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On Entanglements of Flexible and Rodlike Polymers

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ABSTRACT: Values of N_c, the number of chain atoms between "entanglements", were obtained for 62 flexible, semiflexible, and rodlike polymers and plotted against the corresponding values of the characteristic ratio C_∞ or the Kuhn step length A. It was found that the polymers are nicely divisible into the three groups above. Despite some scatter, the flexible polymers fall in a band about a line described by $N_c \propto C_\infty^2$ or $N_c \propto A^2$ and more specifically, $N_c \cong 10C_\infty^2$ or $N_c \cong (2.5\ \text{Å}^{-2})A^2$. In the case of rodlike polymers, the exponential dependence is less than 1.0, but the scatter prevents closer approximations. The semiflexible polymers fall in between the two extreme classes. When L_c, the chain length between "entanglements", is plotted against C_∞ or A, again a $L_c \propto C_\infty^2$ or $L_c \propto A^2$ relationship is obtained for flexible polymers. However, when R_c, the spatial distance between "entanglements" of flexible chains, is plotted, then relationships of the form $R_c \propto C_\infty$ or $R_c \propto A$ are obtained. The observations are discussed in terms of the "entanglements" being interferences to the translational and rotational mobility of whole rodlike molecules or whole or large parts of flexible macromolecules. The empirical relationships for flexible polymers indicated above are in excellent agreement with recent theoretical expectations in the literature.

Introduction

"Entanglements" appear in molten bulk or highly concentrated solutions of long-chain molecules when these are forced by external force out of their state of equilibrium. In the case of flexible polymers, topological "entanglements" may serve as a valid model, but in the case of rodlike macromolecules, where apparent "entanglements" become manifest in relatively dilute, isotropic solutions, the physical meaning of "entanglements" remains obscure. In the case of rigid-rod polymers, the change in macroscopic behavior conventionally associated with the onset of entangled behavior may better be described in terms of concentration-dependent onset of interference to the free rotational and translational movement of the long rodlike molecules, reflected in rather abrupt decrease in their diffusion constants and an increase in solution viscosity. The interference with free movement, both rotational and translational, of flexible[1-5] as well as rodlike[6-9] chains was recently explained in terms of the reptation model. Comparisons of expectations based on the reptation theory with experimental results now appear in rapid succession. Several pertinent examples are given in ref 10–13.

Besides efforts directed at understanding the physical meaning of "entanglements", which will not be addressed in this work, the question arises as to the reason for the uniqueness to each undiluted polymer of the characteristic molecular weight between "entanglements", M_c, or the corresponding characteristic number of chain backbone atoms, N_c. Dilution of high molecular weight, M, polymers with $M \gg M_c$, does not significantly affect the "entanglement" interaction between polymer chains, as it was experimentally observed[14] that the onset of entangled behavior at a concentration c is well approximated by

$$(cM)_c \cong M_c \tag{1}$$

where $(cM)_c$ is the product of concentration and molecular weight at the point of onset of entangled behavior.

Based on the model of topological "entanglements", several empirical attempts were made in recent years to correlate M_c or N_c with some structural parameters of flexible polymers. The most extensive compilations of data assembled for such correlations are those of Boyer and Miller,[15-20] Privalko and Lipatov,[21-25] and Aharoni.[26-28] A comparison of these references reveals that the approaches adopted by the different authors are fundamentally similar to each other even though some scatter of data points and deviations from expectations exist. We believe that the choice of

$$M_c = 2M_e \tag{2}$$

is a contributing factor to the data scatter, besides the effects of heavy pendant atoms or groups on the correspondence of M_c to N_c. Here, M_e is the molecular weight between "entanglements" as obtained from the plateau modulus G_N^0 of the polymer:[29]

$$G_N^0 = cRT/M_e \tag{3}$$

with R being the molar gas constant and T the absolute temperature. Allowing more accurate ratios of M_c/M_e (usually slightly over 2.0) to be used in the calculations of M_c and N_c from M_e undoubtedly will reduce the scatter of the data. However, due to the paucity of such precise data and in light of the fact that the large majority of M_c and N_c data assembled in this work were obtained from viscosity data of melts or concentrated solutions, all values of M_c obtained from M_e will be calculated according to eq 2 in order to maximize the number of evaluated polymers. In light of the results shown below, we do not believe that the data scatter significantly affects observed trends. In fact, attaching error bars of ±50% to N_c values in Table I did not affect the trends seen in Figures 1–6. Because they so clutter the picture, the error bars were omitted from the figures.

