80) and poly(*n*-hexyl isocyanate) (87), straddling line C, were extrapolated by us from plots of  $\log K$  versus  $a$ . In the first instance, the smallest available  $a$  value was 0.78; and in the second case,  $a = 0.96$  (see Fig. 3). One  $K_\theta$  value reported in the literature<sup>6</sup> for cellulose trinitrate is several times larger than the extrapolated one, leading to a  $\log K_\theta$  value far out of line for the stiff polymers. No experimentally determined  $K_\theta$  value for poly(*n*-hexyl isocyanate) is known to us.

In general, there is a remarkably good agreement between values of  $\log K_\theta$  obtained from plots of  $\log K$  versus  $a$  and experimentally obtained literature values of  $\log K_\theta$ .

Curiously, the three lines in Figure 5 intersect at a single point, describing an "average" polymer whose parameters are  $m_0/z = 14.8$  and  $\log K_\theta = -0.76$ . Employing a value of  $\Phi = 2.5 \times 10^{23}$  in eq. (11), one obtains the value of  $\langle L \rangle / M^{1/2} = 880 \times 10^{-4}$  nm as the expansivity measure of the "average" polymer. Multiplication by  $(42700)^{1/2}$ , the square root of  $M_M$ , intrinsic isoviscosity molecular weight of Millich et al.,<sup>2</sup> yields  $\langle L \rangle = 182 \text{ \AA}$ , which compares well with their value of 160–180  $\text{\AA}$ .

## CONCLUSIONS

The parameters  $K$  and  $a$  in the equation  $[\eta] = KM^a$  are a function of one another. This function is  $\log K = C - Ba$ , with  $C$  and  $B$  being typical of each linear polymer. The  $K$ - $a$  relationship holds over the tested range of  $0.22 \leq a \leq 1.8$  and eight decades of  $K$ . The diminution of  $K$  with improved solvent conceivably reflects the ability of the solvent to uncoil the polymer backbone and drain away from the uncoiled chain.

Under  $\theta$  conditions,  $\log K_\theta = C - (B/2)$  and the parameter  $K_\theta$  are characteristic properties of each polymer. When  $\log K_\theta$  values of many polymers are plotted against their respective  $m_0/z$  values, the data points tend to cluster about three mutually intersecting lines. The common denominator for the polymers associated with each line is their measure of chain flexibility. The lines describe polymers that are highly flexible, of intermediate flexibility, and relatively stiff. This kind of dependence on  $m_0/z$  bears a strong resemblance to the dependence of  $N_c$  on  $m_0/z$ , also differentiated according to chain flexibility.

A secondary effect is observed along the intermediate flexibility line. Here, a group of polymers with relatively high concentration of mass close to, but not on, their backbone are displaced from the line in one direction. Another group of polymers, with large  $m_0/z$  being centered far away from the backbone, are displaced in the opposite direction.

