Hydrodynamic and Optical Properties of Homologous Series of Styrene–Methyl Methacrylate Graft Copolymers

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ABSTRACT: Graft copolymers were prepared which contain mostly short side polystyrene branches (90% by weight) and are considered as comblike polystyrene. Two types of solvent were used: (1) good solvents for linear polystyrene and (2) cyclohexane, in which the theta point for linear polystyrene is 34.8 °C. The theta point for comblike polystyrene in cyclohexane was found to be 16 °C. These comblike macromolecules were represented by wormlike chains with the following characteristics: contour length L, thickness d, persistence length a (measure of stiffness), molecular weight per unit length $M_L = M/L$. Hydrodynamic and optical properties were investigated vs. the length of the main chain $L_A = L$. The rectilinear dependences of D_0L on $L^{1/2}$ and $L/([\eta]M_L)$ on $L^{1/2}$ (D_0 is the coefficient of translational diffusion, $[\eta]$ is the intrinsic viscosity) indicate the absence of long-range interactions. These plots gave a = 21 Å in cyclohexane and a = 45 Å in solvents of the first type. In all solvents d = 45 Å. For linear polystyrene a is 10 Å and d is 5 Å. It was experimentally found for the first time that the sign of the reduced birefrigence $[n]/[\eta]$ changes at small values of the parameter $x = L/a$. These data show that the wormlike chains are thick. The limiting value of $[n]/[\eta]$ (at $x \to \infty$) indicates that the side chains are stiff. Long-range interaction of wormlike chain increases proportionally to M_L (or d) and decreases as $a^{-3/2}$. Hence, it is seen in cyclohexane at temperatures above 16 °C but is not observed in solvents of the first type.

In order to obtain quantitative information on macromolecular chains based on modern theories of hydrodynamic and optical properties of polymer solutions[1,2] it is necessary to have experimental data for broad homologous series. We consider here the main results of hydrodynamic (viscosity, diffusion, sedimentation) and optical (flow birefringence) investigations of homologous series of styrene–methyl methacrylate graft copolymers.

Symbols. The subscript A refers to the poly(methyl methacrylate) backbone. The subscript B refers to polystyrene side chains. Their contour lengths are L_A and L_B, and their molecular weights are M_A and M_B, respectively. One macromolecule consists of a linear backbone chain to which m linear side chains are attached, with the mean distance between them L_A/m along the backbone. The weight fraction of polystyrene is y.

A schematic representation of a macromolecule of graft copolymer with a M_A/M_B ratio of 100 000/2000 = 50 is shown in Figure 1a. This is a typical comblike macromolecule, $L_A \gg L_B$.

Let us assume that in this macromolecule the backbone and side chains obey the random-flight chain model and they have the same stiffness as before coupling. Then the theoretical relation between the unperturbed mean square radius of gyration of the comblike macromolecule $\bar{R}^2_\theta$ and that of the backbone $\bar{R}^2_{\theta,A}$ is:[3]

$$(\bar{R}^2_\theta)_{\text{theor}} = \bar{R}^2_{\theta,A}(1 + (1 - y)^{-1}y^{7/3}(3m - 2)m^{-2}) \quad (1)$$

Our copolymers have short side chains. In that case a wormlike (persistence) model[4] should be used which holds good for describing chain molecules of any length. But here the difference between the wormlike chain and the Gaussian one[5] may be ignored in qualitative estimation. Equation 1 shows that one cannot expect a considerable increase in $\bar{R}^2_\theta$ as compared to $\bar{R}^2_{\theta,A}$ for a macromolecule similar to that shown in Figure 1a (with a great number of side chains).

However, numerous experiments demonstrate[6-11] that dimensions of a comblike macromolecule are much greater than the theta-point dimensions of the homopolymer used as a backbone. There are three different interpretations of this important observation:

1. The stiffness of chains increases markedly when they are consolidated in a comblike structure.[6,7,11,12]

2. The excluded volume effect of a comblike macromolecule is much higher than that of a linear polymer.[13,14]

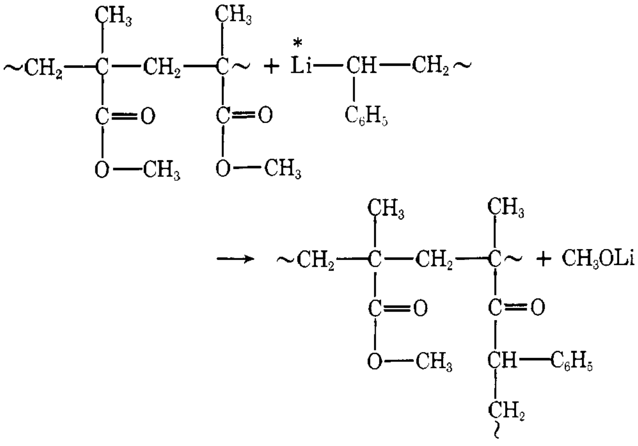
3. The dimensions of the macromolecule determined under theta conditions are not unperturbed.[10,15,16]

We adhere to the first interpretation, at least when considering our copolymers. Their important feature is a close arrangement of branches. These form about 0.9 of the macromolecular mass, and therefore the branch length is very long compared to the chain length between branches; the average ratio $L_B/(L_A/m)$ is about 8.

In the present paper experimental evidence is offered in favor of this view. The influence of long-range interactions on the dimensions of the comblike macromolecule is also considered. In accordance with Deckers' proposal[8] we treat the macromolecules of our copolymers as comblike polystyrenes since they contain an inconsiderable (no more than 5% by weight) quantity of oxygen.