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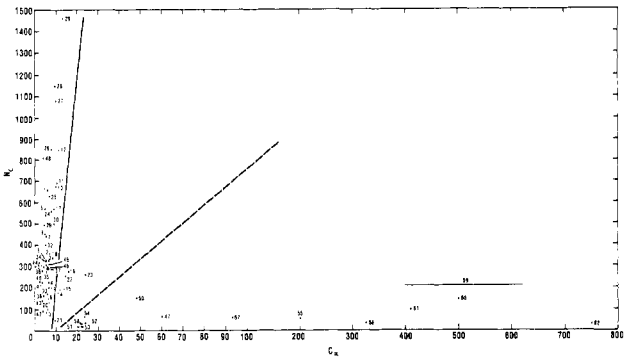

Figure 1. Linear plot of N_c vs. C_∞. Notice change of scale on C_∞ axis.

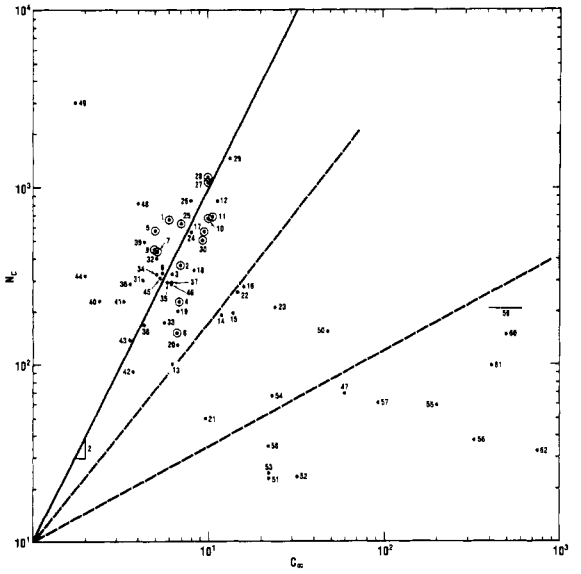

Figure 2. Double-logarithmic plot of N_c vs. C_∞.

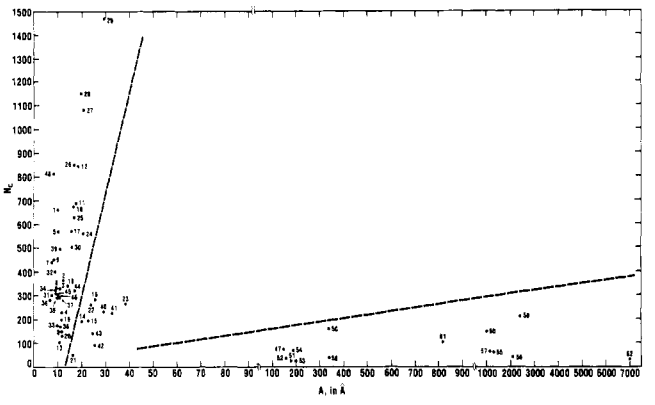

Figure 3. Linear plot of N_c vs. A. Notice two changes of scale on A axis.

Recently, there appeared a new treatment[30] of topological "entanglements" of flexible polymers. For the 15 flexible polymers plotted in Figure 1 of ref 30, there appears to exist a power law of the form

$$G_N^0 A^3/kT \propto (nLA^2)^a \tag{4}$$

with the exponent a being approximately 2. Here, k is Boltzmann's constant, L is the chain contour length, n is the number of chains per unit volume, and A is the Kuhn step length, defined[31] as

$$A = (C_\infty + 1)l \tag{5}$$

where C_∞ is the characteristic ratio and l is the average length of the real or virtual main-chain bond. It should

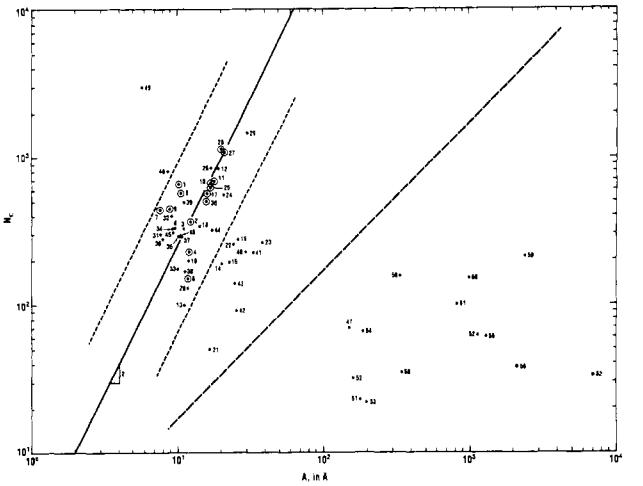

Figure 4. Double-logarithmic plot of N_c vs. A.

