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Chain Flexibility Parameter and Persistence Length of Various Poly(methacrylic acid) Esters

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The theoretical treatments developed by Yamakawa and co-workers on the basis of the wormlike[1] and helical wormlike[2,3] chain models have been frequently used to determine the degree of rigidity of semirigid macromolecules. The latter is expressed by means of the persistence length q, which is conceptually a measure of how far a polymeric chain persists in a given direction. On the contrary, in the case of flexible coils which obey Gaussian statistics, the degree of rigidity is commonly defined by means of the so-called flexibility parameter, which is in fact a measure of the hindrance to internal rotation about the single bonds of the chain.[4] σ represents the ratio $\langle r_0^2\rangle^{1/2}/\langle r_{0,f}^2\rangle^{1/2}$ of the unperturbed root mean square end-to-end distance $\langle r_0^2\rangle^{1/2}$ to the same distance of a hypothetical chain with free internal rotation $\langle r_{0,f}^2\rangle^{1/2}$; it ensues that

$$\langle r_0^2\rangle = \sigma^2\langle r_{0,f}^2\rangle = \sigma^2 n l^2\left(\frac{1+\cos\theta}{1-\cos\theta}\right) \qquad (1)$$

where l is the bond length, θ the supplement of the valence angle, and n the number of bonds. For an infinitely long chain in the coil limit, we have

$$\langle r_0^2\rangle \simeq 2qL \qquad (2)$$

The contour length L is equal to the number of monomer units multiplied by the contribution length of each monomer. It is thus expected from the comparison of eq 1 and 2 that a quadratic dependence of q on σ should be obeyed, as previously mentioned by Kurata and Stockmayer.[4] From a theoretical point of view, comparisons between Flory's rotational isomeric state model and the Kratky–Porod wormlike chain model have been presented by Maedo, Saito, and Stockmayer[5] and by Mansfield.[6] More recently, a detailed comparison between the rotational isomeric state and the helical wormlike cylinder models has been presented by Fujii et al., with particular emphasis on rather flexible chains.[7]

The purpose of the present note is to make use of the Yamakawa–Fujii relationship for the viscosity of wormlike chains to derive values of the persistence length of a series of poly(methacrylic acid) esters (disubstituted asymmetric chains), using experimental results in the ideal Θ state, i.e., in the absence of excluded volume effects. The theory of Yamakawa et al. has been frequently applied to the treatment of the steady-sate transport and dynamic properties of stiff chains such as polynucleotides, polypeptides, cellulose derivatives, poly(n-alkyl isocyanates), etc., but rather less of flexible chains.

Experimental Section

According to Yamakawa and Fujii, the intrinsic viscosity (in $\mathrm{cm^3\cdot g^{-1}}$) of wormlike chains is related to the molecular weight M and the persistence length q through the relationship

$$[\eta] = \frac{\Phi_\infty M^{1/2}}{(M_L/2q)^{3/2}}\left[1 - \sum_{i=1}^{4} C_i\left(\frac{L}{2q}\right)^{-i/2}\right]^{-1} \qquad (3)$$

where Φ_∞ is the theoretical Flory constant for infinitely large molecular weights (2.87×10^{23} in cgs units) and M_L is the molar mass per unit length, so that $M_L = M/L = M_0/h$ if M_0 and h designate the molecular weight of the monomer and the length of the monomer unit, respectively. C_i are coefficients which depend on the ratio $d/2q$, where d is the diameter of the curved cylinder associated with the wormlike chain. The C_i coefficients can be calculated with the aid of the expressions reported in ref 3 for two $d/2q$ ranges: $d/2q < 0.1$ and $0.1 \leq d/2q < 1.0$. Our calculation procedure consists in fitting the experimental $[\eta]$ vs. M curves with the theoretical equation (3) by means of a multiparametric nonlinear least-squares fitting program.[8] Persistence length and chain diameter are kept as adjustable parameters, whereas the length of the monomer unit, equal to 2.5 Å for a vinylic chain, is considered as a constant. Similar procedures have been already used in the analysis of the viscosity results of cellulose derivatives[9] and polyelectrolytes.[10]

As we detected for some samples $d/2q$ values close to the limit of 0.1, at which the C_i coefficients of eq 3 vary, the fittings were performed for the two situations $d/2q < 0.1$ and $0.1 \leq d/2q < 1.0$. The persistence lengths obtained in this way did not generally differ by more than 4%, and the average of the two q values will be retained for further discussion. On the contrary, the difference in the diameter values can reach a factor of about 2. All the fittings of the experimental data are very close and characterized by relative mean square deviations comprised between 0.01 and 0.02.