Experimental Section

The homologous series of graft copolymers was obtained as follows. Poly(methyl methacrylate) fractions were prepared by radical polymerization and fractional precipitation. Six of them with molecular weights from 5 × 10³ to 200 × 10³ were mixed. This mixture was chosen as backbone of the graft copolymer. The reaction between this polar polymer and polystyrenelithium ("living polymer") yields a graft copolymer[17] (the reaction was performed by Dr. G. A. Andreeva).



$$\sim CH_2-C(CH_3)(C{=}O\,O{-}CH_3)-CH_2-C(CH_3)(C{=}O\,O{-}CH_3)\sim + Li-\overset{*}{C}H(C_6H_5)-CH_2\sim \longrightarrow \sim CH_2-C(CH_3)(C{=}O\,O{-}CH_3)-CH_2-C(CH_3)(C{=}O\,CH(C_6H_5)CH_2\sim)\sim + CH_3OLi$$

Investigation of the living polystyrene (before the grafting reaction) showed low polydispersity and a molecular weight of $M_B = 2.2 \times 10^3$ (determined with a vapor-pressure osmometer). Finally, the copolymer was fractionated with a benzene–chlorobenzene–petroleum ether system sensitive to the molecular weight of poly(methyl methacrylate).

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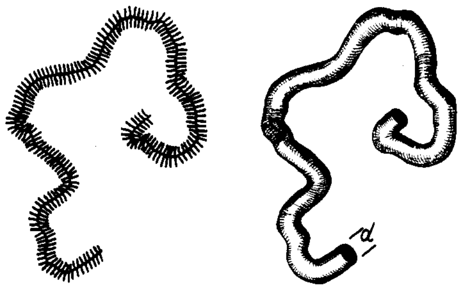

Figure 1. (a, left) Scheme of a comblike macromolecule with the M_A/M_B ratio of 50:1. (b, right) Wormlike chain as a model of comblike macromolecule; d is the thickness of the wormlike chain.

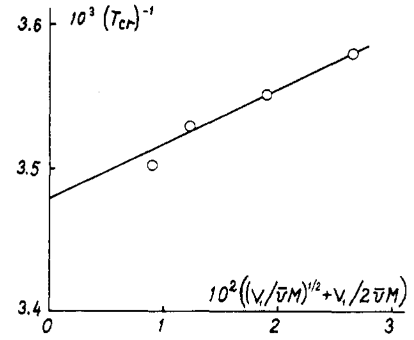

Figure 2. Reciprocal value of critical temperature $(T_{cr})^{-1}$ vs. the parameter $(V_1/\bar{v}M)^{1/2} + V_1/(2\bar{v}M)$.

The molecular weight of fractions was evaluated from the Svedberg formula:

$$M_{SD} = (S_0/D_0)(RT/(1 - \bar{v}\rho_0)) \qquad (2)$$

Here S_0 and D_0 are the limiting sedimentation and diffusion constants (the concentration of solution c g/dL $\rightarrow$ 0), R is the universal gas constant, T is the temperature, ρ_0 is the solvent density, and $\bar{v}$ is the partial specific volume. The average value for our copolymers is $\bar{v}$ = 0.91 cm^3 g^{-1}.

The constants S_0 and D_0 were obtained with the aid of a polarization interferometer. The description and the theory of this method are given elsewhere.[1,18] This technique makes it possible to measure the values of S and D in a region of very low c, so the concentration dependence of $S(c)$ and $D(c)$ is negligible.[18] Butyl acetate was chosen because of its suitable density and high value of the refractive index increment $(dn/dc)_{AB} \simeq 0.2$. The concentration c = 0.04 g/dL was used to determine $D = D_0$ and c = 0.07 g/dL for $S = S_0$. From the investigation of dependence $S^{-1} = S_0^{-1}(1 + K_s c)$ for the first fraction we obtained $K_s = 1.75$; i.e., when C = 0.07 g/dL the difference between S and S_0 is about 10%. When the molecular weight decreases the value of K_s also decreases. Therefore S is close to S_0. The experimental error in molecular weight determination with this method lies below 10%. The data on molecular weight polydispersity were obtained with ultracentrifuge. The calculations of M_w/M_n ratio were performed on the basis of a Gaussian distribution.[19] The weight fraction of polystyrene y was calculated by assuming additivity of the refractive index increment (dn/dc):

$$(dn/dc)_{AB} = (dn/dc)_A(1 - y) + (dn/dc)_B y \qquad (3)$$

The values of (dn/dc) were obtained also with the polarization interferometer. There is an important advantage in this case: we can eliminate the contribution of homopolystyrene and determine[20] the true value of $(dn/dc)_{AB}$. These experiments were carried out in bromoform, whose refractive index n_0 is close to that of polystyrene and of our copolymers. Therefore we could obtain[21] the value of y to within ±0.002.

Flow birefringence Δn was also investigated in bromoform in order to avoid form effects.[1,22] An apparatus with an inner rotor was used. The length of the rotor is 3.05 cm, and the width of the annular gap is 0.0174 cm. The Brace half-shade method was used for measuring Δn. The observed flow birefringence always increased proportionally to the velocity gradient g. The probable uncertainty in $\Delta n/g$ values is no more than 5%. The cylinder apparatus and optical system for these experiments are described elsewhere.[1,22] The relative viscosity η_r was measured with a capillary viscosimeter. All the experiments were carried out at 21 °C.

The principal hydrodynamic and optical characteristics of the fractions are presented in Table I. The heterogeneity of fractions is small both in mass (column 6) and in composition.[23,24] Therefore we calculated M_A and m from the equations:

$$M_A = M_{SD}(1 - y) \qquad (4a)$$

$$m = M_{SD}y/M_B \qquad (4b)$$

The contour length L is the length of a chain which is straightened without breaking the valency angles. The contribution to L corresponding to one monomer unit λ (two C–C bonds of backbone) is equal[1] to $\lambda = 2(1.54) \times 10^{-8} \sin(109°\ 30'/2)$ cm $= 2.52 \times 10^{-8}$ cm. The whole contour length was calculated from the equation:

$$L = L_A = (M_A/M_0)\lambda \qquad (5)$$

The molecular weight of the monomer unit M_0 was computed on the basis of the reaction scheme. We took into account that m monomeric units of backbone were not true methyl methacrylate because their methoxyl groups were cut. The values of L are presented in the seventh column of Table I.