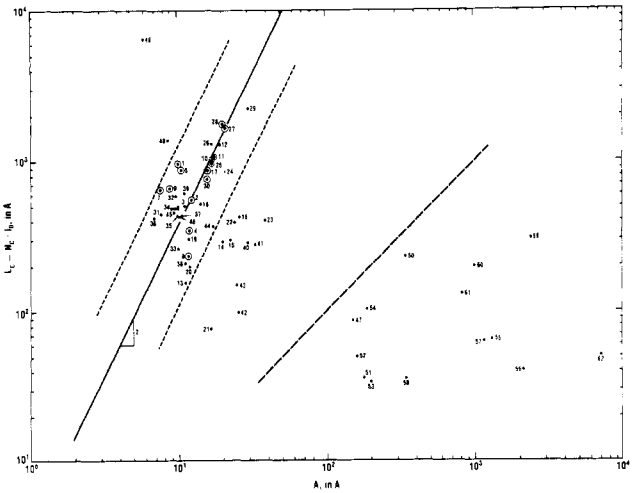

Figure 5. Double-logarithmic plot of L_c vs. A.

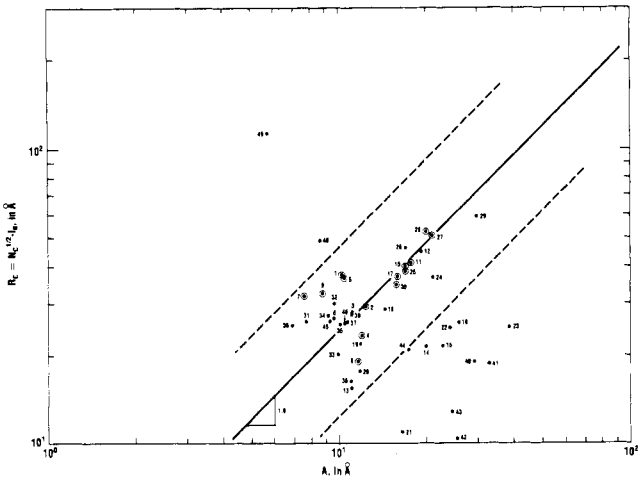

Figure 6. Double-logarithmic plot of R_c vs. A. Data of only flexible and semiflexible polymers are shown; see text.

be recognized that G_N^0 is proportional to $1/N_c$ and that nL, the total length of chain contour per unit volume, is inversely proportional to d^2, the chain cross-sectional area. Thus, proportionality 4 can be recast as

$$A^3/N_c kT \propto (A^2/d^2)^a \tag{6}$$

with the ratio A/d being the axial ratio of the chain Kuhn step length.

In a recent paper, Klein[5] treated the onset of entangled behavior in terms of the reptation and tube reorganization

Table I. Polymers and Their Characteristic Parameters[a]

