Solution Properties of Polymacromonomers Consisting of Polystyrene V. Effect of Side Chain Length on Chain Stiffness

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ABSTRACT: Light scattering and viscosity measurements were made on cyclohexane and toluene solutions of a series of polymacromonomer samples consisting of polystyrene with 65 monomer units in each side chain to determine the z-average mean-square radius of gyration $\langle s^2 \rangle_z$ and the intrinsic viscosity $[\eta]$ as functions of the weight average molecular weight in a range from 2.9×10^5 to 8.6×10^6 . The theta temperature for the polymacromonomer in cyclohexane was determined to be 34.5°C. The $\langle s^2 \rangle_z$ data in this solvent at 34.5°C and toluene at 15°C (a good solvent) were quantitatively described by the wormlike chain with λ^{-1} (the Kuhn segment length) = 36 nm and M_L (the molecular weight per unit contour length) = 25000 nm⁻¹ in the former and with λ^{-1} = 75 nm and M_L = 25000 nm⁻¹ in the latter. The molecular weight dependence of $[\eta]$ in each solvent was also explained by this model chain when the end effect arising from side chains near the main-chain ends was taken into account. The above λ^{-1} values in the two solvents and the previous estimates for polystyrene polymacromonomers with shorter side chains were used to examine the dependence of the backbone stiffness on side chain length. It was found that λ^{-1} increases almost linearly with the side-chain molecular weight for both solvents but with a larger slope in toluene than in cyclohexane.

KEY WORDS Light Scattering / Intrinsic Viscosity / Polystyrene Polymacromonomer / Wormlike Chain / Chain Stiffness /

In previous studies of this series,^{1–4} we found from light scattering and viscosity measurements that two polymacromonomers consisting of polystyrene with 15 and 33 styrene units in each side chain (polymacromonomers F15 and F33) behave like wormlike chains in cyclohexane at the theta temperature and in toluene, a good solvent, at 15°C. The backbone stiffness expressed in terms of the Kuhn segment length λ^{-1} was higher for the F33 polymer, being consistent with the earlier finding^{5–7} that for polymacromonomers consisting of the poly(methyl methacrylate) backbone and polystyrene side chains in toluene (a good solvent), λ^{-1} increases with side chain length. We also found that λ^{-1} is larger in the good solvent than in the theta solvent for both F15 and F33. These findings ought to be theoretically explained in terms of side chain-side chain and side chain-main chain interactions, but at present, we deem it necessary to extend the experimental work to a polystyrene polymacromonomer with a larger side chain length in order to establish the experimental relations between the backbone stiffness and the side chain length in both theta and good solvents.

Thus we prepared polystyrene polymacromonomer samples with 65 side chain units and different main-chain lengths, and determined z-average mean-square radii of gyration $\langle s^2 \rangle_z$ and intrinsic viscosities $[\eta]$ for them by static light scattering and viscometry in cyclohexane at the theta temperature and in toluene at 15°C. In the work reported below, we analyze the results on the basis of the wormlike chain and compare the estimated parameters with those for the F15 and F33 polymacromonomers.

EXPERIMENTAL

Preparation of Polymacromonomer Samples

Styrene was anionically polymerized in toluene using tolyllithium as an initiator, and the reaction was terminated by *p*-chloromethylstyrene (Seimi Chemical Co. Ltd.) to obtain the macromonomer.⁸ Before the termination, an aliquot of the living polystyrene solution was taken out, and linear polystyrene was precipitated by the addition of methanol. Its weight-average molecular weight M_w was 6770 when determined by light scattering in toluene. The crude macromonomer was reprecipitated several times into methanol to remove the excess *p*-chloromethylstyrene. The complete removal of this impurity was confirmed by ¹H NMR, which showed the end group functionality of this macromonomer to be about 75%. The macromonomer thus purified was polymerized in benzene at 38–60°C with azobisisobutyronitrile as an initiator. The monomer concentration was adjusted to 84–87% by weight. The yield of the polymacromonomer changed from 56 to 73% depending on monomer concentration and temperature.

