Dilute-Solution Properties of Polystyrene Polymacromonomer Having Side Chains of over 100 Monomeric Units

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Static and dynamic light scattering and viscosity measurements were made on 12 samples of polymacromonomer F110 consisting of polystyrene with 113 styrene units in each side chain to determine the z-average mean-square radius of gyration, the hydrodynamic radius, and the intrinsic viscosity in cyclohexane at 34.5 °C (the theta temperature) and toluene at 15.0 °C as functions of weight-average molecular weight M_w . Small-angle X-ray scattering experiment was also performed for one sample in the two solvents. The dependence of the three measured properties on M_w in the range 1.9×10^5 – 1.3×10^7 studied were consistently explained by available theories for the wormlike chain with M_L (the molar mass per unit contour length) = 45500 nm^{-1} , λ^{-1} (the stiffness parameter) = 80 nm (in cyclohexane) or 155 nm (in toluene), and d (the chain diameter) = 16–26 nm (depending on the kind of solvent and measured property) when the end effect arising from side chains near the main-chain ends was taken into account. The side-chain length dependence of λ^{-1} , examined with the aid of previous data for three polystyrene polymacromonomers with shorter side chains of 15, 33, and 65 styrene units, was found to be almost quantitatively explained by the theory of Nakamura and Norisuye [*Polym. J.*, **33**, 874 (2001)]. That of d was also discussed in relation to the end-to-end distance of a wormlike side chain.

KEY WORDS: Polymacromonomer / Radius of Gyration / Hydrodynamic Radius / Intrinsic Viscosity / Chain Stiffness / Chain Thickness /

We have studied polymacromonomers consisting of polystyrene (PS) having side chains of 15, 33, and 65 monomeric units (F15, F33, and F65, respectively) in cyclohexane (a theta solvent) and toluene (a good solvent) by static^{1–3} and dynamic^{4,5} light scattering, small-angle X-ray scattering (SAXS),^{6,7} and viscosity measurements.^{3,8} The z-average mean-square radius of gyration $\langle S^2 \rangle_z$, the hydrodynamic radius R_H , and the intrinsic viscosity $[\eta]$ obtained as functions of weight-average molecular weight M_w were explained in a consistent manner by the Kratky-Porod (KP) wormlike chain model,⁹ and the estimated backbone stiffness parameter (or Kuhn segment length) λ^{-1} and chain diameter d were found to depend on the side chain length and the solvent quality, being consistent with observations on different polymacromonomers by other groups.^{10–14} To establish the relations between these molecular parameters and the side chain length, however, further work was highly desirable for polymacromonomers with longer side chains.

The present paper reports an experimental study thus undertaken as an extension of our previous light scattering, SAXS, and viscosity studies to a series of PS polymacromonomer samples (designated F110) with 113 side chain units. The data obtained from these methods are comprehensively analyzed, and the side chain length dependence of λ^{-1} and d is discussed. With regard to the sample preparation, which was actually crucial to the present study, a brief remark may be in order.

For very thick chains, samples with large polymerization degrees N of main chain are needed for an unequivocal

determination of λ^{-1} , but the preparation of such is generally difficult. To circumvent the difficulty, we synthesized a very large quantity of PS macromonomer composed of about 110 styrene units in essentially the same way as that described previously.^{1,3} We then divided it into many parts and polymerized them one by one to find the most suitable condition. PS polymacromonomer samples thus obtained were found to contain components with N larger than 1000, and were carefully fractionated to obtain a series of samples covering a broad range of N .

EXPERIMENTAL

Preparation of Polymacromonomer Samples

Styrene (about 150 mL) was polymerized with benzyl lithium as an anionic initiator in 1 L of toluene and terminated by excess 4-vinylbenzylchloride (VBC). The macromonomer thus obtained was reprecipitated four times to remove unreacted VBC. Its M_w and the weight to number-average molecular weight ratio M_w/M_n were determined by light scattering in cyclohexane at 34.5 °C and size exclusion chromatography (SEC), respectively, to be $M_w = 11900$ and $M_w/M_n = 1.05$.