Results and Discussion

For some polymethacrylates, Θ conditions were determined experimentally and K_Θ values were directly obtained from the viscosity–molecular weight relationship; the experimental $[\eta]_\Theta$ and $\bar{M}_w$ values were treated by the computing procedure presented above. For other polymers, intrinsic viscosities were measured in a few good solvents and K_Θ values were calculated with the aid of several theories which imply extrapolations to zero molecular weight: Stockmayer–Fixman, Kurata–Stockmayer, Cowie, Berry, Kamide–Moore, etc. Eight to ten $[\eta]_\Theta,\bar{M}_w$ pairs were then calculated with the viscosity–molecular weight relationship ($[\eta]_\Theta = K_\Theta \bar{M}_w^{1/2}$), making use of the mean K_Θ obtained from the various theories. The molecular weight range was between 5×10^4 and 10^6. With the exception

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Table I
Characteristics of the Various Polymethacrylates: K_Θ Constants, Average Polydispersity, Flexibility, Persistence Length, and Molar Volume of the Monomer Unit[a]

lateral group	solvent (T, °C)	$K_\Theta \times 10^3$, $cm^3 \cdot g^{-1}$	$\langle \bar{M}_w/\bar{M}_n \rangle$	σ^*	σ^a	q, Å	V, $cm^3 \cdot mol^{-1}$	ref
methyl	4-heptanone (33)	48.0	1.80	1.80	1.79	6.8 ± 0.3	86.5	11
	acetonitile (45)							
ethyl	2-propanol (36.9)	47.5		2.00	1.90	7.9 ± 0.5	102.4	12
butyl	2-propanol (23.7)	37.0		2.06	1.95	8.4 ± 0.5	134.0	12
hexyl	2-propanol (43.0)	43.0		2.29	2.25	10.9 ± 0.4	165.7	13
octyl	1-butanol (16.8)	26.8		2.28	2.07	9.5 ± 0.1	197.4	14
dodecyl	1-pentanol (29.5)	34.8		2.59	2.56	14.4 ± 0.2	260.8	15
2-ethylbutyl	2-propanol (27.4)	33.7		2.12	2.07	8.3 ± 0.4	167.4	16
2,2-dimethylpropyl	various solvents (25)	45.0			2.19	10.4 ± 0.5	154.8	17
triethylmethyl	various solvents (25)	37.0	1.5	2.50	2.23	11.0 ± 0.4	186.4	18
cyclohexyl	1-butanol (23)	44.6	1.2	2.50	2.26	11.1 ± 0.4	153.3	19
	various solvents (25)	(45.0)						
decahydro-β-naphthyl	various solvents (25)	43.0	1.4	2.90	2.56	14.3 ± 0.2		20
menthyl	2-pentanone (25)	43.6	1.5	3.10	2.59	14.8 ± 0.2		21
	various solvents (25)	(44.0)						
4-*tert*-butylcyclohexyl	1-butanol (25)	31.3	1.5	2.26	2.32	11.7 ± 0.3	216.7	22
phenyl	various solvents (25)	57.0	1.6	2.80	2.41	11.8 ± 0.3	135.3	19
naphthyl	various solvents (25)	54.0	1.5	3.10	2.71	16.1 ± 0.2		20
(tetramethylbutyl)phenyl	various solvents (25)	44.5		3.36	2.89	19.1 ± 0.5	272.6	23
2-*tert*-butylphenyl	cyclohexane (18.4)	35.5	1.3	2.60	2.39	12.3 ± 0.3	194.3	21
	various solvents (25)	(35.0)						
4-*tert*-butylphenyl	cyclohexane (25)	43.1	1.4	2.62	2.55	14.6 ± 0.2	194.3	22
	various solvents (25)	(45.0)						
triphenylmethyl (trityl)	various solvents (25)	37.0	1.6	2.97	2.97	20.0 ± 0.2	285.3	24
2-chlorophenyl	various solvents (25)	36.0		2.27	2.28	11.3 ± 0.3	148.0	25
4-chlorophenyl	various solvents (25)	48.0	1.5	2.75	2.51	13.7 ± 0.3	148.0	26
2,4,5-trichlorophenyl	various solvents (25)	26.0	1.2	2.37	2.38	12.4 ± 0.2	178.6	27

[a] σ^* is the flexibility parameter given by the authors; σ is the flexibility parameter calculated with the same value of ϕ according to eq 1 and 4.

of poly(4-(1,1,3,3-tetramethylbutyl)phenyl methacrylate), for which only osmotic pressure experiments have been performed, all the literature data[11-27] are based on weight-average molecular weights. Θ conditions (solvents and temperature), K_Θ values, and average polydispersities $\langle \bar{M}_w/\bar{M}_n \rangle$ (if available) are collected in Table I together with the flexibility σ^* given by the authors.

