Dilute Solution Properties of Polymacromonomer Consisting of Polybutadiene Backbone and Polystyrene Side Chains

Yuji Hatanaka and Yo Nakamura*

Department of Polymer Chemistry, Kyoto University, Katsura, Kyoto 615-8510, Japan

* Corresponding author (E-mail: yonaka@molsci.polym.kyoto-u.ac.jp)

Keywords: polymacromonomer; solution properties; chain stiffness

Abstract

A polymacromonomer consisting of polybutadiene backbone and polystyrene side chains (BS-PM) with the degree of polymerization of side chain $n = 20$ was synthesized by anionic polymerization. Five samples with different molecular weight or main-chain length were prepared. Light scattering and viscosity measurements were taken on dilute solutions of these BS-PM samples in toluene at 15.0 °C and in cyclohexane at 34.5 °C and 29.0 °C. The second virial coefficients of BS-PM in cyclohexane vanished at 29.0 °C, which is lower than the theta temperature, 34.5 °C, of linear polystyrene and polymacromonomer consisting of polystyrene (PS-PM) in the same solvent. This shows that the interaction between side and main chains is appreciable in cyclohexane at 34.5 °C. The mean-square radius of gyration and the intrinsic viscosity in toluene and cyclohexane determined as functions of molecular weight were analyzed with the aid of the theories for the wormlike chain model to determine the stiffness parameter λ^{-1} of the main chain. The values of λ^{-1} for BS-PM in both solvents were smaller than those for PS-PM with the same n, reflecting the wider side-chain spacing. These results are consistent with the prediction of the first-order perturbation theory of Nakamura and Norisuye [Polym J 2002;33:874], which gives the contribution of the segmental interactions among side chains λ_b^{-1} to λ^{-1}. However, the difference of λ^{-1} between BS-PM and PS-PM in each solvent is appreciably larger than the difference of the calculated λ_b^{-1} between BS-PM and PS-PM, suggesting that the difference of the contribution of steric hindrance among side chains to λ^{-1} between these two polymers is appreciable.

1. Introduction

Since brush-like polymers, which have comb-like structure with dense side chains, was found to behave as stiff chains,[1-8] the relations of the main-chain stiffness parameter λ^{-1} to the polymer structure and/or the segmental interactions have been one of the important issues of polymer solution study. We have studied polymacromonomer (PM) with side and main chains both consisting of polystyrene (PS-PM) to determine λ^{-1} in good and theta solvents as functions of the degree of polymerization of side chain n.[9-12] From these studies, we concluded that λ^{-1} is expressed by a sum of two parts, λ_b^{-1} and λ_0^{-1}; the former represents the effects of segmental interactions among side chains and the latter is a constant term. The latter part is considered to be mostly from the steric interactions of side chains.

There are several theories to calculate λ_b^{-1}.[13-16] These theories predict that λ_b^{-1} increases with increasing n and decreases with increasing the side-chain spacing. Increase of λ^{-1} with n was experimentally observed in dilute-solution data for several PM's.[3,6-8] However, decrease of λ^{-1} with increasing the side-chain spacing has not been observed, yet. It is desirable to study λ^{-1} of polymers with different side-chain spacing to check the validity of the theory.

Most of polymacromonomers are synthesized from polymerization of macromonomers with a vinyl group. The side-chain spacing of such polymacromonomers is fixed by two carbon-carbon bonds. If we use a macromonomer with a diene group at the end, we may increase the side-chain spacing.

Here, we report synthesis of a polymacromonomer having a backbone with polybutadiene structure and polystyrene side chains (BS-PM) with $n = 20$ and dilute solution properties of it in toluene and cyclohexane; λ^{-1} in each solvent was determined by analyses of the mean-square radius of gyration $\langle S^2 \rangle$ and the intrinsic viscosity $[\eta]$ determined as functions of molecular weight. The resulted λ^{-1} was compared with the values of λ^{-1} for PS-PM's and with theoretical predictions. The

contributions of λ_b^{-1} and λ_0^{-1} on the experimental values of λ^{-1} are also discussed.

2. Experimental Section

2.1. Polymer Samples

The macromonomer with a diene group was synthesized from the coupling reaction of living polystyrene; styrene was polymerized in toluene with benzyllithium as the initiator and terminated with 6-bromo-3-methylene-1-hexane (**1**).[17] This coupling reagent (**1**) was obtained from the reaction of 1,3-dibromopropane and 2-(1,2-butadienyl) magnesium chloride (**2**) in the presence of Li_2CuCl_4. The Grignard reagent (**2**) was synthesized from chloroprene,[18] which was kindly supplied from Denka Co. Ltd. The weight-average molecular weight M_w and the ratio of M_w to the number-average molecular weight M_n of the macromonomer obtained was determined by MALDI-TOF-MS measurement to be 2270 and 1.03, respectively. From the former value, we found $n = 20.0$. The macromonomer was separated into parts and polymerized one by one with n-butyllithium as the initiator. Since the molecular weight distribution of polymacromonomers were rather broad, they were factionally precipitated with benzene as the solvent and methanol as the precipitant. Finally, six samples with narrow molecular weight distribution were obtained. We observed a single peak at 4.7 ppm on a ^{1}H NMR chart for one of these samples in $CDCl_3$, showing that the main chain is made from the 1,4 linkage, although the ratio of *cis* and *trans* components was not determined. The values of M_w/M_n for these samples were in the range from 1.03 to 1.04, when they were determined by gel-permeation chromatography with the calibration curve for these BS-PM samples. The chemical structure of the BS-PM polymacromonomer is shown in Figure 1 along with the structure of PS-PM.