The polymacromonomer samples prepared were fractionated by repeated fractional precipitation as described previously.¹ Seven fractions (designated below as F65-1, F65-2, ..., F65-7) with different main-chain lengths were chosen for the present work. Weight- to number-average molecular weight ratios were estimated to be 1.09 for F65-3 and F65-4, 1.10 for F65-2, 1.13 for F65-5, and 1.27 for F65-6 by gel permeation chromatography with the M_w -elution volume relation established for this polymacromonomer.

Light Scattering

Light scattering measurements were made on a Fica-50 light-scattering photometer using vertically polarized incident light of 436 and 546 nm in wavelength. The instrument was calibrated with benzene at 25°C and the literature values for the Rayleigh ratio.⁹ Each polymacromonomer solution was made optically clean by centrifugation at 12000 rpm for 1.5 h, carefully sucked with a clean pipette, and transferred into a cylindrical light scattering cell. Intensity data were taken at 15 and 34.5°C for toluene and cyclohexane solutions, respectively; for samples F65-7 and F65-4 in cyclohexane, data were also taken at other temperatures T of 25, 30, 40, and 45°C.

The polymer mass concentration c was calculated from the weight fraction with the solution density ρ , which was determined as a function of T and c for F65-4 using an Anton-Paar DMA 5000 density meter. The results were found to be represented by

$$\rho = 0.87149 + 0.199c \quad (\text{in toluene at } 15^\circ\text{C})$$

$$\rho = 0.76481 - 0.00072(T/^\circ\text{C} - 34.5) + [0.282 + 0.0004(T/^\circ\text{C} - 34.5)]c \quad (\text{in cyclohexane})$$

in units of g cm^{-3} . Specific refractive index increments $\partial n/\partial c$ for F65-7 in cyclohexane at 34.5°C and toluene at 15°C were measured using a modified Schulz-Cantow type differential refractometer. The results were $0.107 \text{ cm}^3\text{g}^{-1}$ at 436 nm and $0.104 \text{ cm}^3\text{g}^{-1}$ at 546 nm in toluene and $0.180 \text{ cm}^3\text{g}^{-1}$ at 436 nm and $0.171 \text{ cm}^3\text{g}^{-1}$ at 546 nm in cyclohexane.

Viscometry

Viscosity measurements were made using Ubbelohde type viscometers. The relative viscosity was evaluated by taking account of the difference between the solution and solvent densities. The Huggins plot,¹⁰ the Fuoss-Mead plot,¹¹ and the Billmeyer plot¹² were combined to determine $[\eta]$ and the Huggins constant k' .

RESULTS

Figure 1 shows the angular dependence of $(Kc/R_\theta)^{1/2}$ for sample F65-7 in cyclohexane at 34.5°C. Here, K is the optical constant and R_θ is the excess reduced scattering intensity at scattering angle θ . Extrapolation of the data points at the respective concentrations gives almost identical intercepts, *i.e.*, equal zero-angle values of Kc/R_θ within experimental error.

The second virial coefficients A_2 obtained for sample F65-7 as a function of T are shown in Figure 2; the A_2 values at the temperatures other than 34.5°C have been evaluated from A_2M_w with the M_w value at 34.5°C. It can be seen that A_2 vanishes at 34.5°C, the theta temperature for linear polystyrene and polymacromonomers F15 and F33 in cyclohexane.^{1,2} For another sample F65-4, the absolute values of A_2 at 30–45°C were less than $8 \times 10^{-6} \text{ cm}^3 \text{ mol g}^{-2}$, being hardly distinguishable from zero. We therefore concluded that the theta temperature of the F65 polymacromonomer in cyclohexane is practically the same as that (34.5°C) of F15 and F33. In fact, the A_2 values for all our samples in the solvent were essentially zero at this temperature. The numerical results of M_w , $\langle s^2 \rangle_z$, and A_2 in cyclohexane and toluene are presented in Tables I and II, respectively.

