ORIGINAL ARTICLE

Effects of side-chain ends on the stiffness and excluded-volume parameters of polymacromonomers

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Light and small-angle X-ray scattering measurements were taken on cyclohexane and toluene solutions of a polystyrene (PS) polymacromonomer (PM) having side chains consisting of 19 styrene residues and an *n*-butyl group (butyl-PS PM) at each end. The second virial coefficient, A_2 , of the butyl-PS PM in cyclohexane was positive in the temperature range of 15.0–34.5 °C, differing from previous results for PS PMs with benzyl ends (benzyl-PS PM) whose A_2 vanished at 34.5 °C. The mean-square radius of gyration, $\langle S^2 \rangle$, for the butyl-PS PM in cyclohexane at 34.5 °C was much larger than that for the benzyl-PS PM with the same side-chain length, indicating large effects of the side-chain ends on intramolecular interactions, whereas the difference in $\langle S^2 \rangle$ between these polymers in toluene at 15.0 °C was quite small. From these data, the stiffness parameter and the excluded-volume strength were determined with the aid of theories for the wormlike chain model. The effects of the side-chain ends on these parameters are discussed according to recently developed theories.

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INTRODUCTION

The second virial coefficient, A_2 , of linear polystyrene (PS) with a butyl end in cyclohexane at the Θ temperature (34.5 °C) was known to increase with decreasing molecular weight, M , when M is lower than 10^4 , which had been considered to be the effects of the three-segment interactions.¹ Yamakawa² interpreted this increase as an effect of chain ends in 1992. Since then, studies were undertaken to address the chain-end effect on A_2 for several kinds of polymers.^{3–9} Among them, PS solutions were the most precisely examined. Because the chain-end effect on A_2 of linear PS with a benzyl end, in contrast to a butyl end, was negligibly small,⁷ the increase in A_2 of PS at low M was ascribed to the effects of the butyl end. Recently, a similar study was carried out on the A_2 of a four-arm star PS with a butyl group at each arm end and showed that the increase in A_2 at Θ with decreasing M begins at a higher value of M than that for linear PS with the same end group.⁸ This study indicates that the chain-end effect becomes more significant with an increasing number of branches. Therefore, one may expect the chain-end effect to be much larger for comb polymers that have many more branches.

Polymacromonomer (PM), a type of comb-branched polymer with dense side chains, is known to behave as a stiff chain in solution because of the interactions between its side chains.^{10–12} We have studied PM consisting of a PS main chain and PS side chains with a benzyl group at each end (benzyl-PS PM) and showed that its A_2 in cyclohexane vanishes at 34.5 °C, which is identical to the Θ temperature of linear PS in cyclohexane.^{13–16} In contrast, the values of A_2 for PM consisting of a polymethacrylate main chain and PS side chains

with a butyl group at each end (PS-MA PM) in d_{12} -cyclohexane were shown to be positive at 20 °C,¹⁷ far below the Θ temperature (40 °C) of linear PS in d_{12} -cyclohexane. Although the butyl end in PS-MA PM may be a primary cause of the positive A_2 , there may be a possible effect on the A_2 of the polymethacrylate main chain. Therefore, it is desirable to pursue further examinations of PM samples consisting of a PS main chain and PS side chains with butyl ends.

We prepared butyl-PS PM samples with side chains consisting of 19 repeating units and determined the mean-square radius of gyration $\langle S^2 \rangle$, the particle scattering function $P(\theta)$, and A_2 as functions of M for the samples in toluene and cyclohexane. By analyzing these data, the excluded-volume parameter, B , and the chain-stiffness parameter, λ^{-1} , were determined. Effects of the side-chain ends on B and λ^{-1} are discussed with the aid of current theories.

EXPERIMENTAL PROCEDURE

Samples

The macromonomer was obtained by anionic polymerization of styrene in a high-vacuum apparatus as follows. A hexane solution of *n*-butyllithium was added to styrene in toluene in a round-bottom flask. When the color of the solution became yellow, tetrahydrofuran was quickly added to promote the propagation reaction. After 20 h, a tetrahydrofuran solution of vinylbenzyl chloride (supplied from AGC Seimi Chemical Co. Ltd., Kanagawa, Japan) was added at –78 °C. The crude macromonomer was precipitated in methanol from toluene solutions three times to remove residual vinylbenzyl chloride. Introduction of a double bond at the chain end was confirmed by ¹H nuclear magnetic resonance measurement. The weight-average molecular weight, M_w , and the M_w to M_n (number-average molecular weight) ratio of the