The PS macromonomer (about 10 g in each preparation) was polymerized with azobisisobutyronitrile as an initiator at various temperatures 42–60 °C and macromonomer concentrations 54–86% (w/w) in benzene. The highest molecular weight was reached under the following conditions: monomer concentration, 81% (w/w); initiator concentration, 0.024 mol/

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L; polymerization time, 164 h; temperature, 45 °C. Under these conditions, the yield was as high as 77% and the apparent molecular weight estimated from the peak position of SEC with the calibration curve for linear polystyrene was 2.84×10^6 .

The polymacromonomer samples thus obtained were fractionated by repeated fractional precipitation in toluene-methanol mixtures for low molecular weight samples and in cyclohexane for high molecular weight samples. Twelve fractions (designated below as F110-1, F110-2, ..., F110-12 from high to low molecular weight) were chosen for the present study. The values of M_w/M_n for F110-4–F110-9 were in the range 1.09–1.14 when determined from SEC with the calibration curve constructed for this polymacromonomer.

Static Light Scattering

Five solutions with different concentrations were prepared for each sample in the respective solvents. They were made optically clean by use of a membrane filter of 0.45μ pore size. Measurements were made at 15.0 and 34.5 °C (controlled within ± 0.05 °C) for toluene and cyclohexane solutions, respectively, on a Fica-50 light scattering photometer with vertically polarized incident light of 436 or 546-nm wavelength in the manner employed in our previous studies; for samples F110-9 and F110-11 in cyclohexane, data were also taken at other temperatures T of 25, 30, 40, and 45 °C.

Excess reduced scattering intensities R_θ obtained at scattering angles θ between 30 and 150° were analyzed by means of the square-root plot,¹⁵ i.e., $(Kc/R_\theta)^{1/2}$ against $\sin^2(\theta/2)$ or against c (the solute mass concentration) to obtain M_w , $\langle S^2 \rangle_z$, and A_2 (the second virial coefficient), where K denotes the optical constant. The mass concentration was calculated from the gravimetrically determined weight fraction with the solution density ρ . The density increment $(\partial\rho/\partial c)$ was determined by an Anton-Paar DMA5000 densitometer to be 0.200 in toluene at 15 °C and 0.289 in cyclohexane at 34.5 °C. Its values for cyclohexane solutions were found to change with the temperature coefficient $d(\partial\rho/\partial c)/dT = 5.6 \times 10^{-4} \text{ K}^{-1}$ for $25^\circ\text{C} \leq T \leq 45^\circ\text{C}$.

Specific refractive index increments $\partial n/\partial c$ in cyclohexane at 25, 30, 34.5, 40, and 45 °C and in toluene at 15 °C were measured by using a modified Schulz-Cantow type differential refractometer. The results for toluene solutions were 0.107 and $0.103 \text{ cm}^3 \text{ g}^{-1}$ for 436 and 546 nm, respectively, and those for cyclohexane solutions at 34.5 °C were 0.179 and $0.172 \text{ cm}^3 \text{ g}^{-1}$ for 436 and 546 nm, respectively, with the temperature coefficient $d(\partial n/\partial c)/dT$ of $6.0 \times 10^{-4} (\text{cm}^3 \text{ g}^{-1} \text{ K}^{-1})$ for both wavelengths in the T range between 25 and 45 °C.

Small-Angle X-ray Scattering

SAXS measurements were made on sample F110-9 in cyclohexane (34.5 °C) and toluene (25.0 °C) at a beam line BL40B2 in a synchrotron facility SPring8 (Proposal No 2007A1556) to estimate the chain diameter in each solvent. The camera length and the wavelength of the incident X-ray were set to 1.5 m and 0.1 nm, respectively. A test solution in a quartz glass capillary of 1.5 mm in diameter was kept within

± 0.1 °C by circulation of temperature-regulated water through a capillary holder. Four different concentrations were studied for the respective solvents, with intensity data accumulated for 5 min for each. From the scattered X-ray detected on an imaging plate as a two-dimensional image, the excess scattering intensity $\Delta I(\theta)$ at θ was evaluated as described elsewhere.^{6,7} The square-root plot of $[c/\Delta I(\theta)]^{1/2}$ vs. c was used to obtain $[c/\Delta I(\theta)]_{c=0}^{1/2}$, i.e., the infinite dilution value of $[c/\Delta I(\theta)]^{1/2}$.