Figure 3 shows the molecular weight dependence of $\langle s^2 \rangle_z$ for the F65 polymacromonomer in toluene (15°C)

Figure 1. Angular dependence of $(Kc/R_\theta)^{1/2}$ at indicated c for polymacromonomer sample F65-7 in cyclohexane at 34.5°C.

Figure 2. Temperature dependence of A_2 for sample F65-7 in cyclohexane.

Table I. Results from light scattering and viscosity measurements on polymacromonomer samples of F65 in cyclohexane at 34.5°C

Sample	$M_w/10^5$	$\langle s^2 \rangle_z/\text{nm}^2$	$[\eta]/\text{cm}^3 \text{g}^{-1}$	k'
F65-1	85.5	1670	31.4	0.76
F65-2	42.3	790	—	—
F65-3	36.4	641	19.3	0.83
F65-4	20.9	287	14.8	0.87
F65-5	14.5	165	11.9	0.91
F65-6	(9.43) ^a	—	9.9	0.93
F65-7	2.86	—	8.4	0.97

^a In toluene.

Table II. Results from light scattering and viscosity measurements on polymacromonomer samples of F65 in toluene at 15°C

Sample	$M_w/10^5$	$\langle s^2 \rangle_z / \text{nm}^2$	$10^5 A_2 / \text{cm}^3 \text{mol g}^{-2}$	$[\eta] / \text{cm}^3 \text{g}^{-1}$	k'
F65-1	81.6	2970	1.6	64.2	0.45
F65-2	40.6	1270	1.3	—	—
F65-3	36.6	902	1.4	31.9	0.45
F65-4	21.6	394	1.8	21.9	0.54
F65-5	14.7	218	2.6	16.7	0.65
F65-6	9.43	—	2.4	13.9	0.75
F65-7	(2.86) ^a	—	—	11.1	0.93

^a In cyclohexane. **Figure 3.** Molecular weight dependence of $\langle s^2 \rangle_z$ for the F65 polymacromonomer in toluene 15°C (unfilled circles) and in cyclohexane 34.5°C (filled circles). The solid lines represent the theoretical values calculated from eq 1 with the parameters in Table III. **Figure 4.** Molecular weight dependence of $[\eta]$ for the F65 polymacromonomer in the indicated solvents. The symbols are the same as those used in Figure 3. Solid lines, theoretical values calculated from eq 3 with the parameters in Table III; dot-dashed lines, theoretical values for $\delta = 0$.

and cyclohexane (34.5°C). The curves for cyclohexane and toluene solutions have slopes 1.4 and 1.6, respectively, for $M_w < 3 \times 10^6$ and bend down with increasing M_w . Such behavior of $\langle s^2 \rangle_z$ indicates that our polymacromonomer is semiflexible in both solvents.

The numerical values of $[\eta]$ in cyclohexane and toluene are included in Tables I and II, along with those of k' , and the molecular weight dependence of $[\eta]$ in the two solvents is shown in Figure 4. The solid lines closely fitting the data points in the respective solvents rise very gradually up to $M_w \sim 10^6$ and bend up relatively

Figure 5. Plot of $(M_w / \langle s^2 \rangle_z)^{1/2}$ vs. M_w^{-1} for F65 samples in cyclohexane at 34.5°C.

sharply with further increasing M_w . Their slopes reach 0.85 and 0.55 for toluene and cyclohexane solutions, respectively. The very weak molecular weight dependence of $[\eta]$ for low M_w is typical of polymacromonomers.^{3,5,13} The significance of the indicated solid and dashed lines is interpreted in the next section.