macromonomer as determined by matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy were 2.12×10^3 and 1.08, respectively. From the former value, the degree of polymerization of the side chain, n , was calculated to be 19. The macromonomer thus obtained was separated into parts and polymerized one by one in benzene with a radical initiator, azobisisobutyronitrile. Existence of the polymerized components was confirmed by gel permeation chromatography. The crude PM samples were successively reprecipitated to obtain six fractions with narrow molecular-weight distributions. The values of M_w/M_n for these samples were in the range of 1.07–1.13 as estimated from gel permeation chromatography with a calibration curve for this PM.

Measurements

Solutions for light-scattering measurements were made by dissolving each sample in toluene and cyclohexane that had been distilled after refluxing over sodium metal for ~6 h. The toluene and cyclohexane solutions were stirred for 1 day at room temperature and at 34.5 °C, respectively, and filtered using a polytetrafluoroethylene filter with a 0.45-μm pore size.

The densities, ρ , of solutions of butyl-PS PM in cyclohexane and toluene were measured using an Anton Paar DMA5000 densitometer (Anton Paar, Graz, Austria) to obtain the specific volume, $\bar{v}$, which was used to calculate the solution density at a given polymer weight fraction, w , using the expression $\rho = \rho_0 + (1 - \bar{v}\rho_0)\rho_0 w$ with ρ_0 , the solvent density and the mass concentration, c , calculated from ρw . The values of $\bar{v}$ for butyl-PS PM in cyclohexane at 34.5 °C and in toluene at 15.0 °C were 0.945 and 0.919 cm³ g⁻¹, respectively. The refractive index increments, $\partial n/\partial c$, were measured using a modified Schultz-Cantow-type differential refractometer (Shimadzu DR-1, Shimadzu, Kyoto, Japan) at 435.8 nm and were found to be 0.179 and 0.102 cm³ g⁻¹ for butyl-PS PM in cyclohexane at 34.5 °C and in toluene at 15.0 °C, respectively.

Light-scattering measurements were taken with a Fica 50 light-scattering photometer (Fica, Saint Denis, France) with 435.8 nm vertical light at 10 scattering angles, θ , from 30.0° to 142.5°. The reciprocal intensities for each solution were extrapolated to the zero scattering angle by Berry's square-root plot. For each sample, six solutions with different concentrations were prepared to obtain the reciprocal intensity extrapolated to $c=0$.

Small-angle X-ray scattering measurements were taken at a beam line BL40B2 of the synchrotron facility (SPring-8, Hyogo, Japan) with an X-ray of 0.1 nm wavelength and a camera whose distance from the sample to the imaging-plate detector was 1.66 m. Four solutions of differing concentrations were prepared to obtain the reciprocal scattering intensity extrapolated to $c=0$.

Table 1 Properties of butyl-PS PM samples in cyclohexane and toluene

Sample	$10^{-5}M_w$	$[\eta]$ (cm ³ g ⁻¹)	$\langle S^2 \rangle$ (nm ²)	$10^5 A_2$ (cm ³ mol g ⁻²)
Cyclohexane at 34.5 °C				
T19-1	19.1	38.9	792	2.2
T19-2	13.6	30.0	515	2.6
T19-3	9.98	23.7	364	3.3
T19-4	6.01	16.7	189	3.8
T19-5	4.32	13.8	114	4.0
T19-6	2.27	9.36	54 ^a	5.1
Toluene at 15.0 °C				
T19-1	19.2	—	999	2.4
T19-2	14.2	—	625	3.3
T19-3	10.1	—	407	4.0
T19-4	6.05	—	196	4.3
T19-5	4.35	—	130	5.4
T19-6	(2.27) ^a	—	63 ^b	—

Abbreviations: PM, polymacromonomer; PS, polystyrene.

^aValue in cyclohexane.

^bFrom small-angle X-ray scattering measurements.

The temperature of the solution in a capillary with a 1.5-mm diameter was controlled to within ± 0.05 °C by circulating water in a water jacket around the capillary holder. Obtaining each measurement took 3 min. The particle scattering function, $P(\theta)$, was obtained by the previously described method.¹⁸

The results from the scattering measurements along with the intrinsic viscosities, $[\eta]$, in cyclohexane at 34.5 °C measured by a handmade Ubbelohde viscometer are summarized in Table 1.