Dynamic Light Scattering

The autocorrelation function $g^{(2)}(t)$ was determined as a function of t (correlation time), θ (between 20 and 60°), and c using a light scattering photometer ALV/DLS/SLS-5000 equipped with an ALV-5000E correlator and a YAG laser of the wavelength 532 nm. The first cumulant Γ relative to k^2 (the square of the scattering vector) was evaluated from the slope of a plot of $\ln[g^{(2)}(t) - 1]$ against $k^2 t$ according to the relation

$$\ln[g^{(2)}(t) - 1] = \text{const.} - 2\Gamma t + o(t^2)$$

The translational diffusion coefficient D was determined by double extrapolation of Γ/k^2 to $k = 0$ and to $c = 0$. The desired hydrodynamic radius R_H was calculated from the relation $R_H = k_B T / 6\pi\eta_0 D$, where k_B is the Boltzmann constant and η_0 the solvent viscosity.

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,¹⁶ Mead-Fuoss,¹⁷ and Billmeyer¹⁸ plots were used to determine $[\eta]$.

RESULTS

Figure 1 shows A_2 for samples F110-9 and F110-11 in cyclohexane to vanish at a T of 34.5 °C, which coincides with the theta point for cyclohexane solutions of linear polystyrene and PS polymacromonomers F15, F33, and F65.^{1–3}

The unfilled and filled circles in Figure 2 represent the $\langle S^2 \rangle_z$

Figure 1. Temperature dependence of second virial coefficient for PS polymacromonomer samples F110-9 and F110-11 in cyclohexane.

Figure 2. Molecular weight dependence of mean-square radius of gyration for PS polymacromonomer F110 in toluene at 15.0°C (unfilled circles) and cyclohexane at 34.5°C (filled circles) determined by light scattering. Unfilled and filled squares represent previous SAXS results¹⁹ for F110 in toluene and cyclohexane, respectively. Lines show calculated values from different theories (see the text and Table II).

Figure 3. Cross-section plots for sample F110-9 in toluene at 15.0°C (unfilled circles) and cyclohexane at 34.5°C (filled circles).

data plotted double-logarithmically against M_w for the F110 polymer in toluene at 15.0°C and cyclohexane at 34.5°C, respectively. The previous SAXS data¹⁹ for this polymer in toluene and cyclohexane are also shown by the unfilled and filled squares, respectively. The light scattering data in the good and theta solvents are fitted by straight lines with slopes 1.54 and 1.50 (not shown), respectively, while the SAXS data are almost independent of M_w .

Figure 3 shows the cross-section plots²⁰ of $\ln\{k[\Delta I(\theta)/c]_{c=0}\}$ vs. k^2 for F110-9 in cyclohexane (filled circles) and toluene (unfilled circles). The data points for either solvent (in a relatively small k^2 region in toluene) follow a straight line, whose slope gives d (the cylinder diameter) 16 nm in cyclohexane and 20 nm in toluene if equated to $-d^2/16$ (see ref 21 for theoretical discussions on the slope).

The hydrodynamic radii for F110 samples in toluene (unfilled circles) and cyclohexane (filled circles) are plotted double-logarithmically against M_w in Figure 4. The plots for toluene and cyclohexane solutions are almost linear with slopes 0.56 and 0.53, respectively, for $M_w > 4 \times 10^6$, but the slopes for both solutions are about 0.30 for $M_w < 10^6$.

Figure 4. Molecular weight dependence of hydrodynamic radius for F110 in toluene at 15.0°C (unfilled circles) and cyclohexane at 34.5°C (filled circles). Lines show calculated values for the wormlike chain^{25,26} (see Table II for the parameters used).

