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Correlations between Chain Parameters and the Plateau Modulus of Polymers

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ABSTRACT: Plateau modulus, $G_N°$, values of over 50 polymers were correlated with long-distance chain parameters such as M_c, N_c, and L_c and with short-distance chain parameters such as the chain diameter, d, and the Kuhn segment length, A. For the flexible and semiflexible polymers, it was found that essentially no correlation exists between $G_N°$ and any of the long-distance chain parameters. The correlation of $G_N°$ and short-distance chain parameters was marginal with A and reasonably good with A/d for well-behaved flexible and semiflexible polymers: $G_N° \propto A/d$. It was further observed that when $G_N°$ is multiplied by A^3/kT to render the product dimensionless, the correlation of this variable with $(A/d)^2$ is dominated by the magnitude of A^3 and does not reflect the relationship between $G_N°$ and $(A/d)^2$. Plots of the relationship between A and d clearly divide the polymers into four groups: flexible, semiflexible, semirigid, and rigid. The difference in behavior between the more flexible polymers and the more rigid ones appears to be related to the ratio of L_c, the chain contour length between entanglements, to A. In the case of the flexible polymers $L_c \gg A$ and for the rigid polymers $L_c \ll A$.

Introduction

The presence of entanglements or interchain contact points seems to be a prerequisite for a polymeric system to exhibit a plateau modulus, $G_N°$. It is widely accepted[1] that an inverse relationship exists between the plateau modulus and the molecular weight between entanglements, M_e, of a polymer in its elastoviscous state

$$G_N° = c\rho RT/M_e \quad (1)$$

Here ρ is the polymer density under test conditions, R is the gas constant, T is the temperature, and c is a numerical factor solely or largely consisting of the polymer concentration. In the case of linear polymers in the undiluted state, $c = 1.0$. The same relationship holds for cross-linked elastomers, where M_e is the molecular weight between cross-link junctions[2]

$$G_N° = \rho RT/M_e \quad (2)$$

Since the density of most organic polymers is in the neighborhood of 1, a reasonable estimate of M_e for the pure polymer may be obtained from the measured $G_N°$ by

$$G_N° \simeq RT/M_e \quad (3)$$

When the viscosity of fractions of a pure polymer, measured in the molten fluid state, is plotted in log-log scale against the molecular weight, M, of the fractions, a break in the curve is observed at the point where the molecular weight dependence of the viscosity changes over a relatively narrow range from dependence on $M^{1.0}$ to a dependence on $M^{3.4}$. The molecular weight at which the break in the curve occurs is termed the characteristic molecular weight for entanglement, M_c. M_c is observed also in solutions. Here, a high molecular weight polymer is used, with $M \gg M_c$. Comparison of the results obtained in solution and in the melt indicates that[3]

$$(cM)_c = M_c \quad (4)$$

where c is the concentration. When the M_c and M_e values of the same polymers are compared, it is found[4,5] that the ratio M_c/M_e is about 2. Therefore, an approximate value of $G_N°$ can be calculated from the known M_c or M_c estimated from $G_N°$

$$G_N° \cong 2c\rho RT/M_c \quad (5)$$

and for the neat polymer in a weaker approximation

$$G_N° \simeq 2RT/M_c \quad (6)$$

Because the $G_N°$ and M_c values are obtained from two independent measurements, we believe that attempted correlations between the two variables are valid. Similarly, correlations between $G_N°$ and N_c or L_c are valid, N_c being the number of chain backbone atoms or bonds corresponding to M_c and L_c the chain contour length defined by M_c. On the other hand, attempted correlations between pairs of $G_N°$ and M_e values are invalid since both variables of each pair were obtained from the same measurement or the same kind of measurement. By the same token, correlations of $G_N°$ with N_e or $G_N°$ with L_e are also invalid.

The purpose of this work is to determine if correlations between $G_N°$ and M_c, N_c, or L_c are statistically valid and whether there exist better correlations relating $G_N°$ to other chain parameters.

Data Acquisition and Treatment

All plateau modulus values were obtained from the literature. Most were from bulk polymers, but a few were extrapolated from the plateau modulus of polymeric solutions. In several instances the value of $G_N°$ was esti-

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mated from G' values of incomplete curves. Occasionally, a value of $G_N°$ was obtained from the equilibrium compliance $J_N°$ (or $J_e°$, J_e, J_0) by the use of the relationship[1] $1/J_N° = G_N°$. The use of[3] $G_N° = (5/6)J_e°$ does not alter significantly the results, in light of the substantial experimental scatter. In the case of solutions, the viscoelastic data for flexible polymers were obtained from concentrations as high as possible. Special care was taken to ensure that the results of water-soluble polymers are indeed from solutions and not, as is often the case, from visually uniform suspensions of very fine molecular aggregates. The data for rigid polymers were obtained from substantially more dilute solutions, ensuring them to be completely isotropic. Thus, for rigid polymers, the $G_N°$ values refer to isotropic bulk polymers, systems not existing in reality. When the data were derived from G' values, and G'' data were also available, the value of $G_N°$ was obtained by the extrapolation of the G' value at the point where the G' and G'' curves intersect. In the extrapolation, the relationship[3] $G_N° = (G_N°)_{soln}/c^2$ was used, in which c is the volume fraction of polymer in solution and $(G_N°)_{soln}$ is the $G_N°$ value of the solution at that concentration. All plots were made on log–log paper. When plotted, modulus data of polymers considered by Graessley and Edwards[6] were indicated by encircled dots. All other bulk polymers were indicated by solid circles. Modulus data obtained from solution data were indicated by square symbols.

The plateau moduli of a few flexible polymers were out of the range of scatter of all other flexible polymers. These polymers are poly(ethylene oxide) (no. 31 in Table I), poly(ethylene terephthalate) (38), poly(ϵ-caprolactam) (45), poly(hexamethyleneadipamide) (46), polymeric sulfur (49), and (hydroxypropyl)cellulose (53). The low $G_N°$ of poly(ethylene oxide) may be due to aggregation effects in solution and/or too low a molecular weight to support a uniform distribution of entanglements. The molecular weight of the next three polymers was apparently too low to support and uniformly distribute the applied load, leading to premature disruption of the entanglement network and a lower than expected $G_N°$. The lower $G_N°$ of polymeric sulfur may be explained by the usual presence of a substantial amount of cyclic sulfur octamers and by the rapid chain scission and reformation known to occur in molten polymeric sulfur (ref 44 of Table I). The very low $G_N°$ of (hydroxypropyl)cellulose is due to the fact that the bulk polymer was, at least in part, in its thermotropic liquid crystalline state (ref 50 of Table I), known to have a viscosity and modulus much smaller than in the isotropic state. The data of these six polymers are given for the sake of completeness only and should not be considered when the $G_N°$ data of the flexible polymers as a group are evaluated.

The data are listed in two tables. Table I includes polymers previously tabulated in ref 8. For the ease of comparison, we adopted in the present paper the same ordinal numerical code used to identify polymers in that reference. In Table II are listed several additional polymers, the data for which were not available for ref 8. The numerical codes from both tables were used to identify the data points of all polymers in the figures of this work.