RESULTS AND DISCUSSION

Radius of gyration

Double logarithmic plots of $\langle S^2 \rangle$ versus M_w for both cyclohexane and toluene solutions are shown in Figure 1. The values for the toluene solutions are larger than those for the cyclohexane solutions by 5–20%, indicating that toluene is a better solvent for butyl-PS PM than cyclohexane. These results are similar to those observed for PS-MA PM in toluene and cyclohexane.^{17,19}

The unperturbed mean-square radius of gyration, $\langle S^2 \rangle_0$, for wormlike chains with a contour length L is expressed as²⁰

$$\lambda^2 \langle S^2 \rangle_0 = \frac{\lambda L}{6} - \frac{1}{4} + \frac{1}{4\lambda L} - \frac{1}{8(\lambda L)^2} [1 - \exp(-2\lambda L)] \quad (1)$$

where L is related to M by $L=M/M_L$, with the molar mass per unit contour length, M_L . For good solvent systems, the polymer chain is expanded by the excluded-volume effect, which is expressed by the radius expansion factor, α_s . This factor may be calculated by the modified Domb–Barrett equation^{21,22}

$$\alpha_s^2 = [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15} \times [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)] \quad (2)$$

The parameter, $\tilde{z}$ is defined by²²

$$\tilde{z} = \frac{3}{4} K(\lambda L) z \quad (3)$$

with the excluded-volume parameter, z , given by

$$z = \left(\frac{3}{2\pi} \right)^{3/2} (\lambda B)(\lambda L)^{1/2} \quad (4)$$

where B represents the excluded-volume strength. The functional form of $K(\lambda L)$ is given in Yamakawa²². Because α_s is a function of λL and

Figure 1 Molecular-weight dependence of the mean-square radius of gyration for butyl-polystyrene polymacromonomer in toluene at 15.0 °C (filled circles) and in cyclohexane at 34.5 °C (unfilled circles). The lines show the theoretical values for the wormlike chain (see text).

λB , $\langle S^2 \rangle$ can be calculated from $\alpha_s^2 \langle S^2 \rangle_0$ with the parameters λ^{-1} , M_L , and B .

It was impossible to determine these three parameters uniquely using the $\langle S^2 \rangle$ data given in Figure 1. Therefore, we calculated M_L to be 7900 nm^{-1} from the macromonomer molecular weight and the contour length for the unit macromonomer residue, $h_s=0.27 \text{ nm}$, which is known for benzyl-PS PMs.^{13–16} The dashed lines in Figure 1 represent the calculated values from the above equations with $\lambda^{-1}=17 \text{ nm}$ and $B=10 \text{ nm}$ for cyclohexane solutions (lower line) and $\lambda^{-1}=20 \text{ nm}$ and $B=13 \text{ nm}$ for toluene solutions (upper line). Excluding the data for the lowest molecular weight sample, these lines satisfactorily fit the data points. We can estimate B for benzyl-PS PM in toluene to be 8 nm with $n=19$ from the interpolation of the previously obtained values.²³ The value of B for butyl-PS PM in toluene is larger than that for benzyl-PS PM in toluene. Obviously, B for butyl-PS PM in cyclohexane at 34.5°C is also larger than that for benzyl-PS PM ($B=0$).

An explanation of the solid lines in Figure 1 will be given in the next section.