polymer	N_c (ref)	C_∞ (ref)	av l, Å (ref)	A, Å (ref)	l_0, Å	L_c, Å	R_c, Å
1. poly(dimethylsiloxane)	660 (1)	6.0 (2)	1.46 (3)	10.2	1.46	964	37.51
2. polyethylene	364 (4)	7.0 (2)	1.54 (3)	12.3	1.54	561	29.38
3. polypropylene	328 (5)	6.2 (2)	1.54 (3)	11.1	1.54	505	27.89
4. hydrogenated polyisoprene	227 (6)	6.8 (3)	1.54 (3)	12.0	1.54	350	23.20
5. polyisobutene	570 (7)	5.0 (2)	1.54 (3)	10.5	1.54	878	36.77
6. *cis, trans*-polybutadiene	330 (8)	5.5 (2)	1.47 (3)	9.6	1.47	485	26.70
7. *cis*-polybutadiene	440 (9, 10)	5.15 (2)	1.47 (3)	7.6	1.47	647	30.83
8. 1,2-polybutadiene	152 (11, 12)	6.6 (3)	1.54 (3)	11.7	1.54	234	18.99
9. *cis*-polyisoprene	450 (7)	5.0 (2)	1.47 (3)	8.8	1.47	662	31.18
10. polystyrene	673 (5)	10.0 (2)	1.54 (3)	16.9	1.54	1036	39.95
11. poly(α-methylstyrene)	690 (13)	10.5 (2)	1.54 (3)	17.7	1.54	1063	40.45
12. poly(vinyltoluene)	847 (14)	11.4 (2)	1.54 (3)	19.1	1.54	1304	44.82
13. poly(1-vinylnaphthalene)	101 (15)	6.2 (2, 15)	1.54 (3)	11.1	1.54	156	15.48
14. poly(2-vinylnaphthalene)	191 (15)	12.0 (2, 15)	1.54 (3)	20.0	1.54	294	21.28
15. poly(4-vinylbiphenyl)	196 (15)	13.8 (2, 15)	1.54 (3)	22.8	1.54	302	21.56
16. poly(*N*-vinylcarbazole)	278 (16)	15.9 (17)	1.54 (3)	26.0	1.54	428	25.68
17. poly(vinyl acetate)	570 (5)	9.4 (2)	1.54 (3)	16.0	1.54	878	36.78
18. poly(vinyl alcohol)	340 (5)	8.3 (2)	1.54 (3)	14.3	1.54	524	28.40
19. poly(vinyl chloride)	200 (1)	6.7 (2)	1.54 (3)	11.9	1.54	308	21.78
20. poly(acrylic acid)	130 (5)	6.7 (2)	1.54 (3)	11.9	1.54	200	17.58
21. poly(acrylonitrile)	~50 (18)	9.7 (2)	1.54 (3)	16.5	1.54	~77	~10.89
22. poly(acrylamide)	257 (19)	14.8 (20)	1.54 (3)	24.3	1.54	396	24.69
23. poly(tetrafluoroethylene)	264 (5)	24.0 (2)	1.54 (3)	38.5	1.54	407	25.02
24. poly(methyl acrylate)	560 (21)	8.0 (2)	1.54 (3)	21 (47)	1.54	862	36.44
25. poly(methyl methacrylate)	630 (22)	7.0 (2)	1.54 (3)	17 (47)	1.54	970	38.65
26. poly(*n*-butyl methacrylate)	850 (5)	8.0 (2)	1.54 (3)	17 (47)	1.54	1309	44.90
27. poly(*n*-hexyl methacrylate)	1080 (23)	10.0 (2)	1.54 (3)	21 (47)	1.54	1663	50.61
28. poly(*n*-octyl methacrylate)	1150 (5)	10.0 (2)	1.54 (3)	20 (47)	1.54	1771	52.22
29. poly(*n*-dodecyl methacrylate)	1465 (24)	13.4 (2)	1.54 (3)	30 (47)	1.54	2256	58.94
30. poly(2-ethylbutyl methacrylate)	503 (25)	9.3 (2)	1.54 (3)	15.9	1.54	775	34.54
31. poly(ethylene oxide)	300 (1, 8)	4.2 (2)	1.49 (3)	7.7	1.49	447	25.81
32. poly(propylene oxide)	400 (22)	5.1 (2)	1.49 (3)	9.1	1.49	596	29.80
33. poly(tetramethylene oxide)	175 (26)	5.6 (2)	1.52 (3)	10.0	1.52	266	20.11
34. poly(oxyundecanoyl)	⩽326 (5)	5.1 (2)	1.51 (27)	9.2	1.51	⩽492	⩽27.26
35. poly(decamethylene succinate)	290 (5)	5.8 (28)	1.49 (27)	10.1	1.49	432	25.37
36. poly(decamethylene adipate)	280 (5)	3.55 (2)	1.51 (27)	6.9	1.51	423	25.27
37. poly(decamethylene sebacate)	290 (5)	6.1 (28)	1.51 (27)	10.7	1.51	438	25.71
38. poly(ethylene terephthalate)	170 (29)	4.21 (29)	2.135 (27)	11.1	1.25	213	16.30
39. poly(ethylene isophthalate)	495 (29)	4.29 (29)	2.09 (27)	11.1	1.25	619	27.81
40. poly(carbonate of bisphenol A)	230 (14, 30)	2.4 (2)	8.65	29.4 (31)	1.25	288	18.96
41. poly(1:1 ester carbonate of bisphenol A + terephthalic acid)	227 (14)	3.3 (32)	7.68 (32)	33.0	1.25	284	18.83
42. poly(2-methyl-6-phenyl-1,4-phenylene oxide)	92 (33)	3.7 (2)	5.41 (34)	25.4	1.08	99	10.36
43. poly(2,6-dimethyl-1,4-phenylene oxide)	140 (33)	3.55 (35)	5.41 (34)	24.6	1.08	151	12.78
44. poly(ether sulfone of bisphenol A + diphenyl sulfone)	320 (14, 36)	2.0 (37)	5.755 (37)	17.3	1.17	374	20.93
45. poly(ε-caprolactam) (nylon-6)	310 (7, 22)	5.3 (2)	1.49 (27)	9.4	1.49	462	26.23
46. poly(hexamethyleneadipamide) (nylon-66)	292 (38)	6.10 (27)	1.49 (27)	10.6	1.49	435	25.46
47. poly(phenylsilsesquioxane)	70 (39)	60 (39)	2.5 (39)	150 (39)	1.25	88	10.46
48. poly(propylene sulfide), isotactic	810 (40)	4.0 (41)	1.72 (41)	8.6	1.72	1393	48.95
49. polymeric sulfur	~3000 (42)	1.76 (43)	2.06 (43)	5.7	2.06	~6180	~112.83
50. poly[(trifluoroethyl)- + (octafluoropentyl)phosphazene], unfractionated	156 (44)	48 (45)	6.9 (45)	338.1	~1.49	~232	~18.61
51. nitrocellulose	23 (46)	22 (47)	7.75 (48)	178	1.55	36	7.43
52. cellulose acetate, 39.8% acetyl	32 (49)	23.4 (50)	7.75 (48)	160 ± 40 (5)	1.55	50	8.77