DISCUSSION

Mean-Square Radius of Gyration

The mean-square radius of gyration of the unperturbed wormlike chain with a contour length L and a Kuhn segment length λ^{-1} is expressed as¹⁴

$$\langle s^2 \rangle = \frac{L}{6\lambda} - \frac{1}{4\lambda^2} + \frac{1}{4\lambda^3 L} - \frac{1}{8\lambda^4 L^2} [1 - \exp(-2\lambda L)] \quad (1)$$

When $\lambda L > 2$, this equation may be approximated by¹⁵

$$(M / \langle s^2 \rangle)^{1/2} = (6\lambda M_L)^{1/2} (1 + 3M_L / 4\lambda M) \quad (2)$$

where M is the molecular weight and M_L is the molar mass per unit contour length of the chain, *i.e.*, $M_L = M/L$. Equation 2 indicates that λ^{-1} and M_L can be determined from the intercept and slope of a plot of $(M / \langle s^2 \rangle)^{1/2}$ vs. M^{-1} .

Figure 5 shows the plot of $(M_w / \langle s^2 \rangle_z)^{1/2}$ vs. M_w^{-1} constructed from the present $\langle s^2 \rangle_z$ data in cyclohexane at the theta temperature. The data points follow a straight line, which yields $\lambda^{-1} = 36 \text{ nm}$ and $M_L = 25000 \text{ nm}^{-1}$. This M_L is much larger than the previously determined values (6200 and 13000 nm^{-1}) for the polymacromonomers F15 and F33 in the same solvent,¹⁻⁴ reflecting the longer side chains of our polymer. Importantly, however, it yields 0.27 nm for the contour length per main chain residue, a value close to those obtained previously for these polymacromonomers^{1,2} and also that calculated for

linear polystyrene with the all-*trans* conformation.

The solid line for cyclohexane solutions in Figure 3 actually represents the theoretical values calculated from eq 1 with the above parameters. Its satisfactory fit to the filled circles suggests that the effects of chain thickness and chain ends on $\langle s^2 \rangle$ are insignificant in the molecular weight range examined. To confirm this, we estimated the contribution from side chains to $\langle s^2 \rangle$ using the wormlike comb model, in which wormlike side chains with stiffness λ_s^{-1} and contour length L_s are linked to the main chain by completely flexible joints. The equation for $\langle s^2 \rangle$ of this model chain can be found in ref 16 (eqs. 4–6). Using the molecular weight of the side chain along with $M_L = 390 \text{ nm}^{-1}$ and $\lambda_s^{-1} = 2 \text{ nm}$ for linear polystyrene,¹⁷ we find that the contribution from side chains to $\langle s^2 \rangle^{1/2}$ is only about 4.5% for the lowest molecular weight sample (F65-5) examined and becomes negligible with increasing M_w . Hence, it introduces no substantial error in the analysis of the present $\langle s^2 \rangle_z$ data.

In analyzing the toluene data, we employed the curve-fitting procedure, because we anticipated that the condition $\lambda L > 2$ for eq 2 is not satisfied for the two lowest molecular weights. The curve for toluene solutions in Figure 3 shows the best fit obtained with $M_L = 25000 \text{ nm}^{-1}$ and $\lambda^{-1} = 75 \text{ nm}$. This M_L value agrees with that in cyclohexane estimated above. On the other hand, the λ^{-1} value of 75 nm in toluene is more than twice as large as that (36 nm) in cyclohexane, indicating that the polymacromonomer backbone is much stiffer in the good solvent than in the theta solvent. The following remark may be pertinent here with regard to the analysis of the toluene data made without consideration of intramolecular excluded-volume effect.