Appendix I  
Entanglement Parameters

No.	Polymer	$m_0$	$z^a$	$m_0/z$	$N_c$ (reference)
A1	Poly(dimethylsiloxane)	74.1	2	37.1	660 (1)
A2	Poly(tetramethyl- <i>p</i> -silphenylenesiloxane)	208	7	29.7	582 (1)
A3	Polyisobutene	56.1	2	28.1	570 (2)
A4	Hevea (natural) rubber	68.1	4	17.0	500 (3)
A5	Poly- <i>cis</i> -isoprene	68.1	4	17.0	450 (2)
A6	Poly(propylene oxide)	58.1	4	14.6	400 (4)
A7	Poly(ethylene oxide)	44.1	3	14.7	400 (1)
A8	Polyethylene	28.1	2	14.1	364 (5)
A9	<i>cis</i> -1,4-Polybutadiene	54.1	4	13.5	440 (6,7)
B1	Polypropylene	42	2	21.0	328 (3)
B2	Poly(methyl acrylate)	86.1	2	43	560 (8)
B3	Poly(methyl methacrylate)	100.1	2	50	630 (4)
B4	Poly( <i>n</i> -butyl methacrylate)	142.2	2	71.1	~ 850 (3)
B5	Poly( <i>n</i> -hexyl methacrylate)	170.2	2	85.1	1080 (9)
B6	Poly( <i>n</i> -octyl methacrylate)	198.3	2	99.1	~1150 (3)
B7	Poly- $\epsilon$ -caprolactam, nylon 6	113.2	7	16.2	310 (2,4)
B8	Poly( $\epsilon$ -caprolactam sebacic acid)	297	18	16.5	324 (3)
B9	Poly(diethylene adipate)	200.2	10	20.0	310 (4)
B10	Poly(decamethylene succinate)	256.3	16	16.1	290 (3)
B11	Poly(decamethylene adipate)	284.4	18	15.7	280 (3)
B12	Poly(decamethylene sebacate)	340.5	20	17.0	290 (3)
B13	Poly( $\omega$ -hydroxy undecanoate)	184	12	15.3	< 326 (3)
B14	Poly(ethylene terephthalate)	192	10	19.2	320 (10) <sup>b</sup>
B15	Poly(vinyl acetate)	86	2	43	570 (3)
B16	Poly(vinyl alcohol)	44	2	22	340 (3)
B17	Polystyrene	104.1	2	52.0	673 (3)
B18	Poly( $\alpha$ -methylstyrene)	118.1	2	59.1	690 (11) <sup>c</sup>
B19	Polycarbonate of bisphenol A and ethylene	310.3	15	20.2	251 (12)
B20	Poly(tetramethylene oxide)	72	5	14.4	175 (13)
C1	1,2-Polybutadiene	54.1	2	27.0	152 (14,15)

(continued)

## Appendix I (continued)

No.	Polymer	$m_0$	$z^a$	$m_0/z$	$N_c$ (reference)
C2	Polycarbonate of bisphenol A	254.3	12	21.2	114 (16)
C3	Polyacrylonitrile	53.1	2	26.5	~ 50 (17)
C4	Poly(vinyl chloride)	62.5	2	31.2	200 (1)
C5	Poly(tetrafluoroethylene)	100.2	2	50.1	264 (3)
C6	BBB (naphthalene tetracarboxylic acid + diamino benzidine)	410	24	17.0	35 (18)
C7	Polysulfone (Union Carbide)	442	20	22.1	113 (19)
C8	Polyester of bisphenol A and 1,1,3-trimethyl-3-phenylindan-4',5-dicarboxylic acid, PIBPA	516	21	24.6	203 (12)
C9	Poly- <i>p</i> -benzamide	119	6	19.8	38 (20)
C10	Poly(2-ethylbutyl methacrylate)	170.2	2	85.1	503 (21)

<sup>a</sup> Number of backbone chain atoms per repeat unit, *p*-phenyl counts as four atoms, etc.

<sup>b</sup> Indicate that  $M_c$  is lower than 7250 and higher than 5000. The average value of  $M_c = 3200$  was used.

<sup>c</sup> Calculated from  $M_w = 380,000$  and critical concentration of 10.7% (extracted from Fig. 2).

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Appendix II  
 Log  $K_{\theta}$  Values

No.	Polymer	$m_0$	$z$	$m_0/z$	$-\log K_{\theta}$ (reference)
1	Polymethylene	14.1	1	14.1	0.504 (1)
2	Polyethylene	28.1	2	14.1	0.531 (2)
3	Polypropylene, atactic	42	2	21	0.827 (2)
4	Polypropylene, isotactic	42	2	21	0.921 (2)
5	Poly-1-butene	56	2	28	0.910 (2)
6	Poly-1-pentene	70	2	35	0.917 (2)
7	Poly-1-octene	112	2	56	1.163 (2)
8	Natural rubber	68.1	4	17	0.924 (2)
9	Poly- <i>cis</i> -isoprene	68.1	4	17	0.886 (2)
10	Gutta Percha	68.1	4	17	0.667 (2)
11	Polyisobutene	56.1	2	28.1	0.958 (2)
12	Poly- <i>cis</i> -1,4- butadiene	54.1	4	13.5	0.705 (2)
13	Poly- <i>trans</i> - pentamer	68	5	13.6	0.631 (3)
14	Poly(methylene oxide)	30	2	15	0.420 (4)
15	Poly(ethylene oxide)	44.1	3	14.2	0.638 (4)
16	Poly(propylene oxide)	58.1	4	14.6	0.939 (4)
17	Poly(tetra- methylene oxide)	72.1	5	14.4	0.569 (4)
18	Poly(deca- methylene oxide)	156	11	14.2	0.620 (2)
19	Poly(2,6-di- methyl-1,4- phenylene oxide)	120	5	24	0.769 (2)
20	Poly(2-methyl- 6-phenyl-1,4- phenylene oxide)	182	5	36.4	0.959 (2)
21	Poly(2,6-di- phenyl-1,4- phenylene oxide)	244	5	48.8	1.097 (2)
22	Poly(vinyl alcohol)	44	2	22	0.654 (2)
23	Poly(vinyl acetate)	86	2	43	1.054 (2)
24	Poly(vinyl benzoate)	148.2	2	74.1	1.208 (2)
25	Poly(vinyl 4- chloroben- zoate)	182.7	2	91.4	1.137 (2)
26	Poly(vinyl fluoride)	46	2	23	0.893 (2)
27	Poly(vinyl chloride)	62.5	2	31.2	0.904 (2)