Chain cross-sectional areas were obtained from the literature or were calculated by us directly from crystallographic data. Very few chain cross-sectional areas, d^2, were estimated by analogy to other, structurally similar, polymers or from space-filling models. The values of A in Table I were taken from ref 8. Additional A values, in Table II, were obtained from the literature or were calculated from persistence length, q, or characteristic ratios,

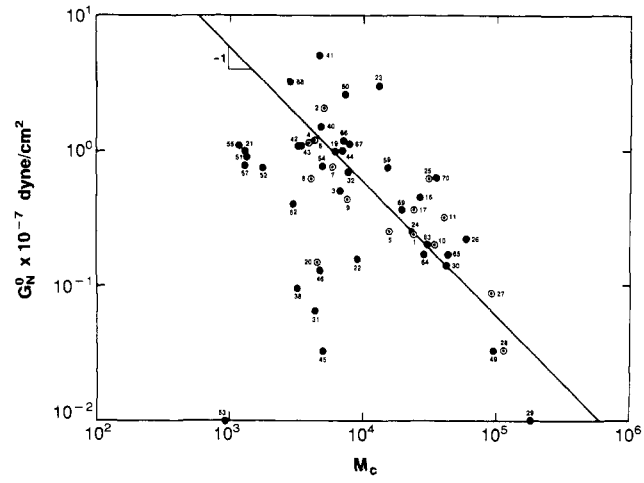

Figure 1. $G_N°$ vs. M_c. Line with slope −1 reflects theoretically expected correlation.

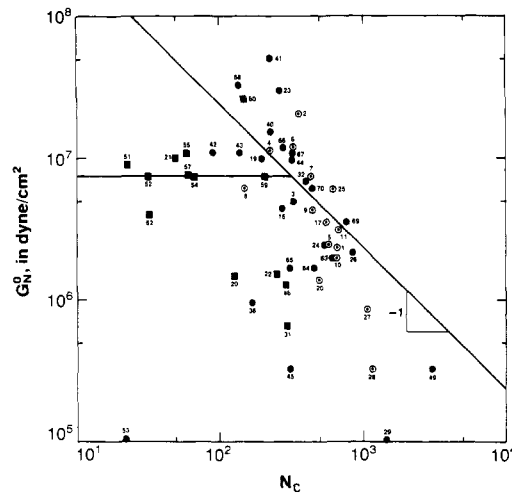

Figure 2. $G_N°$ vs. N_c. Line with slope −1 reflects theoretically expected correlation. Horizontal line indicates the independence of rigid and semirigid polymers from the $G_N°$ vs. N_c relationship.

C_∞. The data sources and specific details for modulus and structural parameters are listed in the references for each table.

It should be noted that $G_N°$ values of a given polymer obtained by different groups are often not the same. The presence of a multiplicity of such values is indicated by the presence of several references for $G_N°$ in the tables. The differences in $G_N°$ values often exceed 100%.

Linear correlation analysis and least-squares curve fitting were performed on all data with the aid of a Sharp EL-5100S scientific calculator and a VAX 11/780 computer made by Digital Equipment Corp. As a rule, data showing power-law behavior were first treated by the method of averages, giving the best power-law dependence of the ordinate variables on the abscissa variables. Subsequent treatment of the data included least-squares analysis and calculations of the standard deviations, σ, of the data points from the modeled power laws.

Results and Discussion

When the $G_N°$ and M_c or $G_N°$ and N_c values of many polymers are paired, one finds that there is practically no correlation between the variables, even when the sample population is limited to flexible and semiflexible polymers only (that is, all polymers in the tables excluding no. 50–62). A glance at Figures 1 and 2 clearly reveals the severity of the data scatter. the $G_N°$ and M_c numerical