Figure 5. Molecular weight dependence of intrinsic viscosity for F110 in toluene at 15.0°C (unfilled circles) and cyclohexane at 34.5°C (filled circles). Solid and dashed lines show calculated values for cylindrical^{27,28} and touched-bead²⁹ wormlike chains, respectively (see Table II for the parameters used).

The molecular weight dependence of $[\eta]$ for the F110 polymer in the two solvents is shown in Figure 5. While for $M_w > 4 \times 10^6$ $[\eta]$ increase in proportion to M_w^ν with $\nu = 0.73$ and 0.68 for toluene and cyclohexane solutions, respectively, it has a minimum around $M_w = 10^6$ in either solvent. We note that no such clear minimum was observed for polymacromonomers with shorter side chains.

The numerical results of M_w , $\langle S^2 \rangle_z$, R_H , and $[\eta]$ for all the F110 samples are summarized in Table I.

DISCUSSION

Radius of Gyration

In our previous studies,¹⁻³ it was shown that the main-chain length dependence of $\langle S^2 \rangle_z$ for three series of polymacromonomers F15, F33, and F65 in cyclohexane at the theta point is accurately described by the familiar expression for the unperturbed cylindrical KP chain of diameter d , i.e., by²²

$$\langle S^2 \rangle = \langle S^2 \rangle_{KP} + (d^2/8) \quad (1)$$

with²³

Table I. Results from static and dynamic light scattering and viscosity measurements on polymacromonomer samples F110 in cyclohexane (CH) at 34.5 °C and toluene (Tol) at 15 °C

Sample	Solvent	$M_w/10^5$	$\langle S^2 \rangle_z / 10^2 \text{ nm}^2$	R_H/nm	$[\eta]/\text{cm}^3 \text{ g}^{-1}$
F110-1	CH	130	27.6	42.6	34.6
F110-2		102	18.4	36.0	28.2
F110-3		84.0	13.5	31.8	24.9
F110-4		61.9	8.7 ₆	27.5	20.9
F110-5		51.7	6.4 ₅	24.3	19.5
F110-6		40.6	4.5 ₄	21.4	15.2
F110-7		25.7	2.4 ₇	17.9	12.5
F110-8		21.9	1.8	16.2	11.7
F110-9		17.9	1.4	15.1	11.1
F110-10		6.80	0.67 ^a	10.8	10.4
F110-11		2.99	0.60 ^a	8.77	11.5
F110-12		1.89	—	7.20	13.3
F110-1	Tol	139	42.3	48.9	60.1
F110-2		104	26.1	40.4	45.9
F110-3		87.8	18.8	37.0	42.0
F110-4		64.7	12.2	31.5	33.5
F110-5		53.3	8.4 ₇	27.4	28.2
F110-6		41.0	6.1 ₅	24.6	24.2
F110-7		27.0	3.2 ₀	19.7	19.6
F110-8		23.0	2.6 ₂	18.1	18.1
F110-9		18.4	1.8	16.9	17.8
F110-10		6.80	0.77 ^a	12.2	16.8
F110-11		3.10	0.72 ^a	9.77	18.1
F110-12		1.99	—	8.37	19.0

^aSAXS results at 25 °C (ref 19).

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

provided the apparent contribution δ of side chains (near the main-chain ends) to the contour length L (see Figure 3 of ref 8) is considered by⁸

$$L = M/M_L + \delta \quad (3)$$

Here, M and M_L denote the polymer molecular weight and the molar mass per unit contour length, respectively.