In the unperturbed state, the values of the average persistence length for the various polymethacrylates range from 7 to 20 Å and, in first approximation, increase with the molecular volume of the lateral group. The diameter values are found to be between 2 and 6 Å. However, a fitting which does not include the length of the monomer unit under the adjustable parameters may be questionable. We refer to the recent paper of Fujii et al.[7] which presents a detailed analysis of the helical wormlike chain model of Yamakawa and co-workers compared to the rotational isomeric state model of Flory. The model parameters, i.e., the Kuhn statistical segment, equal to twice the persistence length, the molar mass per unit length M_L, and the curvature and torsion constants of the helix, are given for a wide variety of polymers. If we consider the monosubstituted and disubstituted asymmetric chains (18 polymers), the average value of the monomer length is equal to 2.58 Å with a standard deviation of 0.25 Å. This allows one to fix with confidence the limits of the range of h values to be used.

It is also worth noting that the microtacticity for most of these polymethacrylates has been previously analyzed.[28,29] The general tendency is a decrease of syndiotacticity with increasing bulkiness of the ester group, poly(methyl methacrylate) having the highest syndiotactic configuration. On the contrary, poly(trityl methacrylate) has a high isotacticity, which can be explained on the basis of steric hindrance effects combined with specific interaction between the phenyl rings.[24] It is precisely this polymer which shows a persistence length close to that of some polymers with heterocyclic rings in the main chain, namely 33 Å for poly(phthaloyl-*trans*-2,5-dimethylpiperazine) in *N*-methyl-2-pyrrolidone[30] and 30 Å for poly(phenylenemethylene-3,5-pyrazole) in dimethylformamide[31] (non-Θ conditions).

The σ values given in Table I were calculated with the aid of eq 1 and 4:

$$K_\Theta = \Phi_\infty[\langle r_0^2 \rangle / M]^{3/2} \tag{4}$$

taking $\Phi_\infty = 2.87 \times 10^{23}$, $l = 1.54$ Å, and $n = 2M/M_0$ in the case of a vinylic unit. In first approximation, $\cos\theta$ has been put equal to $^1/_3$. A correction for polydispersity is not necessary in the present case since the average polydispersity values are of the order of 1.2–1.5. Indeed, if we assume that the distribution of the molecular weights obeys a classical Schulz–Zimm exponential law, the correction on Φ does not exceed 3–4% as long as weight-average molecular weights are considered.[22,24]

Since the contour length L is equal to Mh/M_0, it arises from eq 1 and 2 that

$$q = \frac{\sigma^2 l^2}{h}\left(\frac{1 + \cos\theta}{1 - \cos\theta}\right) \tag{5}$$

The slope of the dependence of q on σ^2, depicted in Figure 1, will thus depend on the choice made to define the parameter h. If h is identified with the projection of the monomer unit along the direction of its first link, i.e., $h = l(1 + \cos\theta) = 2.05$ Å, we can write that

$$q = \sigma^2 l/(1 - \cos\theta) = 2.32\sigma^2 \tag{6}$$

This relationship, previously obtained by Kurata and Stockmayer,[4] considers in fact a contribution of the monomer to the total chain length which is too short with respect to the most frequently accepted value, or 2.5 Å. The problem of the definition of the monomer unit length has already been discussed by Yamakawa.[32] In our case,

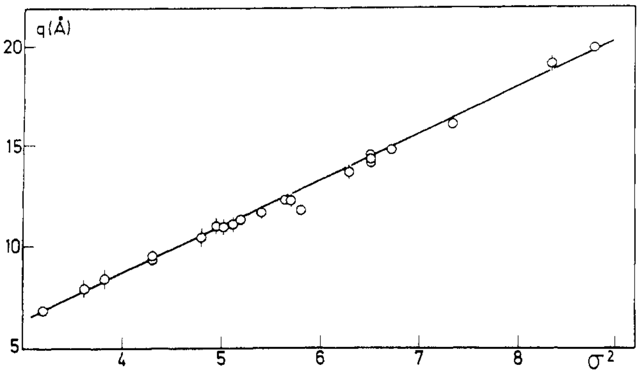

Figure 1. Variation of the persistence length with the square of the flexibility parameter for the various polymethacrylates investigated.