Table I[a]
Polymers and Their Characteristic Parameters Appearing in Ref 8

no.	polymer	A, Å	d^2, Å^2	A/d	M_c	N_c	L_c, Å	$G_N^\circ \times 10^{-7}$, dyn/cm^2
1	poly(dimethylsiloxane)	10.2	43.6 (2)	1.54	24 500	660	964	0.24 (3–5)
2	polyethylene	12.3	18.28 (6)	2.88	5115	364	561	2.06 (3, 7)
3	polypropylene	11.1	34.27 (6)	1.90	6890	328	505	0.50 (8)
4	hydrogenated polyisoprene	12.0	28.5 (9)	2.25	3970	227	350	1.15 (3)
5	polyisobutene	10.5	41.24 (6)	1.63	16 020	570	878	0.25 (3)
6	*cis,trans*-polybutadiene	9.6	19.3 (2)	2.19	4455	330	485	1.20 (3)
7	*cis*-polybutadiene	7.6	20.7 (2)	1.67	5940	440	647	0.76 (3)
8	1,2-polybutadiene	11.7	49.88 (10)	1.66	4110	152	234	0.617 (11)
9	*cis*-polyisoprene	8.8	28.0 (9, 12)	1.66	7650	450	662	0.44 (3, 5)
10	polystyrene	16.9	69.80 (6)	2.02	35 000	673	1036	0.20 (3, 13)
11	poly(α-methylstyrene)	17.7	100 (14)	1.77	40 800	690	1063	0.32 (3)
12	poly(vinyltoluene)	19.1			50 060	847	1304	
13	poly(1-vinylnaphthalene)	11.1			7790	101	156	
14	poly(2-vinylnaphthalene)	20.0			14 725	191	294	
15	poly(4-vinylbiphenyl)	22.8			17 740	196	302	
16	poly(*N*-vinylcarbazole)	26.0	131.02 (15)	2.27	27 050	278	428	0.45 (16)
17	poly(vinyl acetate)	16.0	59.3 (2)	2.08	24 540	570	878	0.36 (3, 5)
18	poly(vinyl alcohol)	14.3			7480	340	524	
19	poly(vinyl chloride)	11.9	27.18 (6)	2.28	6250	200	308	1.0 (17, 18)
20	poly(acrylic acid)	11.9	45.2 (12)	1.77	4690	130	200	0.15 (19)
21	poly(acrylonitrile)	16.5	30.85 (6)	2.97	1330	~50	~77	1.00 (20)
22	polyacrylamide	24.3	45.2 (21)	3.61	9140	257	396	0.156 (22)
23	poly(tetrafluoroethylene)	38.5	27.08 (6)	7.40	13 225	264	407	3.0 (23)
24	poly(methyl acrylate)	21	59.3 (2)	2.73	24 100	560	862	0.25 (24)
25	poly(methyl methacrylate)	17	63.84 (6)	2.13	31 530	630	970	0.62 (3, 24–26)
26	poly(*n*-butyl methacrylate)	17	93.6 (2)	1.76	60 435	850	1309	0.22 (25)
27	poly(*n*-hexyl methacrylate)	21	114.2 (2)	1.97	91 900	1080	1663	0.087 (3)
28	poly(*n*-octyl methacrylate)	20	135.1 (2)	1.72	114 000	1150	1771	0.033 (3)
29	poly(*n*-dodecyl methacrylate)	30	176.6 (27)	2.26	186 350	1465	2256	0.01 (28)
30	poly(2-ethylbutyl methacrylate)	15.9	100 (14)	1.59	42 800	503	775	0.14 (3)
31	poly(ethylene oxide)	7.7	21.50 (6)	1.66	4410	300	447	0.0656 (29)
32	poly(propylene oxide)	9.1	24.47 (6)	1.84	7750	400	596	0.7 (30)
33	poly(tetramethylene oxide)	10.0			2525	175	266	
34	poly(oxyundecanoyl)	9.2			5000	≤326	≤492	
35	poly(decamethylene succinate)	10.1			4650	290	432	
36	poly(decamethylene adipate)	6.9			4400	280	423	
37	poly(decamethylene sebacate)	10.7			4930	290	438	
38	poly(ethylene terephthalate)	11.1	20.0 (2)	2.48	3270	170	213	0.0965 (31)
39	poly(ethylene isophthalate)	11.1			9520	495	619	
40	poly(carbonate of bisphenol A)	29.4	30.89 (32)	5.29	4875	230	288	1.53 (33, 34)
41	poly(ester carbonate of 1 bisphenol A and 2 terephthalic acid)	33.0	30.9 (35)	5.94	4800	227	284	5.07 (36)
42	poly(2-methyl-6-phenyl-1,4-phenylene oxide)	25.4	56.5 (37)	3.38	3350	92	99	1.1 (38)
43	poly(2,6-dimethyl-1,4-phenylene oxide)	24.6	35.52 (39)	4.13	3360	140	151	1.1 (40)
44	poly(ether of bisphenol A and diphenyl sulfone)	17.3	30.9 (35)	3.11	7070	320	374	1.0 (41)
45	poly(ϵ-caprolactam)	9.4	17.86 (6)	2.22	5020	310	462	0.033 (42)
46	poly(hexamethyleneadipamide)	10.6	17.60 (6)	2.53	4730	292	435	0.13 (43)
47	poly(phenylsilsesquioxane)	150			4515	70	88	
48	poly(propylene sulfide), isotactic	8.6			20 000	810	1393	
49	polymeric sulfur	5.7	24.33 (27)	1.26	~96 000	~3000	~6180	0.033 (44)
50	poly[(trifluoroethyl)- + (octafluoropentyl)phosphazene], unfractionated	338.1			29 200	173	~258	
51	nitrocellulose	178	78.5 (45)	20.09	1365	23	36	0.91 (46)
52	cellulose acetate, 39.8%, acetyl	160 ± 40	78.5 (47)	18.06	1800	32	50	0.75 (48)
53	(hydroxypropyl)cellulose, liquid crystalline melt	198	128.61 (49)	17.46	975	22	34	0.01 (50)
54	cellulose tributyrate	186	85.0 (47)	20.17	5000	67	104	0.76 (51)
55	poly(*p*-phenyleneterephthalamide)	1300	38.47 (52)	209.6	1200	60	65	1.1 (53, 54)
56	poly(*p*-benzamide)	2100	38.47 (52)	338.2	750	38	41	
57	poly(benzobisoxazole)	1147	36.6 (55)	185.6	1320	62	63	0.77 (56)
58	poly-BBB (from diaminobenzidine and naphthalenetetracarboxylic acid)	340			1000	35	36	
59	poly(γ-benzyl L-glutamate)	2400	85.2 (12)	260.0	15 400	211	308	0.75 (57)
60	poly(*n*-butyl isocyanate)	1000	76.59 (58)	114.4	7425	150	198	2.6 (59)
61	poly(*n*-hexyl isocyanate)	820			6350	100	132	
62	xanthan polysaccharide	~7000	400 (60)	350	3025	33	51	0.4 (61)

[a] References are as follows: (1) All values of A, N_c, L_c, l, and l_0, together with their respective references are tabulated in Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722. Values of M_c were obtained from the references listed in Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722. Multiple plateau modulus references indicate the existence of more than one G_N° value in the literature. (2) Boyer, R. F.; Miller, R. L. *Rubber Chem. Technol.* **1978**, *51*, 718. (3) Graessley, W. W.; Edwards, S. F. *Polymer* **1981**, *22*, 1329. (4) Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W. *Macromolecules* **1981**, *14*, 1039. (5) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*, 1. (6) Privalko, V. P. *Macromolecules* **1980**, *13*, 370. (7) Raju, V. R.; Menzes, E. V.; Marin, G.; Graessley, W. W.; Fetters, L. J. *Macromolecules* **1981**, *14*, 1668. Value for linear hydrogenated PBD. (8) From compliance data in Plochocki, A. P. *Trans. Soc. Rheol.* **1976**, *20*, 287. (9) Boyer, R. F.; Miller, R. L. *Polymer* **1976**, *17*, 925. (10) Our estimate from data in Tadokoro, H. "Structure of Crystalline Polymers"; Wiley-Interscience: New York, 1979. (11) Sanders, J. F.; Ferry, J. D.; Valentine, R. H. *J. Polym. Sci., Part A-2* **1968**, *6*, 967. (12) Boyer, R. F.;

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V.; Tsvetkov, V. N. *Eur. Polym. J.* **1982**, *18*, 583. (53) From J_e value of isotropic sulfuric acid solution: Chu, S. G.; Venkatraman, S.; Berry, G. C.; Einaga, Y. *Macromolecules* **1981**, *14*, 939. (54) From J_0 values of 2% solution in methanesulfonic acid: Wong, C. P.; Ohnuma, H.; Berry, G. C. *J. Polym. Sci., Polym. Symp.* **1978**, *No. 65*, 173. (55) Estimated from crystallographic data of model compounds in: Wellman, M. W.; Adams, W. W.; Wolff, R. A.; Dudis, D. S.; Wiff, D. R.; Fratini, A. V. *Macromolecules* **1981**, *14*, 935. (56) From J_0 values of 5% (w/v) solution in methanesulfonic acid. Data in ref 54 above. (57) From G' values of PBLG in 1% and 2% concentrations in the helicogenic solvent m-methoxyphenol. MW = 345 000. Data of: Tschoegl, N. W.; Ferry, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 1474. (58) Calculated from crystallographic data in: Shmueli, U.; Traub, W.; Rosenheck, K. *J. Polym. Sci., Part A-2* **1969**, *7*, 515. (59) G' value was calculated from the reduced values of real shear modulus of 10% isotropic solution of PBIC, MW = 65 000, in toluene. Data of: Dev, S. B.; Lochhead, R. Y.; North, A. M. *Discuss. Faraday Soc.* **1970**, *49*, 244. (60) From estimates by Southwick, G. J.; Jamieson, A. M.; Blackwell, J. *Macromolecules* **1981**, *14*, 1728. (61) From G' of 0.5% (w/w) in aqueous solution containing 0.02 mol/dm^3 urea: Ross-Murphy, S. B.; Morris, V. J.; Morris, E. R. *Faraday Symp. Chem. Soc.* **1983**, *18*, 115.