For the polystyrene polymacromonomers F15 and F33 in toluene, excluded-volume effects on $\langle s^2 \rangle_z$ became appreciable when λL exceeded 5–6. This critical λL for the onset of volume effect is comparable to those for linear flexible chains in good solvents, but it is almost one order of magnitude smaller than those for typical stiff chains¹⁸ probably because of the much higher thickness of the polymacromonomer chains. In other words, though polymacromonomers behave like stiff chains, their excluded-volume effects begin to appear at a small λL of about 5 as in linear flexible chains. For our polymacromonomer, this λL corresponds to a molecular weight of 9.4×10^6 , which is slightly larger than the highest M_w studied here. Thus, the above analysis of the toluene data may be rationalized.

Intrinsic Viscosity

A polymacromonomer molecule in solution may be modeled by a cylindrical wormlike chain if its side chains are included as the continuous body, but theoretic-

cal values of $[\eta]$ for the wormlike cylinder model¹⁹ are unavailable for large cylinder diameters d relative to λ^{-1} , *i. e.*, for $\lambda d > 0.2$. In our previous work, Terao *et al.*³ examining the limited information on the cylinder model (capped with hemispheres at both ends) and the theory for the touched-bead model,²⁰ reached the conclusion that the theoretical $[\eta]$ for the former model with $\lambda d > 0.2$ can be replaced in a good approximation by that for the latter model with the bead diameter d_b equal to d . This allows the desired $[\eta]$ for wormlike cylinders with $\lambda d > 0.2$ to be expressed as

$$[\eta] = f(\lambda L, \lambda d) / \lambda^3 M \quad (3)$$

where $f(\lambda L, \lambda d)$ is a known function²⁰ of λL and λd ($= \lambda d_b$). Though $[\eta]$ in this equation is given for the discrete number of beads, we regard it as a continuous function of L .

Terao *et al.*³ further considered that some side chains near the main-chain ends of a polymacromonomer molecule contribute toward apparently increasing the main chain length (see Figure 3 of ref 3), and redefined L by

$$L = M/M_L + \delta \quad (4)$$

where δ stands for the contribution from such side chains to the main-chain contour length ($\delta/2$ from each end). Consideration of the end effect (*i. e.*, the effect of δ) was essential to explain the weak M_w -dependence of $[\eta]$ observed for the polymacromonomers F15 and F33 in cyclohexane and toluene.

Equation 3 with eq 4 contains M_L , λ^{-1} , d , and δ as the parameters, but all of them cannot uniquely be determined from our $[\eta]$ data. In the present analysis, we assumed the λ^{-1} values from the above analysis of $\langle s^2 \rangle_z$, *i. e.*, $\lambda^{-1} = 36 \text{ nm}$ in cyclohexane and $\lambda^{-1} = 75 \text{ nm}$ in toluene, and estimated the other parameters in each solvent by curve fitting. The solid lines for the respective solvents in Figure 4 represent the resulting best-fit theoretical values of $[\eta]$. The agreements between the measured and calculated $[\eta]$ in both solvents are good. A few breaks of each curve in the low molecular weight region are due to the fact that the theoretical $[\eta]$ values for discrete bead numbers are connected by straight lines. The parameters used for the calculation are presented in Table III, along with those determined from $\langle s^2 \rangle_z$. The values of M_L from $\langle s^2 \rangle_z$ and $[\eta]$ in either solvent agree almost perfectly, indicating that our analyses consistently explain the behavior of the two properties.

The dot-dashed lines in Figure 4 refer to the theoretical $[\eta]$ values for $\delta = 0$. Their downward deviations from the data points in the respective solvents are remarkable even at a molecular weight as high as 10^6 , demonstrating the substantial end effects on $[\eta]$. We note that,

Table III. Model parameters for polymacromonomer F65 in cyclohexane and toluene

Solvent	Data	λ^{-1}/nm	$10^{-3}M_L/\text{nm}^{-1}$	d/nm	δ/nm
CH ^a	$\langle s^2 \rangle_z$	36	25.0	—	—
CH	$[\eta]$	36 ^c	26.0	11.5	6
Tol ^b	$\langle s^2 \rangle_z$	75	25.0	—	—
Tol	$[\eta]$	75 ^c	25.0	14	6

^a Cyclohexane at 34.5°C. ^b Toluene at 15.0°C. ^c From $\langle s^2 \rangle_z$.