(continued)

## Appendix II (Continued)

No.	Polymer	$m_0$	$z$	$m_0/z$	$-\log K_\theta$ (reference)
28	Poly(vinyl bromide)	107	2	53.5	1.398 (2)
29	Poly(tetrafluoroethylene)	100.2	2	50.1	0.523 (2)
30	Poly(chlorotrifluoroethylene)	116.5	2	58.3	1.284 (2)
31	Poly(vinylidene fluoride)	64	2	32	1.161 (5)
32	Poly(vinylidene chloride)	97	2	48.5	1.022 (6)
33	Poly(2-vinylpyridine)	105	2	52.5	1.086 (4)
34	Poly(2-vinylpyrrolidone)	111.1	2	58.6	1.131 (4)
35	Poly(vinylcarbazole)	193.2	2	96.6	1.131 (4)
36	Poly(1-vinylnaphthalene)	154.2	2	77.1	1.616 (2)
37	Poly(2-vinylnaphthalene)	154.2	2	77.1	1.189 (2)
38	Polystyrene	104.1	2	52	1.1215 (2)
39	Poly( $\alpha$ -methylstyrene)	118.1	2	59.1	1.141 (2)
40	Poly( <i>m</i> -methylstyrene)	118.1	2	59.1	1.061 (2)
41	Poly( <i>p</i> -methylstyrene)	118.1	2	59.1	1.161 (2)
42	Poly( <i>o</i> -methoxystyrene)	134.2	2	67.1	1.240 (2)
43	Poly( <i>p</i> -methoxystyrene)	134.2	2	67.1	1.207 (2)
44	Poly(4-chlorostyrene)	138.6	2	69.3	1.269 (2)
45	Poly(2-chlorostyrene)	138.6	2	69.3	1.330 (7)
46	Poly(4-bromostyrene)	183	2	91.5	1.324 (2)
47	Poly(2,5-dichlorostyrene)	174.1	2	87	1.450 (2)
48	Poly(3,4-dichlorostyrene)	174.1	2	87	1.149 (2)
49	Poly(2,4-dimethylstyrene)	132.1	2	66	1.194 (8)
50	Poly(4-cyclohexylstyrene)	186	2	93	1.284 (2)
51	Poly(methyl acrylate)	86.1	2	43	1.132 (2)
52	Poly(ethyl acrylate)	100	2	50	1.046 (2)

(continued)