As may be seen from the above equations, $\langle S^2 \rangle$ at high M is determined by λ^{-1} and M_L . The dashed lines in Figure 2 represent the $\langle S^2 \rangle_{\text{KP}}$ values computed with $\lambda^{-1} = 80$ and 155 nm for cyclohexane and toluene solutions, respectively, and $M_L = 45500 \text{ nm}^{-1}$ for both. Their limited fits for $M_w > 4 \times 10^6$ suggest significant effects of d and δ . With the d values from the cross-section plots in Figure 3, δ was estimated to be 7 nm for both cyclohexane and toluene solutions so as to give the closest fit to the data points over the entire M_w range; we note that the two parameters cannot separately be estimated from the present $\langle S^2 \rangle_z$ data. In Figure 2, except for the lowest M_w sample in cyclohexane, the agreements between the thus computed theoretical solid curves and the data points are satisfactory. In the data analysis for toluene solutions, we considered no intramolecular excluded-volume effect, because the Kuhn statistical segment number $\lambda M_w/M_L$ of about 1.9 for the highest molecular weight sample (F110-1) in toluene is smaller than the value (about 3) at which the excluded-volume effect begins to appear.

The main-chain contour length per unit macromonomer is evaluated from the macromonomer molecular weight (1.19×10^4) and M_L ($4.55 \times 10^4 \text{ nm}^{-1}$) to be 0.26 nm, which is close to the values for other PS polymacromonomers (0.26–0.27 nm)^{1–3,22} and that for the all-*trans* conformation of the polymethylene chain (0.25 nm).

We also compare the $\langle S^2 \rangle_z$ data with the prediction from a wormlike comb model, which consists of a wormlike main chain of contour length M_w/M_L ($M_L = 45500 \text{ nm}^{-1}$) and Kuhn length λ^{-1} connected by universal joints with wormlike side chains of contour length l_s and Kuhn length λ_s^{-1} . The expression for $\langle S^2 \rangle$ of this model chain is given in the Appendix of ref 6. We evaluate l_s to be 30.5 nm from the side chain molecular weight divided by M_L of linear PS²⁴ (390 nm^{-1}). We note that the thickness (about 1 nm) of the individual main and side chains has no significant contribution to $\langle S^2 \rangle$. It can be seen in Figure 2 that the dot-dashed lines representing the theoretical $\langle S^2 \rangle$ ($\lambda^{-1} = 80 \text{ nm}$ and $\lambda_s^{-1} = 4 \text{ nm}$ for cyclohexane and $\lambda^{-1} = 155 \text{ nm}$ and $\lambda_s^{-1} = 5 \text{ nm}$ for toluene) give rather better agreement with the data than the solid lines. These λ_s^{-1} values, comparable to the previous estimate^{6,7} (6 nm) for the F15 polymacromonomer in the two solvents, are appreciably larger than that (2 nm) for the isolated PS chain,²⁴ suggesting that the side chains of the polymacromonomer be somewhat stiffened.

Hydrodynamic Radius

The Yamakawa-Fujii theory²⁵ for the translational friction coefficient allows us to calculate R_H for cylindrical wormlike chains as functions of λL and λd . This theory is, however, valid only for L/d larger than about 4 because it does not consider the frictional force from the cylinder ends. This end effect is taken into consideration in the theory of Norisuye *et al.*²⁶ for wormlike cylinders with hemispheres at both ends, but the theory is applicable only to small L/d . In our data analysis, we therefore use the former theory for large M_w and the latter for small M_w .

The theoretical values calculated for F110 from these theories are shown by the solid lines in Figure 4, where M_L and λ^{-1} are fixed to the values from $\langle S^2 \rangle_z$ ($\lambda^{-1} = 80$ and 155 nm in cyclohexane and toluene, respectively, and $M_L = 45500 \text{ nm}^{-1}$ in both) while d and δ are chosen so as to give the closest fit to the data points. The two theoretical curves for either solvent are connected at $M_w \sim 9 \times 10^6$ and closely fit the data points. The parameters used for the computation are summarized in Table II, along with those estimated from $\langle S^2 \rangle_z$. The d values from R_H are appreciably larger than those from $\langle S^2 \rangle_z$ (or SAXS) even though the hydrodynamic estimation of d often involves considerable errors. Similar discrepancies have been found in the analyses of R_H data^{4,5} for polymacromonomers with shorter side chains (see ref 5 for detailed discussions).