Figure 6. Experimental Φ for the F65 polymacromonomer compared with the theoretical curves. Symbols are the same as those used in Figure 3.

as expected, the value of δ for our polymacromonomer (Table III) is considerably larger than those (2.2–4.3 nm) for F15 and F33 with shorter side chains.

In the previous study³ on F15 and F33, we found that the d value determined from $[\eta]$ for each polymer in cyclohexane is almost twice as large as the unperturbed root-mean-square end-to-end distance $\langle r^2 \rangle^{1/2}$ of the linear polystyrene chain with the same contour length as that of each side chain in the polymacromonomer. To examine whether this is also the case for our F65 polymacromonomer, we calculated $\langle r^2 \rangle^{1/2}$ for linear polystyrene with the molecular weight of each side chain of F65 using the wormlike chain model with $M_L = 390 \text{ nm}^{-1}$ and $\lambda^{-1} = 2 \text{ nm}$.¹⁷ The result gave $\langle r^2 \rangle^{1/2} = 5.7 \text{ nm}$, which is very close to a half the d value determined from $[\eta]$ in cyclohexane. We note that essentially the same $\langle r^2 \rangle^{1/2}$ value is obtained when the helical wormlike chain with the known parameter set¹⁹ is used for the polystyrene side chain.

Figure 6 shows the Flory viscosity factor $\Phi = [\eta]M / (6 \langle s^2 \rangle^{3/2})$ plotted against $\log M_w$. It can be seen that Φ 's for both cyclohexane and toluene systems decrease sharply with increasing molecular weight. Similar behavior of Φ was previously observed for F15 and F33,³ but a point to note is that the decrease in Φ with an increase in M_w becomes less pronounced with decreasing side chain length. The solid lines in the figure represent the theoretical values calculated from eqs 1, 3, and 4 with $\lambda^{-1} = 36 \text{ nm}$, $M_L = 25500 \text{ nm}^{-1}$ (the mean of the values from $\langle s^2 \rangle_z$ and $[\eta]$), $d = 11.5 \text{ nm}$, and $\delta = 6 \text{ nm}$ for cyclohexane solutions and $\lambda^{-1} = 75 \text{ nm}$, $M_L = 25000 \text{ nm}^{-1}$, $d = 14 \text{ nm}$, and $\delta = 6 \text{ nm}$ for toluene solutions (note that $\delta = 0$ for $\langle s^2 \rangle_z$). The agreement between the experimental and theoretical values are satisfactory for both solvents, confirming that the cylindrical wormlike chain is a good model for $[\eta]$ of our polymacromonomer.

Dependence of Backbone Stiffness on Side Chain Length

The values of λ^{-1} estimated from $\langle s^2 \rangle_z$ for our polymacromonomers in cyclohexane and toluene are much larger than those for F15 and F33 in the corresponding solvents (see Table 4 of ref 2), ascertaining that λ^{-1} for the polystyrene polymacromonomers in either solvent is an increasing function of side chain length.

Figure 7 shows how λ^{-1} increases with increasing the side chain molecular weight M_{side} . The plotted points approximately follow straight lines for both solvents but

Figure 7. Dependence of λ^{-1} on the side chain molecular weight of polystyrene polymacromonomer. Lines are eye guides.

with a larger slope in toluene than in cyclohexane. The increase in λ^{-1} with M_{side} for toluene solutions suggests that binary excluded-volume interactions between side chains stiffen the polymacromonomers. However, this idea does not explain the stiffness of the polymacromonomers in cyclohexane, because effective binary interactions between segments are known to vanish at the theta point.²¹ The stiffness in the theta solvent may be considered to arise primarily from ternary interactions among side chain segments. This will be discussed in a forthcoming paper on some theoretical basis.

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