Scattering function

The scattering functions of T19-6 in toluene at 15.0°C and in cyclohexane at 34.5°C are illustrated in the Kratky plot shown in Figure 2, that is, the plot of $k^2 P(\theta)$ versus k . The peak height of the data for the toluene solution is lower than that for the cyclohexane solution, as it is for benzyl-PS PM.²⁴ The solid lines are calculated values for the cylindrical wormlike chains²⁵ with the following parameter sets: $M_L=7900 \text{ nm}^{-1}$, $\lambda^{-1}=17 \text{ nm}$, $d=5.4 \text{ nm}$ and $\delta=4.0 \text{ nm}$ in cyclohexane; and $M_L=7900 \text{ nm}^{-1}$, $\lambda^{-1}=20 \text{ nm}$, $d=5.7 \text{ nm}$ and $\delta=5.0 \text{ nm}$ in toluene. Here, d and δ represent the chain diameter and the contribution of the side chains near the main-chain ends to the PM contour length,²⁶ respectively. The calculated values satisfactorily express the data points with the same values of M_L and λ^{-1} as those used for the $\langle S^2 \rangle$ data. The solid lines in Figure 1, which represent the calculated values when the above d and δ are taken into consideration,¹⁸ also satisfactorily fit the $\langle S^2 \rangle$ data. Thus, both $\langle S^2 \rangle$ and $P(\theta)$ are consistently expressed by the cylindrical wormlike chain model with the same parameters. We note that the intramolecular excluded-volume effects are negligible for T19-6. The intrinsic viscosities for butyl-PS PM in cyclohexane at 34.5°C were analyzed by the theory for the wormlike chain model^{27,28} and explained with the parameter set $\lambda^{-1}=17 \text{ nm}$, $B=10 \text{ nm}$, $d=5.6 \text{ nm}$, $\delta=4.0 \text{ nm}$ and $M_L=8200 \text{ nm}^{-1}$, which is essentially the same parameter set as that for $\langle S^2 \rangle$ and $P(\theta)$.

The molecular parameters for butyl-PS PM with $n=19$ along with the interpolated values of B and λ^{-1} for benzyl-PS PM with the same n estimated from the previous results^{13–16,23} are summarized in Table 2. The uncertainty of these parameters is approximately $\pm 5\%$.

Second virial coefficient

Figure 3 shows the temperature dependence of A_2 for T19-3 and T19-4 in cyclohexane. The A_2 values slightly increase with temperature but are always positive in the temperature range studied. This differs from the known behavior of linear PS and benzyl-PS PM in the same solvent in that A_2 decreases with decreasing T and becomes zero at 34.5°C ,^{13–16} but the results are similar to those observed for PS-MA PM.^{17,19}

The molecular weight dependence of A_2 for butyl-PS PM is illustrated in Figure 4, in which the filled and unfilled circles represent the data points for the toluene and cyclohexane solutions, respectively. The data points for the cyclohexane solutions are systematically lower

than those for the toluene solutions, showing that the former solvent is poorer than the latter solvent. However, the order of magnitude of A_2 for both solutions is the same, indicating that cyclohexane is a good solvent for butyl-PS PM.

Figure 2 Kratky plots for butyl-polystyrene polymacromonomer (T19-6) in toluene at 15.0°C (filled circles) and in cyclohexane at 34.5°C (unfilled circles). The lines show the theoretical values for the wormlike chain (see text).

Table 2 Molecular parameters of butyl- and benzyl-PS PM with side chains containing 19 styrene residues in CH at 34.5°C and in Tol at 15.0°C

Polymer	Solvent	$B \text{ (nm}^3\text{)}$	$\lambda^{-1} \text{ (nm)}$	$M_L \text{ (nm}^{-1}\text{)}$	$d \text{ (nm)}$	$\delta \text{ (nm)}$
Butyl-PS PM	CH	10	17	7900	5.4	4.0
	Tol	12	20	7900	5.7	5.0
Benzyl-PS PM	CH	0	12 ^a	—	—	—
	Tol	8 ^a	20 ^a	—	—	—

Abbreviations: CH, cyclohexane; PM, polymacromonomer; PS, polystyrene; Tol, toluene.
^aInterpolated values from previous results.^{13–16,23}

Figure 3 Temperature dependence of the second virial coefficient for butyl-polystyrene polymacromonomer samples in cyclohexane.

Figure 4 Molecular-weight dependence of the second virial coefficient for butyl-polystyrene polymacromonomer in toluene at 15.0 °C (filled circles) and in cyclohexane at 34.5 °C (unfilled circles). The lines show the theoretical values for the wormlike chain (see text).

According to the theory for the wormlike chain,²² A_2 without the effects of the PM ends can be written as:

$$A_2^0 = \frac{N_A L^2 B}{2M^2} h(\hat{z}) \quad (5)$$

In the above equation, N_A represents the Avogadro constant and $h(\hat{z})$ is given by:²

$$h(\hat{z}) = (1 + 7.74\hat{z} + 52.3\hat{z}^{27/10})^{-10/27} \quad (6)$$

The scaled excluded-volume parameter $\hat{z}$ is defined by:

$$\hat{z} = \frac{Q(\lambda L) z}{2.865 \alpha_s^3} \quad (7)$$

The functional form of $Q(\lambda L)$ is given in Yamakawa²².