Table II[a]
Polymers and Their Characteristic Parameters Not Appearing in Ref 8

no.	polymer	C_∞	A, Å	d^2, Å^2	A/d	M_c	N_c	L_c, Å	$G_N^\circ \times 10^{-7}$, dyn/cm^2
63	poly(ethyl acrylate)	8.82 (1)	15.12	73 (2, 3)	1.77	31 280	625	960	0.2 (4)
64	poly(butyl acrylate)	9.00 (5)	15.40	94.08 (2)	1.59	29 500	460	705	0.17 (4)
65	poly(ethylhexyl acrylate)	9.15 (5)	15.63	115 (3)	1.46	44 700	315	485	0.17 (4)
66	poly(carbonate of tetramethylbisphenol A)		29.4 (6)	35.5 (7)	4.93	7 240	280 (8)	350	1.203 (9)
67	poly(ester carbonate of 1 terephthalic acid + 2 tetramethylbisphenol A)		33 (6)	35.5 (7)	5.54	8 000	320 (10)	315 (10)	1.13 (10)
68	poly(ester of bisphenol A and 4,4′-carbonyldibenzoic acid)	3.5 (11)	38.9 (11)	30.9 (7)	7.00	2 900	138 (10)	134 (10)	3.3 (10)
69	poly(ethylene tetrasulfide)	3.5 (12)	8.55 (12)	42.85 (2)	1.31	19 940	767 (4)	1457	0.36 (4)
70	polymeric amorphous selenium	1.015 (13)	4.715	18.97 (14)	1.08	35 300	447	1045	0.63 (4)

[a] References are as follows: (1) Using $A = l_0(C_\infty + 1)$ and $C_\infty = 2\sigma^2$. Data of: Birshtein, T. M.; Ptitsyn, O. B. "Conformations of Macromolecules"; Interscience: New York, 1966; pp 15, 189. (2) From Crystallographic data assembled by: Miller, R. L. In "Polymer Handbook", 2nd Ed.; Brandrup, J., Immergut, E. H. Ed.; Wiley-Interscience: New York, 1975; pp III-1–III-50. (3) Estimated from d^2 progression in methacrylate series and from data in: Privalko, V. P. *Macromolecules* **1980**, *13*, 370. (4) Tobolsky, A. V.; MacKnight, W. J. "Polymeric Sulfur and Related Polymers"; Interscience, New York, 1965; pp 24–26, 46–49, 117–123. Density of amorphous selenium 4.26 g/cm^3; acrylates estimated to be 1.2 g/cm^3. (5) Estimated by analogy to the methacrylate series in Table I from data in: Aharoni, S. M. *Macromolecules* **1983**, *16*, 1722 and Kurata, M.; Tsunashima, Y.; Iwama, M.; Kamada, K. In "Polymer Handbook"; see ref 2 above, pp IV-1–IV-60. (6) Estimated by analogy to polymers no. 40 and 41 in Table I. (7) Estimated by analogy to polymers no. 40 and 41 in Table I and chain cross-sectional area of poly(2,6-dimethyl-1,4-phenylene oxide) in ref 39 of Table I. (8) Calculated from G_N°, density, and structure given in ref 9 below. (9) Wisniewsky, C.; Marin, G.; Monge, P. *Eur. Polym. J.* **1981**, *20*, 691. (10) Prevorsek, D. C.; DeBona, B. T. Morristown, NJ, Dec 1982 Allied Corp. Research Report 82-42. (11) A characteristic ratio of 3.5 was estimated from structure and hindered rotation about the aromatic carbonyl and aromatic oxygen bonds. A virtual bond of 8.65 Å, similar to poly(carbonate of bisphenol A), was assumed. (12) Calculated by assuming weighted amounts of C–C and S–S bonds from characteristic ratios of polyethylene and polymeric sulfur. Value is expected to be lower than $C_\infty = 4.2$ for poly(ethylene sulfide). See Abe, A. *Macromolecules* **1980**, *13*, 541, 546. (13) Estimated from data in Semlyen, J. A. *Trans. Faraday Soc.* **1967**, *63*, 743, using characteristic ratios of sulfur and selenium octamers and linear amorphous sulfur. Also see: Mark, J. E. Curro, J. G. *J. Chem. Phys.* **1984**, *80*, 5262. (14) Wunderlich, B. "Macromolecular Physics"; Academic Press: New York, 1973; Vol. 1, pp 96–100 and Flory, P. J. "Statistical Mechanics of Chain Molecules"; Interscience, New York, 1969; pp 157–159.

values of all 53 polymers in Figure 1 were subjected to linear correlation analysis (for the difference between linear regression and correlation analyses, please consult ref 7 or similar sources) and the sample correlation coefficient, r, was found to be −0.3229. The coefficient of determination, r^2, is 0.1043. Since r^2 defines[7] the proportion of variability in y ($G_N°$ in this case) explained by the linear relationship to x (M_c in this case), its small value indicates that about 90% of the variability of $G_N°$ is unexplained by the variations in M_c. The correlation of $G_N°$ with N_c, in Figure 2, produced values of $r = -0.3246$ and $r^2 = 0.1054$ for the 44 flexible and semiflexible polymers in Tables I and II (numbers 1–49 in Table I and all the polymers in Table II). The extremely poor correlations above, indicating almost total independence of the variables, may be due to any or all of the reasons listed below. (a) Experimentally obtained $G_N°$ values suffer from very large scatter even in cases of well-studied polymers. Differences of 50% in $G_N°$ values of polystyrene (no. 10) and up to 100% in the $G_N°$ values of poly(methyl methacrylate) (no. 25) are recorded in the literature. (b) M_c values suffer from less scatter, but variations of the order of 10% do exist. (c) The M_c/M_e ratio covers a substantial range around 2.[3-5] This causes scatter that would not have existed if equalities 5 and 6 would strictly hold under isothermal conditions. (d) Differences in density of one polymer from the other contribute to the scatter of $G_N° - M_c$ and $G_N° - N_c$ pairs. And, finally, (e) differences in the temperature at which $G_N°$ of the various polymers were determined may contribute to the scatter of the data points. It should be noticed, however, that plots of $G_N°/kT$ against M_c and N_c, meant to eliminate the effects of temperature variation, failed to significantly reduce the scatter of data points in Figures 1 and 2. It is of interest to note that the exclusion of rigid and semirigid polymers from the $G_N° - N_c$ correlation analysis failed to improve the correlation of $G_N°$ with N_c. From the above, one concludes that a substantial fraction of the $G_N°$ and/or M_c data in the literature is of quality too poor for good $G_N° - M_c$ correlations of many flexible polymers. This conclusion carries over also to the relationships of $G_N°$ with N_c and $G_N°$ with L_c. As was shown in the literature,[3-5] the $M_c - M_e$ relationship is not well-defined either. This is despite the generally accepted supposition that M_c/M_e is exactly 2. We believe that poor $G_N°$ data in the literature generate poor M_e values through relationship 1, defining M_e. However, the poor correlations in Figures 1 and 2 do not mean that M_c is not related to $G_N°$. The elucidation of the nature of the $G_N° - M_c$ relationships, and their quality, will have to wait until higher quality experimental data are available. Only at that time firm conclusions concerning the above points can be reached.