The concentration dependence of the cloud point temperature T_{mix} in cyclohexane for fractions 2–5 was also investigated. The critical temperature T_{cr} was obtained from the condition $(\partial T_{mix}/\partial c) = 0$. Figure 2 shows a well-known plot:[25]

$$T_{cr}^{-1} = \theta^{-1}(1 + \psi^{-1}((V_1/\bar{v}M)^{1/2} + V_1/(2\bar{v}M))) \qquad (6)$$

It yields the entropy parameter ψ and the theta temperature for a given polymer–solvent system (V_1 is the molar volume of the solvent). In our case they are: θ = (16.0 ± 0.8) °C and ψ = (0.75 ± 0.10).

Equation 6 is valid for binary systems only. We treated our copolymers as homopolystyrene for the reason stated above. Moreover, Decker[8] found that the second virial coefficient A_2 is equal to zero at the temperature T_{cr} for an infinitely large macromolecule of graft copolymers which were like ours.

Finally we investigated the intrinsic viscosity of some fractions in cyclohexane as a function of temperature (Table II). The intrinsic viscosity in bromoform does not change in the temperature range from 7 to 46 °C.

Table I
Characteristics of Structure and Hydrodynamic and Optical Properties of Macromolecules of Graft Copolymers

Fraction	y	$D_0 \times 10^7$	$S_0 \times 10^{13}$	$M_{SD} \times 10^{-3}$	$([M_w/M_n] - 1)$	$L \times 10^8$	m	$[\eta]$, dL/g bromoform	$([n]/[\eta]) \times 10^{10}$
1	0.860	1.38	22.0	1960	0.25	7500	766	0.74	46
2	0.864	1.51	17.6	1430	0.13	5400	562	0.63	47.5
3	0.869	2.03	112.8	775	0.20	2810	306	0.42	44
4	0.880	3.18	8.3	321	0.13	1070	128	0.245	27.5
5	0.887	4.48	6.1	168	0.13	530	68	0.185	13
6	0.900	6.00	4.05	83.5	0.16	238	34	0.15	0.3
7	0.902	7.13	3.3	57.5	0.20	162	24	0.145	−4.2
8	0.913	7.64	2.95	47.7		120	20	0.14	−5.9
9	0.919	7.71	2.35	37.7		90	16	0.12	−6.5
10	0.918	8.80	1.9	26.0		62	11	0.11	−4.0

Table II
Temperature Dependence of Intrinsic Viscosity in Cyclohexane

Fraction	$[\eta]$ in dL/g at temperatures t in °C: 7.2	10.0	16.0	21.0	28.2	34.5	46.1	66.4	$\beta_{0,\lambda} \times 10^{21}$
2		0.143	0.190	0.246	0.300	0.336	0.390	0.410	1.1
3			0.144	0.166	0.192	0.214	0.260		1.0
4		0.085	0.104	0.110	0.122	0.136		0.170	1.1
5	0.078		0.091	0.098	0.105	0.113	0.109	0.100	1.3
6		0.080	0.086	0.090		0.100	0.108		2.1
9			0.081	0.082	0.089	0.096	0.100		7.5

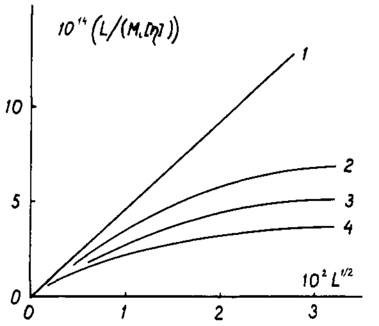

Figure 3. $L/(M_L[\eta])$ vs. $L^{1/2}$ for linear polystyrene according to Berry's data:[31] (1) theta conditions, in cyclohexane at 34.8 °C and in decalin at about 20 °C; (2) in decalin at 40 °C; (3) in decalin at 100 °C; (4) in toluene at 12 °C (a good solvent).

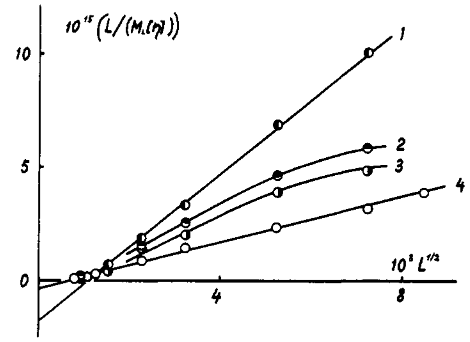

Figure 4. $L/(M_L[\eta])$ vs. $L^{1/2}$ for a styrene–methyl methacrylate graft copolymer (comblike polystyrene); (1) in cyclohexane at 16 °C; (2) in cyclohexane at 34 °C; (3) in cyclohexane at 46 °C; (4) in bromoform at 21 °C.