The dashed lines in Figure 4 show calculated values with the parameters given in Table 2. These lines are close to the data points, although they deviate from the data points for $M_w < 10^6$. To obtain a better fit, we may need to add the following term $A_2^{(E)}$ for the effects of the PM ends on $A_2^{0,2}$:

$$A_2^{(E)} = a_{2,1} M_w^{-1} + a_{2,2} M_w^{-2} \quad (8)$$

The solid lines in Figure 4 show that the calculated values for $A_2^0 + A_2^{(E)}$ with $a_{2,1} = 3.0 \text{ cm}^3 \text{ g}^{-1}$ and $a_{2,2} = 0$ for both of the solutions satisfactorily fit the data points.

Excluded-volume strength

Recently, we proposed a calculation method of B for brush-like segments, which consist of a straight main chain of a length a with Gaussian side chains connected to it at intervals h_s .²³

The excluded volume for the brush-like segments was calculated in terms of a sum of segmental interactions among the side chains. It was shown that the first-order perturbation calculation overestimates B , but the smoothed-density method yields results close to the experimental values. By the latter method, B can be expressed as:

$$B = \frac{1}{a^2} \int \langle 1 - \exp[-W_{12}(\mathbf{r})/k_B T] \rangle d\mathbf{r} \quad (9)$$

In the above equation, $W_{12}(\mathbf{r})$ is the smoothed potential between the brush-like segments as a function of the distance, $\mathbf{r}$, between the

midpoints of the main chain of the brush-like segments. The angular brackets indicate the statistical average. The potential, $W_{12}(\mathbf{r})$, is represented by the sums of the distribution function for the probability of contact among the side-chain segments multiplied by the corresponding cluster integral:

$$\frac{W_{12}(\mathbf{r})}{k_B T} = \beta_2 \sum_{i,j} \sum_{p_i,q_j} P(\mathbf{0}_{p_i,q_j}; \mathbf{r}_{ij}, p_i, q_j) + 2\beta_{01} \sum_{i,j} \sum_{p_i} P(\mathbf{0}_{p_i,n}; \mathbf{r}_{ij}, p_i, n_j) \quad (10)$$

β_2 and β_{01} denote the binary-cluster integral between the middle segments of the side chains and the binary-cluster integral between the segments at the end and the middle of the side chains, respectively. $P(\mathbf{0}_{p_i,q_j}; \mathbf{r}_{ij}, p_i, q_j)$ is the distribution function representing the probability that the segments p_i and q_j (the p th segment of the i th side chain and the q th segment of the j th side chain, respectively) are in contact and given by

$$P(\mathbf{0}_{p_i,q_j}; \mathbf{r}_{ij}, p_i, q_j) = \left(\frac{3}{2\pi b^2} \right)^{3/2} \frac{1}{(p_i + q_j)^{3/2}} \exp \left[-\frac{3r_{ij}^2}{2b^2(p_i + q_j)} \right] \quad (11)$$

where b is the length of the Gaussian segment of the side chain. We note that $\mathbf{r}_{ij}$, the distance between the connected points of the i th and j th side chains to the main chains of two brush-like segments, is a function of $i, j, \mathbf{r}$ and the directions of the two brush-like segments, although this is not indicated for clarity. The factor, 2, in front of β_{01} in Equation (10) comes from the two cases in which the contacting side-chain end belongs to one of two brush-like segments.

Using $\beta_2 = 0$ and $\beta_{01} = 0.1 \text{ nm}^3$ for the (linear) butyl-end PS in cyclohexane at 34.5 °C,⁸ we obtain $B = 7.3 \text{ nm}$, which is $\sim 30\%$ smaller than the experimental value (10 nm) for butyl-PS PM in cyclohexane. This is rather different from the case for benzyl-PS PM in toluene, in which the calculated value was close to the experimental value. In the present calculation, the side-chain ends are assumed to distribute around the main chain according to the Gaussian distribution. However, the butyl groups may tend to be located around the surface of the molecule by the segregation of the end groups from the styrene residues. In other words, the PM molecule may be surrounded by a shell of the end groups. This shell may increase the excluded volume of a brush-like segment.