53. (hydroxypropyl)cellulose	22 (52)	24.5 (48)	7.75 (48)	198	1.55	34	7.27
54. cellulose tributyrate	67 (53)	23 (54)	7.75 (48)	186	1.55	104	12.69
55. poly(*p*-phenyleneterephthalamide)	60 (55)	200	6.5 (47)	1300 (47)	1.08	65	8.37
56. poly(*p*-benzamide)	38 (56)	325	6.5 (47)	2100 (47)	1.08	41	6.66
57. poly(benzobisoxazole)	62 (57)	93 (57)	12.2 (57)	1147	1.02	63	8.03
58. poly-BBB (from diaminobenzidine + naphthalenetetracarboxylic acid)	35 (58)	22 (59)		340 (59)	1.02	36	6.03
59. poly(benzyl glutamate)	211 (60)	400–622 (61)		2400 (47)	1.46	308	21.21
60. poly(*n*-butyl isocyanate)	150 (62)	~500 (63)	2.0 (64)	1000 (47)	1.32	198	16.17
61. poly(*n*-hexyl isocyanate)	100 (65)	~410 (63)	2.0 (64)	820 (66)	1.32	132	13.20
62. xanthan polysaccharide	33 (67)	750 (68)	9.4 (69)	~7000	1.55	51	8.90

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model of de Gennes.[32-34] Using experimental data of Daoud et al.,[35] Klein concluded that N_c', which is essentially a characteristic distance for the onset of entangled behavior, is related to the concentration c as

$$N_c' \simeq \frac{(18\pi^2)^{1/2}}{B} c^{-1.25} \quad (7)$$

where B "is a constant depending on the monomer size, its specific partial volume, and the characteristic ratio for the polymer".[5,36] Closer observation[36] indicates that N_c' is a linear and direct measure of R_c, the spatial distance between entanglements, and that N_c' is dependent on L_c, the chain contour length between entanglements, through a direct squared power relationship. Since N_c' is directly dependent on C_∞,[5,36] the relationships C_∞–R_c and C_∞–L_c are expected to follow those of N_c'–R_c and N_c'–L_c. Furthermore, because N_c is a characteristic multiple of N_c', the dependence of N_c on C_∞ is expected to be similar to the dependence of N_c' on C_∞. A preliminary compilation of experimental data by Aharoni[37] revealed such a direct relationship between N_c and C_∞.

The data in ref 15–28 and 30 demonstrate apparent empirical relationships between N_c and some, obvious or obscure, structural parameters of the polymeric chain. The large majority of the data were limited to what is conventionally termed flexible polymers. In the following, we present a compilation of N_c data for flexible polymers as well as rigid and semirigid ones. A strictly empirical attempt will be made to find whether relationships between N_c and C_∞ or A exist and whether they conform to the prediction of Klein.[5] No quantitative and detailed explanation of the behavior of specific polymers will be attempted at present.

Experimental Section

Most N_c values were obtained from M_c values in the literature. Chain backbone atoms were counted as one per $-CH_2-$, $-CHX-$, or $-CX_2-$ groups, two per amide or ester group, four per each para-aromatic or aliphatic ring, etc. Several N_c values were determined in our laboratories from viscosity vs. concentration log–log plots of data obtained from solutions of polymers of known weight-average molecular weight, M_w, which was in all cases much larger than M_c. The polymers were obtained from chemical supply houses or synthesized in our laboratories, and their M_w values were determined from intrinsic viscosity measurements and Mark–Houwink equation coefficients K and a in the literature (mostly in ref 28, 38, and 39, with additional specific data appearing in the references to Table I). Solvents were of reagent grade or better and used as received. Viscosity measurements were made with a Nametre direct-readout viscometer or with Cannon-Ubbelohde internal dilution glass viscometers, starting with the 700 series and decreasing the capillary bore with diminishing viscosity.