## Appendix II (Continued)

No.	Polymer	$m_0$	$z$	$m_0/z$	$-\log K_\theta$ (reference)
53	Poly(isopropyl acrylate)	114	2	57	1.036 (2)
54	Poly(methyl methacrylate)	100.1	2	50	1.311 (2)
55	Poly(ethyl acrylate)	114	2	57	1.318 (2)
56	Poly( <i>n</i> -butyl methacrylate)	142.2	2	71.1	1.469 (2)
57	Poly( <i>n</i> -hexyl methacrylate)	170.2	2	85.1	1.377 (2)
58	Poly(cyclohexyl methacrylate)	168	2	84	1.468 (2)
59	Poly(2-ethyl-butyl methacrylate)	170.2	2	85.1	1.444 (2)
60	Poly( <i>n</i> -octyl methacrylate)	198.3	2	99.1	1.523 (2)
61	Poly(dodecyl methacrylate)	254	2	127	1.475 (2)
62	Poly( <i>p</i> -biphenyl methacrylate)	238	2	119	1.357 (9)
63	Poly(methyl butacrylate)	142.2	2	71.1	1.244 (2)
64	Poly(ethylene terephthalate)	192	10	19.2	0.796 (2)
65	Poly(decamethylene adipate)	284.4	18	15.7	1.0 (2)
66	Poly decamethylene sebacate	340.5	20	17.0	0.658 (2)
67	Poly( $\omega$ -hydroxy undecanoate)	184	12	15.3	0.733 (2)
68	Poly(decanediol sebacate)	340	22	15.5	0.569 (2)
69	Polyester of isophthalic acid and 3-oxo-isobenzofurane-1,1-diphenylene	448	16	28	0.710 (2)
70	POLA, poly[4, 4'-isopropylidene diphenylene-1,1, 3-trimethyl (-3-phenylindan-4',5-dicarboxylate)]	506	21	24.1	0.807 (10)
71	Nylon 6, polycaprolactam	113.2	7	16.2	0.681 (2)
72	Nylon 66, Poly(Hexamethylene adipamide)	226.4	14	16.2	0.721 (2)

(continued)

## Appendix II (Continued)

No.	Polymer	$m_0$	$z$	$m_0/z$	$-\log K_\theta$ (reference)
73	Poly( $\gamma$ -benzyl L-glutamate)	219	3	73	1.233 (2)
74	Polyacryloni- trile	53.1	2	26.5	0.660 (2)
75	Polymethacry- lonitrile	67.1	2	33.6	0.658 (4)
76	Polyacrylam- ide	71	2	35.5	0.585 (2)
77	Poly(N,N-di- methylacryl- amide)	101	2	50.5	1.108 (2)
78	Poly(9'-fluorene- 4-dianiline terephthalam- ide)	478	17	28.1	0.388 (2)
79	Polycarbonate of bisphenol A	254.3	12	21.2	0.713 (2)
80	Cellulose trini- trate	297	5	59.4	0.886 (2), 0.32 <sup>a</sup>
81	Amylose	162	5	32.4	0.947 (2)
82	Poly[2,2'-(1,4- phenylene)-6, 6'-bis(3-phenyl- quinoxaline)], PPQ	484	16	30.3	0.60 <sup>a</sup> (11)
83	Phenol-formal- dehyde, novo- lak	106	4	26.5	0.785 (12)
84	Polyacenaph- thalene	152	2	76	1.341 (13)
85	Poly(isobutyl- dioxopyrrol- idine)	153	2	76.5	0.879 (2)
86	Poly( <i>p</i> -tolyl- dioxopyrrol- idine)	187	2	93.5	1.125 (2)
87	Poly( <i>n</i> -hexyl isocyanate)	127	2	63.5	0.50 <sup>a</sup>
88	Poly(propylene sulfide)	74.1	4	18.5	1.222 (2)
89	Poly(hexene-1 sulfone)	148	3	49.3	1.276 (14)
90	Poly(2-methyl- pentene-1 sulfone)	148	3	49.3	1.041 (14)
91	Poly(bicyclo- heptane sul- fone)	158	3	52.7	1.53 (15)
92	Poly(bisphenol A diphenyl sulfone)	442	20	22.1	0.839 (16)
93	Poly(dimethyl- siloxane)	74.1	2	37.1	1.107 (2)

(continued)

## Appendix II (Continued)

No.	Polymer	$m_0$	$z$	$m_0/z$	$-\log K_\theta$ (reference)
94	Poly(methyl-phenyl siloxane)	136	2	68	1.288 (17)
95	Poly(phenyl-silsesquioxane)	129	2	64.5	0.658 (2)
96	Poly(vinyl-ferrocene)	213	2	106.5	1.275 (18)

<sup>a</sup> Extrapolated from  $a$ -vs.  $-\log K_\theta$  curve.

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