Discussion

In previous papers[6,7,11,12] we have suggested that the increasing stiffness is the only factor responsible for $\overline{R}^2{}_\theta$ being greater than $\overline{R}^2{}_{\theta,A}$. This was based on the following experimental facts: (a) The dimensions of the comblike macromolecule coincide in all the solvents used.[6] It should be emphasized that they were good solvents for the parent homopolymers. (b) The values of the second virial coefficients (obtained from light scattering) are very near zero.[6] (c) The experimental value of the segmental optical anisotropy $(\alpha_1 - \alpha_2)_{AB}$ greatly exceeds the expected value.[12,26]

Now we have a homologous series and can supplement our arguments. This homologous series contains macromolecules with backbones varying from very short to very long. In such cases it may be preferable to use the model of a wormlike chain[4] in which the stiffness has a uniform value at all points (Figure 1b). It is characterized by the contour length L, the effective diameter d ("thickness"), and the persistent length a, which is the measure of the chain stiffness.[4]

We first consider the hydrodynamic data. There is general similarity in functional form among numerous interpretations of the dependence of D_0 or $[\eta]$ on L for unperturbed chains, at least in the Gaussian region.[1,27,28] We use the Hearst–Stockmayer[29] and Hearst[30] results. According to their suggestion, a wormlike chain of uniform thickness is approximated by touching spheres on the chain. In that case the effective Stokes diameter of an element is equal to the spacing between elements along the contour of the chain and is interpreted as the diameter of the chain d. Taking into account eq 2, their equations can be rewritten in the following form:

$$D_0L = 1.843kTL^{1/2}/(3\pi\eta_0(2a)^{1/2}) + kT(\ln(2a/d) - 1.431)/(3\pi\eta_0) \quad (7)$$

$$L/(M_L[\eta]) = L^{1/2}/(\Phi(2a)^{3/2}) + 0.926(\ln(2a/d) - 1.431)/(\Phi 2a) \quad (8)$$

where Φ is 2.2×10^{21}, $k = R/N_A$, N_A is Avogadro's number, $M_L = M/L$ is the molecular weight of the unit length, and η_0 is the solvent viscosity. We analyzed eq 7 and arrived at the conclusion that eq 7 and 8 are correct for macromolecules of any stiffness if condition $a \geqslant d$ is observed. The absence of long-range interaction is necessary to apply eq 7 and 8 strictly. The excluded volume effect increases rapidly when the molecular weight (length) of the macromolecule increases. In this case the plot of $L/(M_L[\eta])$ vs. $L^{1/2}$ should be a curve approaching the abscissa with increasing L. In our opinion the rectilinear character of this plot in the region $L \gg a$ indicates definitely a negligible excluded volume effect in a certain polymer–solvent system, at least for a nondraining macromolecule. This is shown in Figure 3, where such plots are represented (according to Berry data[31]) for polystyrene as cyclohexane at 34.8 °C, in decalin at the theta-point (straight line 1), in decalin at 40 °C (curve 2) and at 100 °C (curve 3), and in toluene at room temperature (curve 4). Just as expected, the greater the power of the solvent, the greater is the deviation from straight line 1. The slope and the intercept of this line give the values $a = 10 \times 10^{-8}$ cm and $d = 5 \times 10^{-8}$ cm which other methods also usually yield for polystyrene.[1,32]

Similar plots for our data are shown in Figure 4: (1, 2, 3) in cyclohexane at 16, 34, and 46 °C, respectively; and (4) in bromoform at 21 °C. Although the deviation of plots 2 and 3 from the straight line is not so pronounced as in Figure 3, one can see an excluded volume effect for the copolymer in cyclohexane at 34 and 46 °C. In contrast, the straight line 4 indicates that no appreciable excluded volume effect occurs in bromoform. It should be noted that plots 1 and 4 are straight lines not only in the Gaussian region but also in the region $L \simeq a$. This is evidently caused by the nondraining character of the thick macromolecules of copolymer.

The diffusion constant data may be discussed in a similar manner. They form also a straight line for our copolymer in butyl acetate, as shown in Figure 5.

Thus, we neglect the excluded volume effect in solvents good for the parent homopolymers (bromoform, butyl acetate) and estimate the main parameters a and d of a wormlike chain which is the model of our homologous series (see Table III). The slopes of plot 4 in Figure 4 and the plot in Figure 5 give a value of the persistence length which exceeds more than fourfold the value of a for the parent homopolymers. The in-

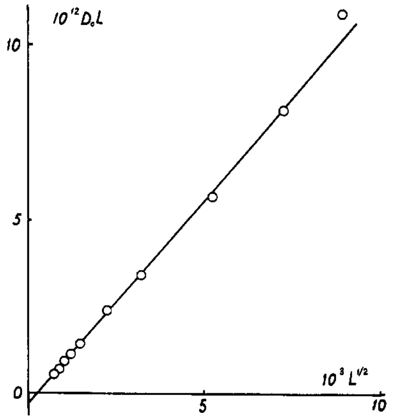

Figure 5. D_0L vs. $L^{1/2}$ in butyl acetate.

Table III[a]

Method	a	a/d	d	a_B
$[\eta]$	48 ± 2	1.1	45 ± 10	>25
D_0	41 ± 2	0.9	45 ± 10	>25
$([n]/[\eta])_{x<10}$		0.4	120 ± 20	
Form effect in ref 39		$\leqslant$0.8		
$([n]/[\eta])_{x\to\infty}$				40

[a] Persistent length a and Thickness d of the wormlike chain representing the macromolecule of graft copolymer. Persistent length a_B of the side chain. All values are determined in good solvents for parent homopolymers and are expressed in units of 10^{-8} cm.

tercepts indicate that the diameter of these macromolecules is great: $(a/d) \simeq 1$. The good agreement between the values of a and d obtained by using two different physical phenomena, translational and rotatory movements, should be emphasized.

These values of a and d describe uniform comb-type polymers. But in reality our copolymers do not form strictly homologous series. They contain 8–14% of methyl methacrylate units (Table I). Therefore the mass per unit contour length M_L changes from $M_L = 2.6 \times 10^{10}$ for the first fraction to $M_L = 4.2 \times 10^{10}$ for the last one. Some compensation for this demerit is achieved by substituting the true values M_L for each fraction but not the average value $\overline{M}_L = (3.4 \pm 0.6) \times 10^{10}$ in eq 8. Note that eq 7 does not contain the value of M_L.