Results and Discussion

Values of N_c, C_∞, and A for 62 polymers are listed in Table I. Average values of virtual bond length l, used in calculating A from C_∞ (or vice versa, occasionally), as well as average actual bond length, l_0, used to calculate L_c, the critical chain length associated with N_c

$$L_c = N_c l_0 \quad (8)$$

are all listed in the table. The data were plotted in linear and log–log plots, with the points identified by the code number of the polymers as listed in the table. Figure 1 is a linear N_c vs. C_∞ plot. Figure 2 is a log–log representation of the same data. In Figure 3 values of N_c are linearly plotted against A, and in Figure 4 the same data are plotted logarithmically. In Figure 5 the L_c vs. A data are plotted on a log–log scale. Linear plots of L_c vs. A and L_c vs. C_∞ were rather similar to the corresponding N_c plots and were not, hence, reproduced here. Note that the lines in Figures 1 and 3 and the dashed lines in Figures 2, 4, 5, and 6 were drawn only as guides to the eye and have no significance by themselves. The circled points in Figure 2, 4, and 5 are for polymers appearing in Figure 1 of the paper by Graessley and Edwards[30] for which we have N_c values. It should be noticed that the plots relating N_c to C_∞ relate dimensionless values, possibly supporting a claim for universality. All plots indicate a division of the polymers into three main groups. Typical is Figure 1. Here, on the left-hand side are concentrated polymers conventionally termed as flexible polymers. On the lower right-hand side appear the polymers commonly denoted as rigid polymers. In between the full and dashed lines, delineating respectively the regions of flexible and rigid polymers, there appear several polymers that may be called semirigid or semiflexible. In Figure 1 the semiflexible polymers are nos. 14, 15, 16, 21, 22, and 23. In Figure 2 points 50 and 54 are added. The difference between the two figures clearly indicates the poor definition of the transition from the rigid to the semirigid domains. When plotted in terms of N_c vs. A, points 50 and 54 move from the semiflexible to the rigid domain, again demonstrating the poor definition of these two regions.

The position of isotactic poly(propylene sulfide) (48) and polymeric sulfur (49) is out of the scattered band of flexible polymers in the log–log Figures 2, 4, and 5, reflecting rather high values of N_c coupled with small values of C_∞ and A. The reasons for the small C_∞ and A values are the relatively long S–S and S–C bonds and the weak attraction between backbone atoms, resulting in C_∞ (and A) values smaller than encountered usually among aliphatic polymers having C–C, C–O, or C–N bonds along their backbone.[31,40,41]

Semiflexible (or semirigid) polymers are divisible into two groups. One group contains polymers with short backbone bonds encountering stiff resistance to their rotation. This resistance can be due to steric effects of very bulky pendant groups directly attached to polyvinyl backbone (polymers 14, 15, and 16) or strong side-group interactions, as in the case of polymers 21, 22, and 23. These polymers appear in the semiflexible domain when N_c is plotted against C_∞. The second group of semiflexible polymers is characterized by long virtual bonds containing para-aromatic rings connected by highly flexible swivels in the form of an ether oxygen or carbonate group. Because of their highly flexible swivels, the aromatic polyethers and polycarbonates, nos. 40–44, all exhibit remarkably small C_∞ values, indicating tight coils (cf. references in Table I). This is the reason for their appearnace deep in the flexible polymer domain when N_c is plotted against C_∞.[42] However, when the long virtual bonds of these polymers are being considered, as when N_c is plotted against A, then their points are shifted into the domain of semiflexible polymers (except for the poly(ether sulfone) no. 44, which does not quite make it). It is interesting to notice that, depending on whether C_∞ alone is considered, polymers 40–44 may be viewed as flexible[43,44] tight coils or stiff[44,45] tight coils.

The important features of Figures 1–5 are the following: (a) the N_c vs. C_∞ and N_c vs. A relationships hold true immaterial of whether the plots are linear or double logarithmic; (b) despite the substantial scatter in the flexible polymer domain, there exists an overall trend that is consistent with a power law behavior with an exponent of about 2; (c) in the rigid and semiflexible domains, the data scatter is so large that at present one can conclude only that in the rigid polymer domain the exponent is less than unity. Thus, the slope of the flexible polymers solid lines

in Figures 2 and 4 indicate that

$$N_c \propto C_\infty^2 \tag{9}$$

and

$$N_c \propto A^2 \tag{10}$$

These proportionalities are in excellent agreement with the theoretical expectations of Klein.[5] As shown below, a linear relationship between C_∞ and R_c is demonstrated for flexible polymers, again in perfect agreement with theory.[5]

Purely empirical numerical estimates from Figures 2 and 4 yield

$$N_c \cong 10C_\infty^2 \tag{11}$$

and

$$N_c \cong (2.5\ \text{Å}^{-2})A^2 \tag{12}$$

affording us a simple way to evaluate N_c of flexible polymers directly from their structural parameters C_∞ or A and overcoming a drawback associated with the absence of a method to estimate N_c.[46] In light of the scatter of the presently available data, a refinement of the exponent is neither possible nor warranted.