Until now we have dealt with attempted correlations of $G_N°$ with *long-distance* chain parameters such as M_c, N_c, and L_c. We have found that the correlations, even when limited to flexible and semiflexible polymers only, are nonexistent or poor at best. We shall now direct our attention to *short-distance* chain parameters such as the average chain diameter and the Kuhn segment. The average chain diameter, d, is defined as $(d^2)^{1/2}$, where d^2 is the chain cross-sectional area. The Kuhn segment length A is twice the persistence length, q, for flexible chains obeying Gaussian statistics. A/d is the axial ratio of the Kuhn segment. Not counting several polymers whose $G_N°$ values fall substantially below the range of expectations (e.g., no. 31, 38, 45, 46, 49, and 53) or whose d^2 area is out of the range of all other polymers (no. 62), we are left with 46 statistically well-behaved polymers. Linear correlation

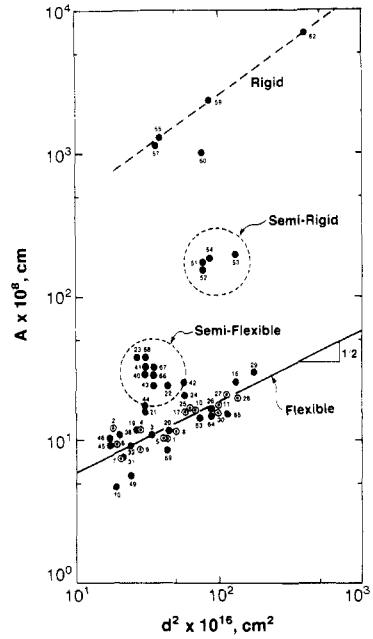

Figure 3. Relationship between A and d for four groups of polymers.

analysis of the relationship between $G_N°$ and $1/d$ of the 46 polymers produced an extremely small coefficient of determination, $r^2 = 0.1367$. The results of the correlation of $G_N°$ and d were the same, naturally, but with the sign of the correlation coefficient being negative. The analysis of the correlation between $G_N°$ and A was carried only for the 44 flexible and semiflexible polymers in Tables I and II. The resulting value of $r^2 = 0.3427$ indicates a marginal correlation between $G_N°$ and A.

In a previous paper[8] we have shown that for flexible polymers there exists a proportionality of the form

$$N_c \propto A^2 \tag{7}$$

or, to be exact, $A^2 = 0.44N_c - 10.55$. For the 36 flexible polymers in ref 8, the correlation coefficient was obtained as $r = 0.830$ and the coefficient of determination $r^2 = 0.689$. For the same 36 polymers the correlation of N_c with $C_\infty{}^2$ resulted in $r^2 = 0.585$. Attempted correlations of N_c with A or A^3 resulted in r^2 values much smaller than for the $N_c - A^2$ correlation. A plot of $G_N°$ against A^2 gave, for the flexible and semiflexible polymers, a data point scatter very much the same as seen in Figures 1 and 2.

The values of the Kuhn segment lengths, from Tables I and II, are plotted in Figure 3 against the corresponding values of d^2. The slope of the straight line passing through the flexible polymers data points is 0.5. In a similar plot[9] where A is plotted against d^4, the slope of the line is 0.25. This indicates a proportionality of

$$A \propto d \tag{8}$$

Linear correlation analysis of the 35 flexible polymers in Figure 3 resulted in $r^2 = 0.6848$, a rather good correlation of A and d considering the diversity of polymers and polymer families, the various sources of data, and the fact that polymeric sulfur (49) and selenium (70) were also included in the sample population. Interestingly, all 15 data points of the polymers selected by Graessley and Edwards[6] were nicely scattered around the line $A \propto d$, with 13 of them within one standard deviation $\sigma = 3.018$, from the line. The dependence of A on d to several other powers, including $d^{4/3}$ and $d^{2/3}$, was tested with a resulting decrease in r^2 and increase in σ. The linear dependence of A on d for flexible polymers is expected from simple

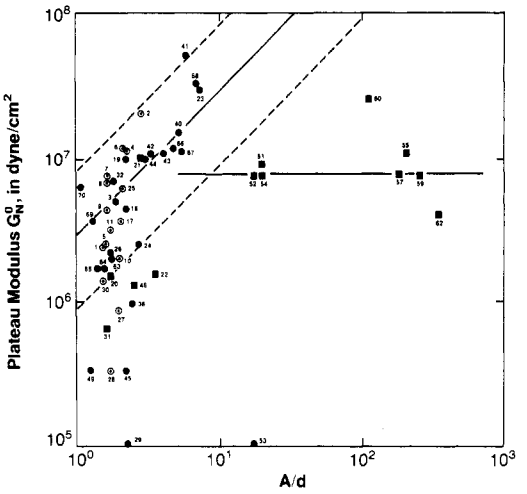

Figure 4. Plateau modulus plotted against A/d. Only flexible and semiflexible polymers between the dashed lines were analyzed statistically.

geometrical considerations. Because proportionality 8 holds for over half the polymers in the sample population, it is not unexpected that the correlation of A with A/d will produce rather large r^2 values for the whole population. Values of A were thus correlated with A/d for 53 polymers in Tables I and II, producing a coefficient of determination $r^2 = 0.8053$. A least-squares analysis indicated that the dependence of A on A/d, or vice versa, is linear. It will be shown later that the relationship between L_c and A strongly affects the behavior of polymeric chains. First, however, we shall devote our attention to flexible and semiflexible polymers alone.

Plateau modulus values in Tables I and II were plotted against A/d, $(A/d)^2$, and $(A/d)^3$. Figure 4, for $G_N°$ vs. A/d, is typical since the three plots bear substantial similarity to one another. From the 44 flexible and semiflexible polymers, the $G_N°$ values of only 33 polymers were considered of acceptable quality to be subjected to statistical analysis. Least-squares analysis favored the relationship

$$G_N° \propto A/d \tag{9}$$

with the relationship of $G_N° \propto (A/d)^2$ coming a close second. The relationship $G_N° \propto (A/d)^3$ showed a poor third. For the 33 tested polymers (no. 1–11, 16, 17, 19–21, 23–26, 30, 32, 40, 42–44, 63–69) between the dashed lines in Figure 4, the correlation coefficient of $G_N°$ with A/d was $r = 0.8552$ and the coefficient of determination $r^2 = 0.7314$. The equation relating $G_N°$ (in units of 10^7 dyn/cm^2) to A/d is

$$G_N° = -0.2961 + 0.4096A/d \tag{10}$$

When the number of tested polymers was expanded to all 44 flexible and semiflexible ones, the quality of the correlations decreased somewhat. In this case, the correlation coefficient of the $G_N° - A/d$ relationship was $r = 0.7999$, and $r^2 = 0.6398$. The correlation between $G_N°$ and $(A/d)^2$ was almost as good, with $r = 0.7871$ and $r^2 = 0.6195$. From the discussion above, and as will be shown below, proportionality 9 is believed by us to be valid. It may be that additional, better quality, data will tilt the balance in favor of a $G_N° - (A/d)^2$ relationship. In any case, both these dependencies are far superior to any of the correlations between $G_N°$ and any of the long-distance chain parameters or $G_N°$ and any individual short-distance parameter such as A or d alone.