Intrinsic Viscosity

Although the wormlike cylinder is a suitable model for polymacromonomer molecules, its theoretical $[\eta]$ elaborated by Yamakawa, Fujii, and Yoshizaki^{27,28} is available only for

Table II. Molecular parameters explaining different properties for polymacromonomer F110 in cyclohexane (CH) and toluene (Tol)

Property	Solvent	Model	M_L/nm^{-1}	λ^{-1}/nm	d/nm	δ/nm
$\langle S^2 \rangle_z$		C ^a			16	7
R_H	CH	C	45500	80	24	5
$[\eta]$		C			15	13
$[\eta]$		TB ^b			16.5	9
$\langle S^2 \rangle_z$		C			20	6
R_H	Tol	C	45500	155	26	5
$[\eta]$		C			21	14
$[\eta]$		TB			21.5	11

^aCylindrical chain, ^bTouched-bead chain.

$\lambda d \lesssim 0.2$. For the previously studied polymacromonomers F15, F33, and F65, the λd values were all out of this range, and we used the Yoshizaki-Nitta-Yamakawa theory²⁹ based on the touched-bead wormlike model for analyses of experimental $[\eta]$ data with the bead diameter equated to d ,^{3,8} because the difference in $[\eta]$ between the two hydrodynamic models diminishes with increasing λd and becomes at most $\pm 5\%$ at $\lambda d = 0.2$.

Table II shows λd for our polymacromonomer F110 to be just about this boundary value (0.13–0.20 from $\langle S^2 \rangle_z$ and 0.17–0.30 from R_H), so that we may use the both models for the analysis of $[\eta]$. The solid and dashed lines in Figure 5 represent the calculated values from the cylindrical and touched-model theories, respectively, where the d and δ used are the best-fit values presented in Table II while λ^{-1} and M_L are fixed to those from $\langle S^2 \rangle_z$. This comparison allows a few points to be made. 1. The theoretical curves, solid and dashed, satisfactorily fit the data points for both cyclohexane and toluene solutions. 2. In particular, the cylinder model explains the minima of $[\eta]$ around $M_w \sim 10^6$. The left end of each line corresponds to the value for the rigid sphere (for the given parameter set); the solid line for cyclohexane ends at a low M of 9.1×10^4 simply because δ happens to be close to d . 3. The d values based on the two models and that from $\langle S^2 \rangle_z$ (or SAXS) in each solvent are close to one another, so that, as expected, the cylinder and touched-bead model theories give essentially the same results when $\lambda d \sim 0.2$. It should be noticed that the d values from $[\eta]$ are close to those from $\langle S^2 \rangle_z$ or SAXS as was found to be the case for the F15 polymer in cyclohexane and toluene.

The observed minimum of $[\eta]$ in either solvent can be expected from the theory for rigid spheroid cylinders,^{28,30} which is written

$$[\eta] \propto \frac{d^2 p^3}{p - (\delta/d)} F(p) \quad (4)$$

if the chain-end effect is taken into consideration by eq 3. Here, p is the axis ratio defined by L/d and $F(p)$ is a known function of p . For $\delta/d = 0.51$ – 0.87 (see Table II) eq 4 predicts that $[\eta]$ has a minimum at $p = 1.3$ – 2.0 and hence at $M_w = 6 \times 10^5$ – 9×10^5 for F110 in agreement with the experimental data in Figure 5. Since the gradual upswing of $[\eta]$ with lowering M_w arises from the factor $(p - \delta/d)^{-1}$ in eq 4, the significant effect of δ is apparent at low molecular weights.

Figure 6. Main-chain stiffness parameter λ^{-1} plotted double-logarithmically against polymerization degree n_s of side chain for PS polymacromonomers in toluene at 15.0°C (unfilled circles) and cyclohexane at 34.5°C (filled circles). Crosses and triangles are literature data for PMMA-PS polymacromonomers.^{11,14} Solid and dashed lines show calculated values of λ^{-1} and λ_b^{-1} , respectively (see the text).