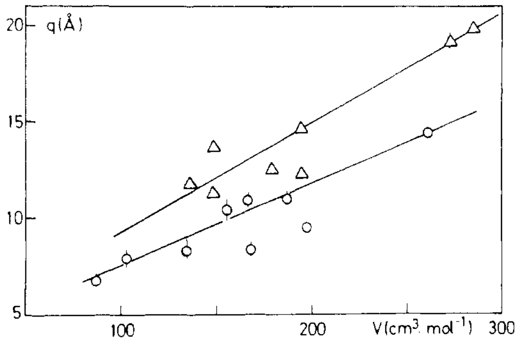

Figure 2. Influence of the molar volume of the methacrylic ester group on the persistence length in the case of aliphatic (○) and aromatic (△) esters.

we preferred to take the average of two lengths forming a valence angle equal to $(\pi - \theta)$, so that $h = 2l \cos (\theta/2) = 2.5$ Å. This is equivalent to considering the contour length as that of the fully extended chain in the all-trans conformation. Hence, eq 5 becomes $q = 1.89\sigma^2$. Experimentally, we found on Figure 1 a slope close to 2.3, as expected from eq 6, in spite of the fact the determination of the persistence length by fitting has been performed with the value of 2.5 Å for the length of the monomer unit. We presently have no explanation for this apparent discrepancy. This study however indicates that the analysis previously applied to stiff polymeric chains and based on the classical Kratky–Porod wormlike chain model can be easily extended to the limit of flexible coils. Application of the Yamakawa–Fujii relationship for viscosity thus appears powerful to quantitatively determine the value of the persistence length of rather flexible chains.

As previously attempted with the σ parameter,[24] we verified the correlation between the persistence length values and the molar volume of the ester group. The latter has been calculated with the aid of the data collected by Van Krevelen and Hoftyzer[33] and the molar volume V reported in Table I is in fact the sum of the contributions of the main-chain methacrylic group and of the lateral ester group. A rather satisfactory linear variation is observed in the case of the aliphatic series whereas the scatter of the points is somewhat larger for the aromatic series (Figure 2). For an identical molar volume value, the supplement of rigidity found in the case of aromatic esters is specifically related to strong interactions between the π-electron atmosphere of the aromatic rings.[19,20] A similar linear correlation between q and V, not presented inthe present study, has been obtained with monosubstituted asymmetric chains of the vinylic type, including poly(vinyl halides), poly(vinyl esters), polyacrylates, polystyrene, and derivatives. Poly(vinyl alcohol) and poly(acrylonitrile) alone depart markedly therefrom.

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Registry No. Poly(methyl methacrylate) (homopolymer), 9011-14-7; poly(ethyl methacrylate) (homopolymer), 9003-42-3; poly(butyl methacrylate) (homopolymer), 9003-63-8; poly(hexyl methacrylate) (homopolymer), 25087-17-6; poly(octyl methacrylate) (homopolymer), 25087-18-7; poly(dodecyl methacrylate) (homopolymer), 25719-52-2; poly(2-ethylbutyl methacrylate) (homopolymer), 25087-19-8; poly(2,2-dimethylpropyl methacrylate) (homopolymer), 34903-87-2; poly(triethylmethyl methacrylate) (homopolymer), 34032-79-6; poly(cyclohexyl methacrylate) (homopolymer), 25768-50-7; poly(dodecahydro-β-naphthyl methacrylate) (homopolymer), 33774-32-2; poly(methyl methacrylate) (homopolymer), 30847-50-8; poly(4-*tert*-butylcyclohexyl methacrylate) (homopolymer), 34903-89-4; poly(phenyl methacrylate) (homopolymer), 25189-01-9; poly(naphthyl methacrylate) (homopolymer), 39296-32-7; poly((tetramethylbutyl)phenyl methacrylate) (homopolymer), 76033-34-6; poly(2-*tert*-butylphenyl methacrylate) (homopolymer), 52734-65-3; poly(4-*tert*-butylphenyl methacrylate) (homopolymer), 29696-27-3; poly(trityl methacrylate) (homopolymer), 27497-74-1; poly(2-chlorophenyl methacrylate) (homopolymer), 36876-19-4; poly(4-chlorophenyl methacrylate) (homopolymer), 34149-11-6; poly(2,4,5-trichlorophenyl methacrylate) (homopolymer), 40921-83-3.

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