In Figure 4 the ordinate $G_N°$ is in units of dyn/cm^2 and the abscissa A/d is dimensionless. To render the correlation dimensionless, $G_N°$ should be multiplied by some

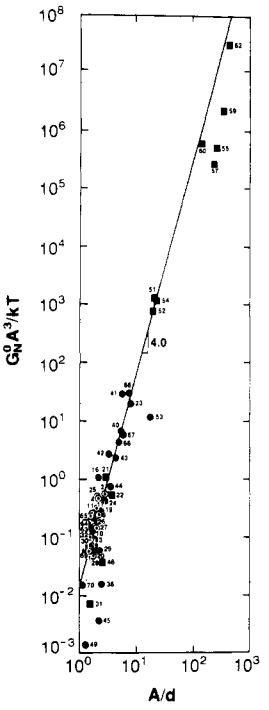

Figure 5. $G_N°A^3/kT$ vs. A/d.

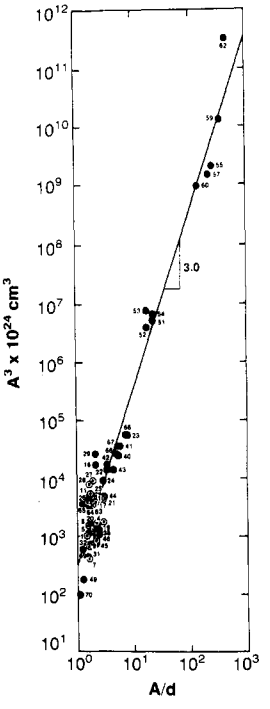

Figure 6. A^3 vs. A/d.

factor having the units cm^2/dyn. In Figure 1 of their treatment of the plateau modulus of flexible polymers, Graessley and Edwards[6] elected to use A^3/kT as the multiplication factor for $G_N°$. Their abscissa variable nLA^2 is essentially identical with our $(A/d)^2$ because nL is the total chain length per unit volume (including the "free" volume), which closely approximates the inverse of d^2.

To render the ordinate variable dimensionless, it is not necessary to multiply $G_N°$ specifically by A^3/kT. This multiplier can be replaced, for instance, by l_0^3/kT, where l_0 is an average backbone bond distance, of the order of 1.5 Å for hydrocarbons. Taking polystyrene as an example, $A^3 = 4826.81$ Å^3 and $l_0^3 = 3.65$ Å^3 ($l_0 = 1.54$ Å). The large values of A^3 tend to dominate, at least the appearance of, the plots in which $G_N°$ is multiplied by multiplication

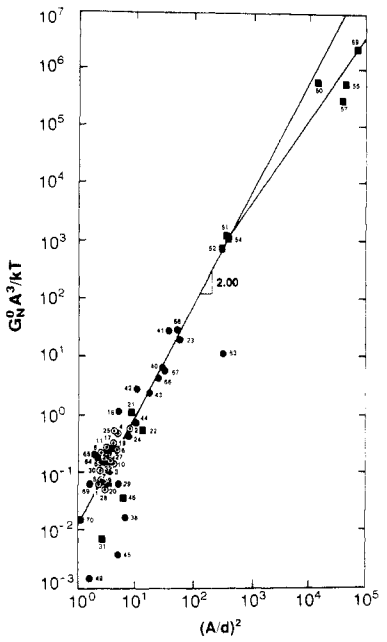

Figure 7. $G_N^\circ A^3/kT$ vs. $(A/d)^2$. Plot fundamentally the same as Figure 1 of Graessley and Edwsards.[6]

factors containing A^3. In Figure 5, for example, $G_N^\circ A^3/kT$ is plotted against A/d. In Figure 6, A^3 alone is plotted against A/d. The similarity of the plots is obvious, even though the slope of the $G_N^\circ A^3/kT$ line is larger by one power than the slope of the A^3 line. A plot of $G_N^\circ A^3/kT$ against $(A/d)^2$, in Figure 7, is similar in nature and in conclusions to the plot in Figure 5, again indicating a dependence of $G_N^\circ A^3/kT$ on $(A/d)^2$ to one power higher than the dependence of A^3 on $(A/d)^2$

$$G_N^\circ A^n \propto (A/d)^{n+1} \tag{11}$$

Figure 6 as well as a plot of A^3 vs. $(A/d)^2$ not reproduced here indicate a relationship of

$$A^n \propto (A/d)^n \tag{12}$$

Division of proportionality 11 by proportionality 12 results in

$$G_N^\circ \propto A/d \tag{9}$$

in agreement with the conclusion previously reached on the basis of the statistical analysis of the G_N° vs. A/d model. Plots of $G_N^\circ A^2$ and $G_N^\circ A^2/kT$ against A/d and $(A/d)^2$, not reproduced here, all lead to an identical conclusion. Linear correlation analysis of all 53 polymers in Tables I and II yielded $r = 0.9080$ and $r^2 = 0.8245$ for the correlation between $G_N^\circ A^3/kT$ and A/d. For the correlation between $G_N^\circ A^3/kT$ and $(A/d)^2$, only the 48 flexible, semiflexible, and semirigid polymers were considered. In this case $r = 0.8960$ and $r^2 = 0.8028$ were obtained. The numerical difference between the corresponding results are not large, but because the rigid polymers were included in the A/d correlation and omitted from the $(A/d)^2$ correlation, it is felt that the differences are significantly in favor of proportionality 9. Interestingly, the correlation of $G_N^\circ A^3$ with $(A/d)^2$ yielded $r = 0.8977$ and $r^2 = 0.8059$. These values are almost identical with the values obtained from $G_N^\circ A^3/kT$ vs. $(A/d)^2$. This indicates that the presence or absence of kT in the ordinate variable has practically no effect on the results. It should be noted that our Figure 7 contains the same ordinate and abscissa variables as Figure 1 of Graessley and Edwards,[6] and the same conclusions drawn here should be drawn from their figure too.

On the basis of the above, it is our belief that the large values of the coefficients of determination, r^2, obtained in the $G_N^\circ A^3$ and $G_N^\circ A^3/kT$ correlations with A/d and $(A/d)^2$ merely reflect (a) the above mentioned large coefficient of determination of the corresponding correlations of A^3 with A/d and $(A/d)^2$, and (b) the domination of the $G_N^\circ A^3$ and $G_N^\circ A^3/kT$ correlations by A^3.