Thus we treat our polymers as a homologous series with the average distance between the neighboring points of attachment $L/m = (7.6 \pm 1.4) \times 10^{-8}$ cm.

Next to be considered are the flow birefringence data. Theoretical investigations[33-35] predict the following properties of a plot of the optical anisotropy of wormlike (persistent) chains vs. the parameter $x = L/a$: it increases directly proportionaly to x from zero (the region of stiff rods), then it bends over in approaching the limit value (the region of the "semistiff" behavior), and finally it remains unchanged (the Gaussian region). Figure 6 gives only the main features of this plot, since in the experiment the reduced flow birefringence $[n]/[\eta]$ is measured but not the optical anisotropy. Equations relating $[n]/[\eta]$ to segmental optical anisotropy $(\alpha_1 - \alpha_2)$ are based on some concept of the chain conformation.

In the range of low x the flow birefringence is only an orientational effect. With increasing x the change in $[n]/[\eta]$ results both from the increase in optical anisotropy and from the change in geometrical asymmetry of the macromolecule $p(x)$. For a realistic macromolecular chain with the diameter d the value of $p(x)$ can be calculated[36] from the equation:

$$p(x) = (a/d)(2(x - 1 + e^{-x}))^{1/2} \tag{9}$$

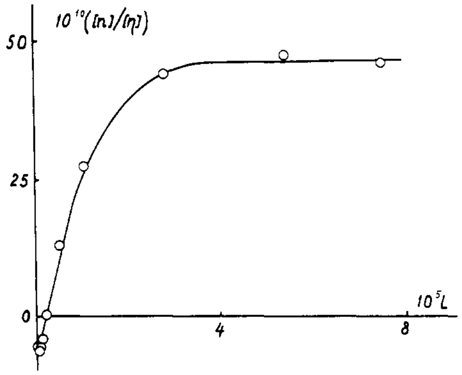

Figure 6. Reduced birefringence $[n]/[\eta]$ vs. L in bromoform.

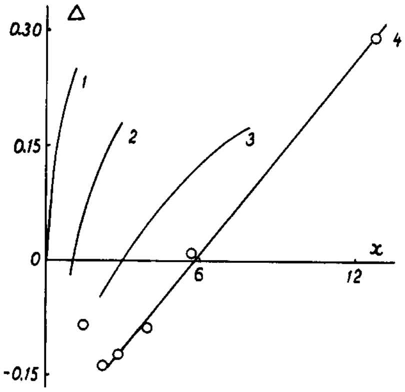

Figure 7. Reduced birefringence divided by its maximum value $\Delta = ([n]/[\eta])/([n]/[\eta])_{x\to\infty}$ vs. x. Theoretical curves:[36] (1) $(a/d) = \infty$; (2) $(a/d) = 1$; (3) $(a/d) = 0.5$; (4) the experimental dependence.

In this case the dependence of $[n]/[\eta]$ on x is represented by a family of curves, each of them corresponding to a certain a/d ratio. The lower the a/d ratio, the lower is the initial slope of the curve and the greater is the intercept x_0 on the abscissa. At $x = x_0$ the geometrical asymmetry is $p(x) = 1$ and the flow birefringence should change its sign. Hence, the ratio a/d can be determined from an experimental plot of $[n]/[\eta]$ vs. x. In Figure 7 the initial part of the plot in Figure 6 and theoretical plots[36] are represented in coordinates $\Delta \equiv ([n]/[\eta])/([n]/[\eta])_{x\to\infty}$ vs. x. We used two equivalent calculations of a/d. Substitution of the values $p = 1$ and $x = 5.8$ into eq 9 yields $(a/d) = 0.32$. A comparison of the theoretical derivative

$$(\partial\Delta/\partial x)_{p=1} = (6/25)(1 - e^{-x})(1 - e^{-5x/6})(a/d)^2 \tag{10}$$

with the slope of the experimental plot yields $(a/d) = 0.42$.

With subsequent increase of x the deformation of macromolecular coil arises and "semistiff" behavior in flow birefringence is displayed. It is impossible to define uniquely the value of x after which the orientational theory[36] is not applicable. Also, there is no sure theoretical location of the beginning of the Gaussian region. We can only establish that the higher the chain stiffness the greater the length L at which $[n]/[\eta]$ reaches the limit value. This limit was observed at $L = 1000 \times 10^{-8}$ cm for linear polystyrene[37] and at $L = 2800 \times 10^{-8}$ cm in the case of our comblike polystyrene (Figure 6); that is, the latter has a noticeably stiffer backbone. It is to be emphasized that we compared the experimental plots without any supplementary model concepts.

In the Gaussian region the optical anisotropy of macromolecular chains (irrespective of their stiffness) does not change with increasing L, and $(\alpha_1 - \alpha_2)$ is proportional to the experimental value of $[n]/[\eta]$:[38]

$$(\alpha_1 - \alpha_2) = (45kTn_0/4\pi(n_0{}^2 + 2)^2)([n]/[\eta]) \tag{11}$$

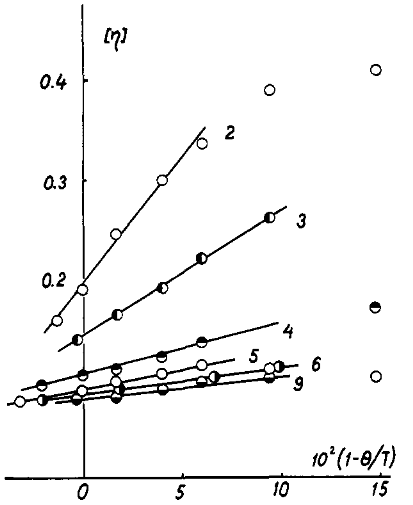

Figure 8. Intrinsic viscosity $[\eta]$ vs. parameter $(1 - \theta/T)$ for a graft copolymer in cyclohexane; figures at the straight lines correspond to fraction numbers.