Main Chain Stiffness

Figure 6 shows that the backbone stiffness for a series of PS polymacromonomers in toluene (the unfilled circles), a good solvent, is systematically higher than that in cyclohexane (the filled circles), a theta solvent, for given n_s (the polymerization degree of side chain) and that both are increasing functions of n_s . As indicated by the theoretical solid curves, this n_s -dependence of λ^{-1} is almost quantitatively explained by Nakamura and Norisuye's theory,³¹ which reads

$$\lambda^{-1} = \lambda_0^{-1} + \lambda_b^{-1} \quad (5)$$

where λ_0^{-1} is the intrinsic backbone stiffness and λ_b^{-1} is the contribution arising from side chain–side chain interactions, given by

$$\lambda_b^{-1} = \frac{1}{8\pi} \left(\frac{n_s}{h} \right)^2 \beta_2 \quad (\text{good solvent}) \quad (6)$$

$$\lambda_b^{-1} = 0.02334 \left(\frac{n_s}{b} \right)^2 \frac{\beta_3}{h^3} \quad (\text{theta solvent}) \quad (7)$$

In the calculation of the solid curves, we have used the following parameters: h (the monomeric contour length of the main chain) = 0.27 nm , b (the effective bond length of each side chain, i.e., of linear PS) = 0.74 nm , β_2 (the binary cluster integral) = 0.034 nm^3 in toluene,³² and β_3 (the ternary cluster integral) = $4 \times 10^{-3} \text{ nm}^6$ in cyclohexane,^{33–35} and $\lambda_0^{-1} = 12$ and 8 nm in toluene and cyclohexane,³¹ respectively.

The dashed lines representing λ_b^{-1} in Figure 6 are fairly close to the data points for the respective solvents at $n_s > 50$, but their slope of 2 predicted by eqs 6 and 7 are much higher than those of the experimental relations even in this large n_s region. The exponents predicted by other theories are in a range from 1.62 to 2,^{36–38} being similar to that of eqs 6 and 7. Evidently, experimental data for longer side chains are needed to determine the asymptotic slopes.

Figure 6 includes the early data (the crosses) of Wintermantel *et al.*¹¹ for polymacromonomers consisting of the poly(methyl methacrylate) (PMMA) backbone and PS side chains in toluene (a good solvent) and also the recent results

from the same group¹⁴ for the PMMA-PS polymacromonomers in d_8 -toluene and d_{12} -cyclohexane at 20 °C (the unfilled and filled triangles, respectively) determined from the angular dependence of small-angle neutron scattering intensity; note that d_{12} -cyclohexane is a poor solvent¹⁴ but not a theta solvent for the polymacromonomer when judged from the magnitude of positive A_2 .¹⁴ Although these recent λ^{-1} values are much smaller than the earlier ones, they are still larger than ours. This comparison (with our polymacromonomers) may be rationalized if, as theoretically shown, λ^{-1} and hence λ_b^{-1} for relatively large n_s are determined predominantly by interactions between or among side chains³¹ (*i.e.*, PS chains). Hence, a remark may be pertinent here.

It is known that the butyl group attached at one end of linear PS leads to non-negligible effects on A_2 near or at the theta point.^{39,40} This end effect must be non-trivial in polymacromonomers having many side chain ends (unlike our benzyl end side chains). The positive A_2 of the PMMA-PS polymacromonomers in d_{12} -cyclohexane may be caused by such effects of the butyl ends in addition to interactions between PS and PMMA units of different molecules. These interactions between or among unlike groups could lead to larger λ^{-1} , and may also affect the side chain conformation.

Chain Thickness

The average values of d estimated from $\langle S^2 \rangle_z$, R_H , and $[\eta]$ for our PS polymacromonomers^{3–8,19} in cyclohexane (the filled circles) and toluene (the unfilled circles) are shown as functions of n_s in Figure 7. Each circle has a large error (maximum error $\pm 29\%$ for F110 in cyclohexane), but, as is the case with λ^{-1} , d is larger in the good solvent than in the theta solvent and is definitely an increasing function of n_s in either solvent. The crosses and triangles representing the data of Schmidt's group^{11,14} for the aforementioned PMMA-PS polymacromonomers show similar trends.