Interestingly, a combination of relationships 11 and 12 reveals that for flexible polymers, the magnitude of A in angstrom (Å) units is, on the average, twice the magnitude of C_∞.

In an attempt to gain deeper insight into the N_c–C_∞ and N_c–A relationships, the spatial distances between intermolecular "entanglements", R_c, were calculated. For random flexible coils the distance R_c is[36,47]

$$R_c = N_c^{1/2} l_0 \tag{13}$$

Numerical values of L_c and R_c for all 62 polymers in this study are listed in Table I, but it must be emphasized that for rigid or semirigid chains not following random coil statistics, the value R_c obtained according to eq 13 has no obvious physical meaning.

Values of R_c of flexible polymers plotted against A are shown in Figure 6. Data of semiflexible polymers are shown merely for comparison and will not be discussed further. Despite the observed scatter, similar to that for flexible polymers in Figure 4, the flexible polymers fall in a band about a line described by the relationship

$$N_c^{1/2} l_0 = R_c \cong 2.5A \tag{14}$$

Noting that for the flexible polymers falling within the band the average bond distance is about 1.5 Å, relationships 5, 11, 12, and 14 indicate a direct and linear relationship of

$$R_c \cong (10\ \text{Å})C_\infty \tag{15}$$

for flexible polymers. That is, the larger is C_∞, the larger the spatial distance between intermolecular interference with free movement. Figure 6 further indicates that for flexible chains, where eq 13 holds, these interferences, i.e., "entanglements", start at spatial distances of about 15 Å and increase with A. Interferences occurring at such spatial distances are overcome by relaxations[5] taking sufficiently long time to be measurable under the time/temperature/stress/concentration conditions of the experiment. These relaxations are the ones associated with "entanglements" or with reptation under constraints in the reptation–tube reorganization model.

Rigid-backbone polymers do not conform to eq 13. In isotropic solutions, where N_c can be determined, the spatial distance between "entanglements" corresponds to L_c, the length of the rodlike molecule between "entanglements". The L_c–R_c relationship among the two kinds of semiflexible polymers stands in between eq 8 and 13 and because of its complexity will not be dealt with in this work. L_c values of rigid polymers are plotted against A in Figure 5. These data are too scattered to follow a particular L_c vs. A curve, but they do show a low exponential dependence of less than 1.0 and a minimal L_c value of 34 Å ((hydroxypropyl)cellulose). Polymers with stiffer backbones such as the aromatic polyamides 55 and 56 or the poly(*n*-alkyl isocyanates) 60 and 61 possess larger values of both L_c and A. The increased spatial distance between "entanglements" of rigid-backbone macromolecules appears to be a mere logical extension of the increase in R_c with C_∞ of flexible chains: the larger is C_∞, the larger is R_c ($=L_c$ in the case of rigid rods) immaterial of the category of the polymer. The linear relationship between R_c and A indicates that, at least for flexible polymers, the "entanglement" concentration is sensitive to long-range chain extension, in addition to the local rigidity effects reflected in the R_c vs. C_∞ relationship.

From the above one can draw the following conclusions: When two flexible polymers with chains of comparable length $L \gg L_c$ are compared, the one with the larger C_∞ (or A) will have the larger N_c. This means that in solution, the concentration at which relationship 1 is satisfied and entangled behavior becomes apparent is higher for the more expanded coils of larger C_∞. In the bulk, where $c = 1.0$, relationship 1 is satisfied once the chain length L surpasses L_c; here, too, L_c (or N_c) increases together with C_∞ (or A) according to proportionalities 9 and 10. Whether in the bulk or in solution, the "entanglement" concentration of flexible coil polymers decreases with increased C_∞ (or A). Although the data for rigid-rod macromolecules suffer from much more scatter, one can reach the conclusion that in isotropic solutions of such molecules there exists a direct relationship between C_∞ (or A) and L_c (which is the same as R_c for rodlike molecules). Because of the imposed anisotropy in the bulk or concentrated solutions of rodlike macromolecules, the above observations and discussion are expected to remain valid only for the isotropic case.

The direct dependence of N_c on C_∞ (or A) and the corresponding inverse dependence of the "entanglement" concentration on the chain expansion instruct us that the "entanglements" can be considered as intermolecular interferences to the translational and rotational motion of whole coils or large portions of them, or whole rodlike macromolecules. The loci of interference, which serve also for the transmission of force through the system, are points at which sections of different macromolecules fail to intersect each other. This simple visualization is applicable to isotropic solutions of rodlike macromolecules as well as to concentrated solutions and bulk flexible polymers. In the latter case, stress-induced tube reorganization may correspond to the interference with motion indicated above.