In the following, an attempt will be made to rationalize the apparent dependence of G_N° on A/d, at least for flexible polymers. The data in Figure 3 and similar plots[9] show a clear distinction between flexible, semiflexible, semirigid, and rigid polymers. This distinction is based solely on the relationship between A and d, two parameters associated only with the structural features of the chain. Employing the values of l_0 for all 46 flexible polymers in this work and in ref 8, one calculates an average bond length of $l_{0,a} = 1.542$ Å. From the relationship $L_c = l_0 N_c$, we obtain $L_c = (1.542 \text{ Å})N_c$. It was demonstrated in ref 8 that for flexible polymers

$$N_c \cong (2.5 \text{ Å}^{-2})A^2 \tag{13}$$

Putting it all together, one obtains

$$L_c \cong (1.542 \text{ Å})(2.5 \text{ Å}^{-2})A^2 \text{ (Å}^2) = (3.855 \text{ Å}^{-1})A^2 \text{ (Å}^2) = 4A^2 \tag{14}$$

where the units of L_c and $4A^2$ are in Angstroms. This means that for an "average flexible polymer" with solely or mostly tetrahedral carbon–carbon backbone bonds for $A = 5$ Å, $L_c = 100$ Å and for $A = 30$ Å, $L_c = 3600$ Å. These values are in an order of magnitude agreement with values available for individual polymers.

For flexible polymers, the Kuhn segment length equals twice the persistence length, q. From its definition, the persistence length can contain no less than two actual or virtual backbone bonds. Therefore, A should contain no less than four such bonds. For average flexible polymers, this amounts to 4×1.542 Å $= 6.168$ Å and a minimum length of

$$L_{ca} = 4(6.168)^2 = 152 \text{ Å} \tag{15}$$

The ratio of the smallest L_{ca} to the smallest A_a for the "average flexible polymer" is, then,

$$L_{ca}/A_a = 152/6.168 = 25 \tag{16}$$

As expected, this ratio is somewhat smaller than the average ratio obtained from all the flexible polymers in Tables I and II.

For 10 semiflexible polymers in this work and in ref 8, the average value of l_0 was calculated to be $l_{0,a} = 1.211$ Å. Because they are clustered closely together in Figure 3, no proportionality of A to d was derived. With average values for the 10 polymers, an average $N_{ca} = 227$ was found, from which an average $L_{ca} = 227(1.211 \text{ Å}) = 275$ Å was obtained. The average value of A was found to be $A_a = 29.4$ Å. From this, a ratio of

$$L_{ca}/A_a = 9.35 \tag{17}$$

characteristic of an "average semiflexible polymer" is obtained. For the four semirigid cellulose derivatives, the following average values were calculated: $l_{0,a} = 1.55$ Å, $N_{ca} = 36$, $L_{ca} = 55.8$ Å, and $A_a = 180.5$ Å. These lead to a ratio of

$$L_{ca}/A_a = 0.31 \tag{18}$$

for an "average semirigid polymer". The average bond length for 10 rigid polymers in ref 8 and in this paper was found to be $l_{0,a} = 1.259$ Å. Average $N_{ca} = 91.5$, $L_{ca} = 115.2$

Å, and A_a = 1650 Å were calculated. From these a ratio of

$$L_{ca}/A_a = 0.07 \quad (19)$$

for an "average rigid polymer" is obtained. It is obvious that substantial differences exist between the L_{ca}/A_a ratios of the four polymer groups.

We can now propose an explanation as to why the rigid and, to a lesser extent, semirigid polymers show a behavior different from the flexible and semiflexible polymers in the correlations of $G_N°$ with N_c and $G_N°$ with A/d (Figures 2 and 4) and in the relationships of $G_N°A^3/kT$ with A/d and $(A/d)^2$ in Figures 5 and 7. In the two latter figures, the power dependence of $G_N°A^3/kT$ on A/d or $(A/d)^2$ was reduced by one power upon moving from the region of flexible and semiflexible polymers to the region of rigid and semirigid ones. This indicates, in agreement with Figures 2 and 4, that upon moving into the region of semirigid and, especially, rigid polymers, $G_N°$ becomes independent of A/d and, for these polymers, the dependency $G_N°A^n \propto (A/d)^n$ reflects only proportionality 12 shown above to exist among all polymer groups tested. Relationships 18 and 19 state that for rigid and semirigid polymers the length of the polymeric chain between entanglements, L_c, is far smaller than the distance A. This means that the points along the chain at which stress is transmitted from one chain to another, and at which constraints on free chain mobility are imposed, are far closer to each other than the length A. Therefore, as the distance L_c becomes smaller than A, the plateau modulus $G_N°$ loses its dependence on A/d. This holds true whether the modulus was measured in the bulk or extrapolated from solution measurements. A developing dependence of $G_N°$ on L_c or L_c/d is likely to substitute the dependence on A/d, but at present we have no supporting evidence for this.

In the case of flexible and semiflexible polymers, $L_c \gg A$, and the magnitude of the plateau modulus is dependent on A/d. This is congruent with the observations of the Soviet school[10,11,12] that the smallest chain segment of flexible polymers apparently moving as an individual entity has a length typically of the order of A. It is possible that for cases where $L_c \gg A$, the magnitude of $G_N°$ is a reflection of the number of bonds along the Kuhn segment and of their resistance to torsional rotation. At present we have no support for this idea.

There is one final point worth mentioning. It is important to recognize that the appearance of the plateau modulus is not necessarily dependent on the presence in the system of "conventional" entanglements requiring chain bending, twisting, folding, and the such. Relatively dilute fully isotropic solutions of rodlike entities were demonstrated to develop a plateau modulus once a certain concentration limit was surpassed. Among these systems one finds aqueous solutions of tobacco mosaic virus (M = 39 × 10^6, L = 3000 Å)[13] and rodlike micelles of certain detergent molecules (cetylpyridinium salicylate, M = 441, micellar length 5500 Å).[14,15] Neither of the above rodlike entities can bend or deform, and "entanglements" between them appear to be simply contact points that block or retard the motions of the rodlike particles in solution. The solution behavior of the rigid polymers mentioned in this paper is visualized to be similar to the behavior of these rodlike entities.

Conclusions

When literature $G_N°$ values of many flexible and semiflexible polymers are correlated with long-distance chain parameters such as M_c, N_c, or L_c, the data pairs are found to be uncorrelated or very poorly correlated. The reasons for the lack of correlation are many. When $G_N°$ values are correlated with short-distance chain parameters such as A or d, and especially A/d, the variable pairs correlate far better. It is further shown that when $G_N°$ is multiplied by A^3/kT and plotted against A/d or $(A/d)^2$, with both ordinate and abscissa being dimensionless, it is the multiplication factor A^3/kT (or A^3 alone) that dominates. This results in a dependence of the form $G_N°A^n/kT \propto (A/d)^{n+1}$ or $G_N°A^n \propto (A/d)^{n+1}$. These dependencies obscure the dependence

$$G_N° \propto A/d$$

which we believe is the one correctly describing the relationship between $G_N°$ and A/d.

The relationship between L_c and A explains the difference in behavior of flexible and semiflexible polymers on one hand and rigid and semirigid polymers on the other. In the case of flexible polymers, $L_c \gg A$ and $G_N°$ is dependent on A/d. In the case of rigid polymers, $L_c \ll A$ and $G_N°$ is independent of A/d.