Then, we can determine segmental optical anisotropy $(\alpha_1 - \alpha_2)$. From the value of $[n]/[\eta] = 46 \times 10^{-10}$ (Figure 6) we obtained $(\alpha_1 - \alpha_2)_{AB} = 520 \times 10^{-25}$ cm³.

We also investigated[39] the form effect in dioxan. It permits the estimation of the a/d ratio $(a/d) \leqslant 0.8$. Thus, the values of a/d that follow from hydrodynamic and optical investigations are in good agreement. The large diameter of the comblike macromolecule $d \simeq a$ evidently results from the total mass of the side chains. Their contour length is $L_B = 21$ (2.52) $\times 10^{-8}$ cm and they should be sufficiently straightened to cause such a large d.

We can estimate the stiffness of a side chain by two different methods. We model each side chain (homopolystyrene) as a persistent chain. Its first element is directed perpendicularly to the backbone at the point of attachment. This model permits the calculation of the contribution of each chain to the optical anisotropy of the whole macromolecule and then the derivation of the expression for the segmental optical anisotropy of a comblike macromolecule:[7]

$$(\alpha_1 - \alpha_2)_{AB} = (2a/\lambda)((a_{\parallel} - a_{\perp})_A - 2a_B y(a_{\parallel} - a_{\perp})_B(1 - e^{-3L_B/a_B})/(12(1 - y)L_B)) \quad (12)$$

Here $(a_{\parallel} - a_{\perp})_A$ and $(a_{\parallel} - a_{\perp})_B$ are the known[40] optical anisotropies of the monomer units of the parent homopolymers. This expression yields $a_B = 40 \times 10^{-8}$ cm. The other method of estimation of a_B postulates the equality $d/2 \simeq (L_B)_{\perp}$ where $(L_B)_{\perp}$ is the projection of the side chain on the perpendicular to the backbone. According to Porod:[4]

$$(L_B)_{\perp} = a_B(1 - e^{-L_B/a_B}) \quad (13)$$

Hence it follows that $a_B \geqslant 25 \times 10^{-8}$ cm.

All the foregoing considerations indicate that the stiffness of the homopolymer chains increases considerably with their coupling in a comblike structure as shown in Figure 1.

Now we discuss the viscosity data obtained in cyclohexane solution. Let us again consider Figure 4. Plot 1 gives $a = (21 \pm 2) \times 10^{-8}$ cm and $d = (45 \pm 10) \times 10^{-8}$ cm in cyclohexane. In our opinion it is natural that the diameter of a wormlike chain is invariant in all solvents. But its stiffness depends on the power of the solvent for homopolystyrene. In cyclohexane at temperatures below the theta-point for linear polystyrene (θ = 34.8 °C) the polymer–polymer interaction exceeds considerably the polymer–solvent interaction. As a result, the neighboring polystyrene chains can "stick together" and some defects can appear along the backbone. Therefore the value of a for a comblike polystyrene in cyclohexane is lower than in other solvents. It exceeds the value of a for homopolystyrene only twofold, and the long-range interaction appears at temperatures above 16 °C as can be seen from the curvilinear character of plots 2 and 3 in Figure 4. Hence, it is necessary to consider possible calculations of long-range interaction and to compare their results with experimental data.

The first variant is long-range interaction of the wormlike macromolecule (Figure 1b). The excluded volume effect of the wormlike chain was calculated elsewhere.[41] The expansion factor $\alpha_R \equiv (\overline{R}^2/\overline{R}^2_{\theta})^{1/2}$ is related to the excluded volume parameter z by the equation

$$\alpha_R{}^2 = 1 + (67/70)Kz \quad (14)$$

where K is the tabulated function of relative contour length $L/2a = x/2$. If the chain is long enough, K tends to $4/3$ and eq 14 coincides with the result of the strict theory:[42]

$$\overline{R}^2{}_{\text{lin}} = \overline{R}^2{}_{\text{lin},\theta}(1 + (134/105)z + \ldots) \quad (15)$$

Parameter z can be represented by the expression:[41]

$$z = (3/2\pi)^{3/2}(2a)^{-3/2}\beta l^{-2}L^{1/2} \quad (16)$$

The chain can be divided into equal elements by any method but z remains invariable. The length of each element is l and its excluded volume is β. Near the theta point it can be assumed[2,43] that:

$$\beta = \beta_0(1 - \theta/T) = \gamma\psi(1 - \theta/T) \quad (17)$$

Equation 16 shows that the long-range interaction depends not only on the chain length but also on its stiffness. An excluded volume effect appears because two elements cannot occupy the same point in space at the same time. Therefore the chain thickness is an essential factor in the generation of long-range interaction. The value γ reflects the influence of the chains thickness or, strictly speaking, its own volume upon z. We attempt to connect γ with molecular parameters.