The polymacromonomer chain diameter may be related to the end-to-end distance $\langle r^2 \rangle_{KP}^{1/2}$ of each side chain by

$$d = (2\langle r^2 \rangle_{KP})^{1/2} \quad (8)$$

Figure 7. Dependence of d on n_s for PS and PMMA-PS polymacromonomers. The symbols are the same as those used in Figure 6. Lines show the values calculated from eq 8 with eq 9 for wormlike side chains with $\lambda_s^{-1} = 6$ nm in cyclohexane and 9 nm in toluene and $M_L = 390 \text{ nm}^{-1}$ (in the two solvents).

if the side chains are modeled by the unperturbed KP chain and if their end-to-end vectors are independent of one another (consistent with our wormlike comb model). Here, $\langle r^2 \rangle_{KP}$ is given by

$$\langle r^2 \rangle_{KP} = \frac{l_s}{\lambda_s} - \frac{1}{2\lambda_s^2} [1 - \exp(-2\lambda_s l_s)] \quad (9)$$

The solid lines fitting the unfilled and filled circles in Figure 7 represent eq 8 with eq 9 for wormlike side chains with $\lambda_s^{-1} = 6$ nm in cyclohexane and 9 nm in toluene and $M_L = 390 \text{ nm}^{-1}$ (in both). While the λ_s^{-1} of 6 nm in cyclohexane is essentially consistent with the previous^{6,7} and present analyses of $\langle S^2 \rangle_z$ (6 nm for F15 and 4 nm for F110) based on the wormlike comb model, that of 9 nm in toluene is appreciably larger than the values of 5–6 nm from $\langle S^2 \rangle_z$. At present no reasonable explanation can be made for this difference, but these λ_s^{-1} values are definitively larger than 2 nm for the isolated, unperturbed PS chain,²⁴ indicating that the side chains of PS polymacromonomers are extended or stretched by interactions between or among them as is the case for the dense polymer brushes on a flat surface.⁴¹ Labeling experiments to see the dimensions of a side chain is intriguing to get direct information on the side chain conformation.

The data points for toluene and cyclohexane solutions in Figure 7 vary as n_s^a with $a = 0.75$ and 0.65, respectively. The former exponent happens to be close to the scaling theory values 0.72–0.75.^{36,37,42}

CONCLUSIONS

We draw the following conclusions from the present work on polymacromonomer F110 consisting of PS with 113 side-chain units in cyclohexane (a theta solvent) and toluene (a good solvent).

1. The molecular weight dependence of $\langle S^2 \rangle_z$, R_H , and $[\eta]$ is explained quantitatively by the wormlike chain with $\lambda^{-1} = 80$ nm (in cyclohexane) or 155 nm (in toluene) and $M_L = 45500 \text{ nm}^{-1}$ (in both solvents) though d and δ are allowed to vary depending on the property. The d values determined from the cross-section plot and $[\eta]$ are close to each other, whereas those from R_H are considerably larger than them.
2. The n_s -dependence of λ^{-1} , examined with the aid of previous data^{1–8} for PS polymacromonomers with shorter side-chain lengths, is satisfactorily described by Nakamura and Norisuye's theory³¹ if the intrinsic backbone stiffness is properly chosen. No scaling relation is adequate in the range of n_s below 110.
3. The chain thickness is larger in the good solvent than in the theta solvent. Its n_s -dependence is explained by the relation $d = 2^{1/2} \times$ (the end-to-end distance of the KP chain) with a linear mass density of 390 nm^{-1} and a Kuhn segment length λ_s^{-1} of 6 nm in cyclohexane or 9 nm in toluene. The λ_s^{-1} value of 6 nm in cyclohexane is consistent with the previous and present analyses of $\langle S^2 \rangle_z$ for F15 and F110 based on the wormlike comb model, whereas that of 9 nm in toluene is appreciably larger than the corresponding estimates (5 nm

for F110 and 6 nm for F15) from $\langle S^2 \rangle_z$. This difference between the λ_s^{-1} values in the good solvent remains to be seen.

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