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Registry No. Poly(ethyl acrylate), 9003-32-1; poly(butyl acrylate), 9003-49-0; poly(ethylhexyl acrylate), 9003-77-4; (carbonic acid)·(tetramethyl bisphenol A) (SRU), 38797-88-5; (carbonic acid)·(tetramethyl bisphenol A) (copolymer), 52684-16-9; (carbonic acid)·(terephthalic acid)·(tetramethylbisphenol A) (polymer), 99828-65-6; (4,4'-benzophenonedicarboxylic acid)·(bisphenol A) (SRU), 41706-32-5; (4,4'-benzophenonedicarboxylic acid)·(bisphenol A) (copolymer), 38783-58-3; poly(ethylene tetrasulfide), 32128-89-5; selenium, 7782-49-2; polyethylene, 9002-88-4; polypropylene, 9003-07-0; poly(isobutene), 9003-27-4; polybutadiene, 9003-17-2; polyisoprene, 9003-31-0; polystyrene, 9003-53-6; poly(α-methylstyrene), 25014-31-7; poly(vinyltoluene), 9017-21-4; poly(1-vinylnaphthalene), 25135-12-0; poly(2-vinylnaphthalene), 28406-56-6; poly(4-vinylbiphenyl), 25232-08-0; poly(*N*-vinylcarbazole), 25067-59-8; poly(vinyl acetate), 9003-20-7; poly(vinyl alcohol), 9002-89-5; poly(vinyl chloride), 9002-86-2; poly(acrylic acid), 9003-01-4; poly(acrylonitrile), 25014-41-9; polyacrylamide, 9003-05-8; poly(tetrafluoroethylene), 9002-84-0; poly(methyl acrylate), 9003-21-8; poly(methyl methacrylate), 9011-14-7; poly(*n*-butyl methacrylate), 9003-63-8; poly(*n*-hexyl methacrylate), 25087-17-6; poly(*n*-octyl methacrylate), 25087-18-7; poly(*n*-dodecyl methacrylate), 25719-52-2; poly(2-ethylbutyl methacrylate), 25087-19-8; poly(ethylene oxide), 25322-68-3; poly(propylene oxide), 25322-69-4; poly(tetramethylene oxide), 25190-06-1; poly(oxyundecanoyl) (SRU), 25735-90-4; poly(oxyundecanoyl) (homopolymer), 3669-80-5; poly(decamethylene succinate) (SRU), 28726-53-6; poly(decamethylene succinate) (homopolymer), 27517-29-9; poly(decamethylene adipate) (SRU), 25212-79-7; poly(decamethylene adipate) (homopolymer), 28552-31-0; poly(decamethylene sebacate) (SRU), 25482-94-4; poly(decamethylene sebacate) (homopolymer), 27514-86-9; poly(ethylene terephthalate), 25038-59-9; poly(ethylene isophthalate) (SRU), 26948-62-9; poly(ethylene isophthalate) (homopolymer), 26810-06-0; (carbonic acid)·(bisphenol A) (SRU), 24936-68-3; (carbonic acid)·(bisphenol A) (homopolymer), 25037-45-0; (bisphenol A)·(terephthalic acid)·(carbonic acid) (polymer).

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Determination of Correlation Lengths in Swollen Polymer Networks by Small-Angle Neutron Scattering

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ABSTRACT: The analogy between semidilute polymer solutions and swollen polymer networks is reviewed and some implications of current theories are considered. Small-angle neutron scattering has been used to measure a characteristic correlation length in randomly cross-linked polystyrene gels at swelling equilibrium in cyclohexane over the range 308–333 K and in toluene at ambient temperature. The equilibrium polymer volume fraction ranged from ca. 0.01 to 0.3, depending on the cross-link density and the solvent used. These results, together with those from earlier quasi-elastic light scattering measurements, were compared with reported scaling laws for polymer solutions. Although similar behavior was noted, the presence of permanent cross-links restricts the region wherein strong excluded volume effects are evident.

Introduction

Considerable insight into the understanding of highly swollen polymer networks, gels, has been obtained from an analogy with semidilute polymer solutions.[1] In a gel the macromolecules are connected by permanent junctions, the chemical cross-links, while in solutions only transient junctions occur, i.e., entanglements or other constraining interactions. In the spirit of this analogy, it is anticipated that it will only be in the very low-frequency properties that polymer solutions will display a different behavior to gels, that is, when the probing frequency is smaller than the reciprocal lifetime of the transient junctions in the solution. Consequently, the recent advances in polymer solution behavior theory should, in principle, be applicable to gels.

Contemporary theories of semidilute/concentrated solutions express the properties in terms of a fundamental length, ξ, being the radius of a volume inside which intramolecular effects are dominant and beyond which intermolecular effects prevail.[1-12] Static properties and equilibrium thermodynamics are discussed in terms of a static correlation length, ξ_c, while dynamic properties (e.g., as measured by quasi-elastic light scattering (QELS)) are characterized by a hydrodynamic screening length, ξ_h; these two parameters have been assumed to be identical with or at least directly proportional to each other. The detailed relation between the two parameters has been discussed by Muthukumar and Edwards.[51]

For a high degree of polymerization the short-range structure of the macromolecule is relatively insignificant, and universal laws that are a function of temperature, concentration, and interaction parameter can be derived for the global properties of the solution or gel and the characteristic length scales of the macromolecules (ξ or R_g, where R_g is the radius of gyration). Characteristic lengths may be measured directly or extracted by some model-dependent analysis of observable properties. Scattering experiments using light, X-rays, or neutrons are particularly useful since between them they cover a wide range of spatial and temporal resolution. The static scattering law, $S(\mathbf{Q})$, analyzed as a function of scattering vector $\mathbf{Q}$ can provide mean equilibrium dimensions while the first cumulant of the dynamic scattering law, $S(\mathbf{Q},t)$, may provide a cooperative diffusion coefficient that is subsequently interpretable in terms of ξ_h.

We describe here the results of measurement of ξ_c by small-angle neutron scattering (SANS) for randomly cross-linked polystyrene networks at equilibrium swelling at different thermodynamic conditions. Comparisons are made with available data for polymer solutions and our previously reported values for ξ_h obtained by QELS. The results are discussed in the framework of existing ideas on the correlation length, ξ, a précis of which is given in the next section, and the applicability of scaling laws to swollen polystyrene networks is examined.

Theoretical Background

The formulation of a comprehensive theory of polymer solutions and gels requires a thorough theoretical and experimental understanding of ξ. We attempt this here by providing an overview, in précis form, of current ideas on the nature of ξ, and we start with an isolated unperturbed macromolecule. The conformation of such a molecule is exactly describable by rotational isomeric state theory[13] and to all practical purposes is a random walk. In solution, the conformation is expanded by repulsive interactions between topologically remote segments of the chain (with respect to the contour length) that become spatially proximate. The molecule now adopts a self-avoiding walk,[14,15] wherein different segments cannot coincidentally occupy the same volume element of the solution, the well-known excluded volume effect. The theory and description of such self-avoiding walks and the interplay between temperature and solvent in influencing polymer conformation in dilute solutions are at a high level of development.[14]

In the discussion of the conformation of an individual molecule in more concentrated solutions, there have been two main approaches. Edwards uses a self-consistent field

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