Long-range interactions of two types of macromolecules are compared: linear ("thin") and comblike ("thick") polystyrene. As before the latter is modeled by a wormlike chain. The excluded volume caused by the interaction of two independent particles is proportional[44] to their own volume u

$$\gamma = 4\nu u \quad (18)$$

where the coefficient ν depends on the asymmetry of the colliding particles. It is natural to choose the length of independent element for a macromolecular chain as $l = 2a$ (the Kuhn segment). Then the values ν for the polymers compared are not far from each other:[44] $\nu_{\text{thin}} \simeq \nu_{\text{thick}}$. Moreover, the value of ψ_{thick} obtained from Figure 2 is close to ψ for homopolystyrene in cyclohexane. Three numerical results were obtained for the latter value: $\psi = 1.06$,[45] 0.703,[46] and 0.65,[47] i.e., on the average $\overline{\psi}_{\text{thin}} = (0.8 \pm 0.2)$. Hence, the difference between both types of macromolecules is only in their own volumes. These volumes can be correctly obtained from the partial specific volume: $u = \bar{v}M/N_A$. The ratio of the γ parameter for thick and thin chains (calculated for an arbitrary but identical length of elements l) is:

$$\gamma_{\text{thick}}/\gamma_{\text{thin}} = M_{\text{L,thick}}/M_{\text{L,thin}} = 1/(1 - y) \quad (19)$$

The temperature dependence of intrinsic viscosity is represented in Figure 8 as $[\eta]$ vs. $(1 - \theta/T)$. The slope of each plot H yields the expansion factor for the intrinsic viscosity $\alpha_\eta \equiv ([\eta]/[\eta]_\theta)^{1/3}$:

$$H = (\alpha_\eta{}^3 - 1)[\eta]_\theta/(1 - \theta/T) \quad (20)$$

According to Yamakawa and Tanaka,[48] z can be determined from $\alpha_\eta{}^3$:

$$\alpha_\eta{}^3 = 1 + 1.06z \quad (21)$$

We suppose that the plot of α_η^3 vs. $(L/2a)$ is of the same character as the plot of α_R^3 vs. $(L/2a)$. Bearing in mind the difference between the limiting values of the numeral coefficients in eq 14 and 21, we can write for small z:

$$\alpha_\eta^3 = 1 + 1.06(3/4)Kz = 1 + 0.80Kz \tag{22}$$

Combination of eq 22, 16, 17, and 20 gives:

$$\beta_0 = H(2a)^{3/2}l^2/(0.80(3/2\pi)^{3/2}[\eta]_\theta KL^{1/2}) \tag{23}$$

The values of $(\beta_0)_{l=\lambda}$ are represented in the last column of Table II. The mean value is $(\bar{\beta}_0)_{\text{thick},\lambda} = 1.3 \times 10^{-21}$. The contribution of fraction 9 was not taken into account because in this case $L_A \simeq L_B$ and the comblike model is not suitable.

The value $(\bar{\beta}_0)_{\text{thin},\lambda} = 1.0 \times 10^{-22}$ was calculated from the data on the excluded volume of polystyrene monomer unit obtained in cyclohexane at temperatures from 32.2 to 60.1 °C.[49] Indeed, the $(\lambda_{\text{thick}}/\lambda_{\text{thin}})$ ratio is close to the $1/(1-y)$ ratio.

Let us compare the behavior of the same macromolecules in bromoform. In this solvent just as in cyclohexane the excluded volume effect of comblike ("thick") macromolecules is $1/(1-y) = 9$ times higher than that of "thin" homopolystyrene. But this increase is compensated by a tenfold decrease because of greater stiffness: $(48/10)^{3/2} \simeq 10$. Consequently, the long-range interaction is not detected.

This example demonstrates a possibility of disagreement between intra- and intermolecular interactions for stiff-chain polymers. Indeed, the elements of the same rodlike macromolecule do not touch each other, but the existence of one rod excludes some volume for another rod. In other words, the condition $\alpha = 1$ can be observed even if the second virial coefficient A_2 does not vanish. But if A_2 is zero, the macromolecule of a homopolymer assumes unperturbed dimensions. This indeed is the main principle of the choice of experimental conditions for measuring unperturbed dimensions of macromolecules.

The second variant is long-range interaction of a true comblike macromolecule (Figure 1a).[13,14] It is assumed that the stiffness of its chains are the same as those inherent in the homopolymers. A strict calculation of the low excluded volume effect leads to the next equation[14] for the mean square radius of a comblike macromolecule:

$$\overline{R}^2 = \overline{R}^2_\theta(1 + (134/105)(y/(1-y))^2z + \ldots) \tag{24}$$

where $\overline{R}^2_\theta$ describes its unperturbed dimensions and z is related to the backbone only. The calculation in ref 14 is applied only in the limiting case for a large number of branches with a branch length very long compared to the chain length between branches. This is our case for the six first fractions. Equation 24 predicts that the long-range interaction of a comblike macromolecule is more unlikely than that of a linear macromolecule (see eq 15) because of the factor $(y/(1-y))^2$. In the case of our macromolecules the relative expansion $(\overline{R}^2/\overline{R}^2_\theta - 1)^{1/2}$ should be about eight times higher than that of their backbones. This is much greater than the experimental value.

Finally, the third variant of calculating long-range interactions was suggested by Benoit and co-workers.[10] They derived two separate dependences of α and A_2 on the local segment density and arrived at a conclusion that the theta point has no physical meaning. Consequently, they postulated that α^2 is the ratio between $\overline{R}^2$ in the considered solvent and calculated value $(\overline{R}^2_\theta)_{\text{theor}}$ but not the experimental expansion factor $\alpha^2 = \overline{R}^2/\overline{R}^2_\theta$. On the other hand, an Orofino–Flory calculation[50] (with approximation within 4%) predicts even for high local segment density unperturbed macromolecular dimensions if A_2 is zero.

If any additional term is introduced into an expression for the total free energy of mixing,[10,15,16] this term should be included in equations both for α and for A_2. Therefore a direct correlation between α and A_2 similar to that of Orofino–Flory (see eq 29 in ref 50) can be obtained. Hence, the above-mentioned important rule may be inferred: if A_2 is zero, macromolecular dimensions are unperturbed.