B for butyl-PS PM in the toluene solutions was also calculated by Equations (9) and (10) using $\beta_2 = 0.033 \text{ nm}^3$ for linear PS²⁹ and $\beta_{01} = 0.32 \text{ nm}^3$ for butyl-end PS,⁹ both in toluene at 15.0 °C. The obtained value was 9.0 nm, which is smaller than the experimental value (12 nm). This may also be attributed to the deviation from a Gaussian distribution for the location of the end groups. We obtain $B = 7.8 \text{ nm}$ for benzyl-PS PM in toluene using Equations (9) and (10) with the above β_2 and $\beta_{01} = 0$. This value of B is quite close to the interpolated value (8 nm) for $n = 19$ from the previous results.

Stiffness parameter

In Table 2, values of λ^{-1} for butyl-PS PM with $n = 19$ in cyclohexane at 34.5 °C and in toluene at 15.0 °C are compared with the interpolated values for benzyl-PS PM with the same n from the previous results.^{13–16} The value of λ^{-1} for butyl-PS PM in toluene agrees with the value for benzyl-PS PM in the same solvent. In contrast, λ^{-1} for butyl-PS PM in cyclohexane is appreciably larger than that for benzyl-PS PM in the same solvent. This difference (5 nm) between the λ^{-1} values for butyl- and benzyl-PS PM in cyclohexane must be due to the effects of the side-chain ends.

In the previous study,³⁰ λ^{-1} was expressed as a sum of the part from the interactions among the side-chain segments, λ_s^{-1} , and the other contributions, λ_0^{-1} .

$$\lambda^{-1} = \lambda_0^{-1} + \lambda_s^{-1} \quad (12)$$

The values of λ^{-1} for PS PMs with n larger than 50 were almost quantitatively expressed by the first-order perturbation theory for λ_s^{-1} .³⁰ According to this theory, the contribution of interactions between the middle and end segments of the side chains can be expressed by the following equation:

$$(\lambda_s^{-1})_E = \frac{n}{4\pi h_s^2} \beta_{01} \quad (13)$$

If we use $\beta_{01}=0.10\text{ nm}^3$ for the butyl-end PS in cyclohexane at 34.5°C ⁸ in the above equation along with $h_s=0.27\text{ nm}$, we obtain $(\lambda_s^{-1})_E = 2.1\text{ nm}$, which is approximately half of the difference between the λ^{-1} values for butyl-PS PM and benzyl-PS PM in cyclohexane. This suggests that the contributions from the two-segment interaction between the side-chain ends, the two-segment interaction between the side-chain end and the main-chain, and the three-segment interaction among a side-chain end and two middle side chains cannot be ignored.

If we calculate the effect of the side-chain end on butyl-PS PM in toluene using Equation (13) with $\beta_{01}=0.32\text{ nm}^3$,⁹ the value for the butyl-end PS, we obtain 6.6 nm for $(\lambda_s^{-1})_E$. Because the difference in λ^{-1} between benzyl- and butyl-PS PMs in toluene is zero, as shown in Table 2, the above value does not agree with the experimental results. If the side-chain end groups tend to distribute outside of the PM molecule, the probability of contact between the side-chain end segment and middle side-chain segment may be smaller than that calculated from the random-distribution approximation. The disagreement in the calculated λ^{-1} and the observed value may be ascribed to this approximation.

CONCLUSIONS

The properties of dilute solutions of PS PMs with a butyl group at each side-chain end were studied. It was shown that this polymer behaves as if it is in a good solvent even in cyclohexane, known as the theta solvent for PSs. The values of B for butyl-PS PM were larger than those for benzyl-PS PM with the same side-chain length, both in cyclohexane and toluene. This parameter was calculated based on the smoothed-density model, which gave a value of B close to the experimental value for benzyl-PS PM in toluene. However, values $\sim 30\text{--}40\%$ smaller than the experimental values were obtained for butyl-PS PM both in cyclohexane and toluene, even when effects from side-chain ends were taken into consideration. This disagreement was ascribed to the deviation in the distribution of the side-chain end groups from the Gaussian distribution. The value for λ^{-1} for butyl-PS PM in cyclohexane was also larger than that for benzyl-PS PM with the same side-chain length. Half of this difference was explained as the effect from side-chain ends by the first-order perturbation theory for λ^{-1} . The other half was ascribed to other interactions: the binary interaction between side-chain ends, the binary interaction between the side-chain end and the main chain, and the ternary interaction among the two middle side-chain segments and one side-chain end segment. The distribution of side-chain deviating from the Gaussian distribution may partly cause the disagreement between the experimental and theoretical values of λ^{-1} .

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