Registry No. Polybutadiene (homopolymer), 9003-17-2; polyethylene (homopolymer), 9002-88-4; polypropylene (homopolymer), 9003-07-0; polyisobutylene (homopolymer), 9003-27-4; polyisoprene (homopolymer), 9003-31-0; polystyrene (homopolymer), 9003-53-6; poly(2-methylstyrene) (homopolymer), 25014-31-7; poly(vinyltoluene) (homopolymer), 9017-21-4; poly(1-vinylnaphthalene) (homopolymer), 25135-12-0; poly(2-vinylnaphthalene) (homopolymer), 28406-56-6; poly(4-vinylbiphenyl) (homopolymer), 25232-08-0; poly(*N*-vinylcarbazole) (homopolymer), 25067-59-8; poly(vinyl acetate) (homopolymer), 9003-20-7; poly(vinyl alcohol) (homopolymer), 9002-89-5; poly(vinyl chloride) (homopolymer), 9002-86-2; poly(acrylic acid) (homopolymer), 9003-01-4; poly(acrylonitrile) (homopolymer), 25014-41-9; poly(acrylamide) (homopolymer), 9003-05-8; poly(tetrafluoroethylene) (homopolymer), 9002-84-0; poly(methyl acrylate)

(homopolymer), 9003-21-8; poly(methyl methacrylate) (homopolymer), 9011-14-7; poly(*n*-butyl methacrylate) (homopolymer), 9003-63-8; poly(*n*-hexyl methacrylate) (homopolymer), 25087-17-6; poly(*n*-octyl methacrylate) (homopolymer), 25087-18-7; poly(*n*-dodecyl methacrylate) (homopolymer), 25719-52-2; poly(2-ethylbutyl methacrylate) (homopolymer), 25087-19-8; poly(ethylene oxide) (SRU), 25322-68-3; poly(propylene oxide) (SRU), 25322-69-4; poly(tetramethylene oxide) (homopolymer), 24979-97-3; poly(oxyundecanoyl) (SRU), 25735-90-4; 11-hydroxyundecanoic acid homopolymer, 25656-55-7; poly(decamethylene succinate) (SRU), 28726-53-6; 1,10-decanediol–succinic acid copolymer, 27517-29-9; 1,10-decanediol–adipic acid copolymer, 28552-31-0; poly(decamethylene adipate) (SRU), 25212-79-7; poly(decamethylene sebacate) (SRU), 25482-94-4; poly(ethylene terephthalate) (SRU), 25038-59-9; poly(ethylene isophthalate) (SRU), 26948-62-9; poly(carbonate of bisphenol A), 24936-68-3; poly(1:1 ester carbonate of bisphenol A–terephthalic acid), 31133-78-5; poly(2-methyl-6-phenyl-1,4-phenylene oxide) (SRU), 25805-39-4; poly(2,6-dimethyl-1,4-phenylene oxide) (SRU), 24938-67-8; poly(ether sulfone of bisphenol A–diphenyl sulfone) (SRU), 25135-51-7; nylon 6, 25038-54-4; nylon 66, 32131-17-2; 1,10-decanediol–sebacic acid copolymer, 27514-86-9; isotactic poly(propylene sulfide) (homopolymer), 70573-38-5; sulfur, 7704-34-9; 1,2-ethanediol–isophthalic acid copolymer, 26810-06-0; nitrocellulose, 9004-70-0; cellulose acetate, 9004-35-7; (hydroxypropyl)cellulose, 9004-64-2; cellulose tributyrate, 39320-16-6; poly(*p*-phenyleneterephthalamide) (SRU), 24938-64-5; poly(*p*-benzamide) (SRU), 24991-08-0; bisphenol A–carbonic acid copolymer, 25037-45-0; poly(benzyl glutamate) (SRU), 25038-53-3; poly(*n*-butyl isocyanate) (homopolymer), 25067-04-3; poly(*n*-hexyl isocyanate) (homopolymer), 26746-07-6; xanthan gum, 11138-66-2; poly(2-methyl-6-phenyl-1,4-phenylene oxide) (homopolymer), 27616-03-1; poly(2,6-dimethyl-1,4-phenylene oxide) (homopolymer), 25134-01-4; poly(phenyleneterephthalamide) (copolymer), 25035-37-4; poly(*p*-benzamide) (homopolymer), 25136-77-0; poly(3,3′-diaminobenzidine–naphthalenetetracarboxylic acid) copolymer, 25971-81-7; poly(benzyl glutamate) (homopolymer), 25014-27-1.

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