In conclusion, we have pointed out shortcomings in the common approach to macromolecules with any type of branching. We suggest that comblike macromolecules with markedly different length of side chains L_B or weight fraction y should be considered as an individual type of polymer. Their characteristics can be obtained from investigations of homologous series in which only the length of the main chain L_A changes.

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Solution Properties of Poly(*n*-butyl isocyanate). 1. Characterization and Intrinsic Viscosity Behavior Over an Extended Molecular Weight Range

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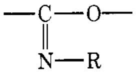
ABSTRACT: The intrinsic viscosity behavior of poly(*n*-butyl isocyanate) (PBIC) has been examined over the molecular weight ($\overline{M}_w$) range of 2.5×10^4 to 12.5×10^6 g mol^{-1} in carbon tetrachloride, tetrahydrofuran, and chloroform. At low molecular weights ($<10^5$) PBIC exhibits rodlike behavior while at high molecular weight (10^7) the molecular posture of this polymer appears to be essentially that of a wormlike chain in tetrahydrofuran and chloroform. However, the $[\eta]$–M characteristics of high molecular weight PBIC in CCl_4 do not support the wormlike chain model. The gel permeation chromatographic behavior of PBIC was examined. A nonlinear calibration was found, a reflection of the changing chain posture with increasing molecular weight.

Poly(*n*-butyl isocyanate) (PBIC) is a polymer which has been found to exhibit rodlike behavior[1] up to a molecular weight of about 10^5. Its structure is similar to that of the polypeptides except for the absence of hydrogen bonding. Chain stiffness was first indicated by Shashoua, Sweeny, and Tietz[2,3] who found abnormally high intrinsic viscosities for relatively low molecular weight anionically synthesized polyisocyanates. Since then, chain stiffness has been observed by studying the dilute solution properties of PBIC and other poly(*n*-alkyl isocyanates). These measurements have examined both the dilute solution equilibrium and hydrodynamic properties of these polymers. All of these measurements, i.e., osmometry, light scattering, dielectric, electric dichroism, electric birefringence, rotatory diffusion, and intrinsic viscosity, have clearly demonstrated[1] the stiff-chain molecular posture possessed by the poly(*n*-alkyl isocyanates).

The origin of the chain stiffness of the poly(*n*-alkyl isocyanates) is at present not totally clear. The presence of the amide unit was considered by Schneider, Furusaki, and Lenz,[4] and they proposed the possibility of partial double bond character imposing coplanarity along the backbone. Troxell and Scheraga[5] later concluded from studies of the dichroism of PBIC solutions subjected to external electric fields that the double bond character of the backbone was too weak to explain the chain stiffness. Steric hindrance, however, is a strong argument in explaining chain stiffness. This is based, in part, on the similarity in structure between the poly(*n*-alkyl isocyanates) and the peptide poly-L-proline. Poly-L-proline exists predominantly in the rigid trans-helical conformation even though hydrogen bonding is absent due to the lack of hydrogens at the peptide nitrogens.[6] Recently, Tonelli[7] completed potential energy calculations which suggest that chain flexibility which accumulates as molecular weight increases is due to helix reversal sites along the chain. A chemical basis for this was suggested by Schneider, Furusaki, and Lenz[4] through a second possible repeat unit involving the flexible ether linkage, i.e.,



$$-\underset{\underset{\textstyle N-R}{\|}}{C}-O-$$

Evidence for this grouping has not been found for polyisocyanates prepared from monoisocyanate monomers. However, this may be due to a lack of an analytical technique capable of detecting this group at low concentration levels, probably less than 0.1%. There is another possibility which could influence the solution properties in the same manner as induced flexibility. This could be branching in the polymer due to diisocyanate species present in the monoisocyanate monomer. As in the case of the ether linkage, no evidence for the presence of a diisocyanate monomer has been found.

Basically, the conformation of PBIC has been described by most authors as being helical and rigid at low molecular weight ($<10^5$), with a decrease in rigidity, but a retention of high elongation at higher molecular weights. The conformational model invoked to describe this trend is usually that of a rigid rod changing to a "wormlike" stiff chain. In this study, viscosity and light-scattering data for PBIC are presented over a molecular weight range (2.5×10^4 to 1.25×10^7) which encompasses both the clearly defined rodlike and a possible wormlike chain region in which there are enough "persistence length" units so that the chain could appear in some properties to be a Gaussian chain.

Experimental Section

The samples used were those used in previous studies.[8–12] Detailed discussions of the procedures used in their synthesis and characterization have been given.[8–12] The $\overline{M}_w$ values of two PBIC samples were determined with a low-angle light-scattering photometer operating at angles from 15 to 150°. The refractive index increment, dn/dc, was determined in tetrahydrofuran. Ultracentrifuge data were also obtained for $\overline{M}_w$ and $\overline{M}_z$ determinations. A specially designed[13] Zimm-type Couette low-shear viscometer was used in addition to commercial variable-shear capillary viscometers.

A gel permeation chromatograph was built by combining the Waters ALC/GPC 501 with its high-pressure 1000 psi pump, a 2.5 mL syphon, and a dual detector combining the UV (at 254 nm) and refractive index detectors. One each of the following 4-ft Styragel columns were used: 5×10^6 Å; 7×10^5 to 5×10^6 Å; 10^6 Å; 1×10^5 to 7×10^5 Å; 3×10^5 Å; 10^5 Å; 3×10^4 Å; 10^4 Å; 10^3 Å; and 250 to 100 Å. This column set provided a near-linear calibration for polystyrene from 2×10^4 to 10^7 molecular weight. This column set had a plate count of 500 ppf at the flow rate of 1 mL min^{-1}. The solvent was chloroform at ambient temperature. Sample preparation and operating conditions were identical to those discussed previously.[14,15] Polystyrene standards used for column calibration were from this laboratory[13] and commercial sources.

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