〈Figure 1〉

4

2.2. Measurements

For light-scattering measurements, from five to eight solutions with different concentrations were prepared for each polymer-solvent system. The weigh fraction w of the solute in each solution was determined gravimetrically. The mass concentration c was calculated by multiplying w by the solution density ρ, which was calculated as a function of w from the following equation,

$$\rho = \rho_0 + (1 - \bar{v}\rho_0)w\rho_0$$

The specific volume $\bar{v}$ for this polymacromonomer in toluene at 15.0°C, in cyclohexane at 29.0°C, and in cyclohexane at 34.5°C were determined by Anton-Paar densitometer DMA5000 to be 0.9195, 0.9282, and 0.9331 cm^3 g^{-1}, respectively. The values of $\bar{v}$ for cyclohexane solutions at other temperatures T were calculated by an approximated linear relation of $\bar{v}$ vs T. The solutions for light-scattering measurements were made optically clean by passing through a teflon filter with the pore size of 0.45 μm.

A Fica 50 light scattering photometer was used for the measurements with the incident light of 436 nm wavelength to obtain the Rayleigh ratio R_θ at the scattering angle θ. Berry's square-root plots[19] of $(Kc/R_\theta)^{1/2}$ vs k^2 and $(Kc/R_\theta)^{1/2}$ vs c were used to obtain M_w, the second virial coefficient A_2, and the mean-square radius of gyration, where K and k indicate the optical constant and the magnitude of the scattering vector, respectively. The specific refractive index increments $\partial n/\partial c$ for the toluene solution at 15.0°C and the cyclohexane solution at 29.0 and 34.5°C were determined by a Shimadzu DR-1, a Shulz-Cantow type differential refractometer to be 0.1071, 0.1800, and 0.1749 cm^3 g^{-1}, respectively, for 436 nm of the incident light. The values of $\partial n/\partial c$ of cyclohexane solutions at the other T were calculated by an approximated linear relation of $\partial n/\partial c$ vs T.

Small-angle X-ray scattering (SAXS) measurements were taken to determine $\langle S^2 \rangle$ of the lowest molecular weight samples in cyclohexane at 34.5°C at a beam line BL40B2 of the synchrotron facility SPring-8. The wavelength and the camera length were chosen to be 0.1 nm and 3 m, respectively. A capillary cell, whose temperature was controlled within ±0.1 degrees by circulating water, was used for the measurements. The scattering image detected by an imaging plate was circularly averaged to obtain the scattering intensity as a function of the scattering angle. The scattering data were analyzed by the same way as the light-scattering data.

The intrinsic viscosities for toluene and cyclohexane solutions were measured using a conventional capillary viscometer of the Ubbelohde type.

3. Results and Discussions

3.1. Second Virial Coefficient

The plot of A_2 against T for a sample BS2 in cyclohexane is shown in Figure 2. The theta temperature where A_2 vanishes became 29.0°C. This is lower than the theta temperature 34.5°C for PS-PM[10-12] and linear polystyrene in cyclohexane. The values of A_2 for three samples in cyclohexane at 34.5 °C were about 1.1×10^{-5} cm^3 mol g^{-2}. Since A_2 for PS-PM was zero, the segmental interactions between polystyrene side chains vanish in this solvent. Therefore, the positive A_2 of BS-PM, which has the same side chains as PS-PM, in cyclohexane at 34.5 °C can be ascribed to the repulsive interaction between side-chain and main-chain segments.

⟨Figure 2⟩

3.2. Radius of Gyration

In Figures 3 and 4, values of $\langle S^2 \rangle$ for BS-PM in cyclohexane at 34.5 °C and 29.0 °C and in toluene at 15.0 °C, respectively, are plotted double logarithmically against M_w. The dot-dashed line in Figure 3 shows the values for PS-PM with the same

side chain length ($n = 20$) in cyclohexane at 34.5 °C calculated with the following molecular parameters; the molecular weight per unit contour length $M_L = 8800$ nm^{-1} and $\lambda^{-1} = 11.5$ nm. The dot-dashed line in Figure 4 represents the calculated values for PS-PM with $n = 20$ using $M_L = 8800$ nm^{-1}, $\lambda^{-1} = 19.5$ nm, and the excluded-volume strength $B = 8.5$ nm. Each parameter for PS-PM was estimated by interpolation of the parameter obtained as a function of n from the previous studies.[9-12] The method of calculation of $\langle S^2 \rangle$ is described below. If we compare at the same M_w, $\langle S^2 \rangle$ of BS-PM is larger than that for PS-PM with the same n reflecting longer main chain of BS-PM than that for PS-PM, because of the larger side-chain spacing.

⟨Figures 3 and 4⟩

Since A_2 of BS-PM in cyclohexane vanishes at 29.0 °C, $\langle S^2 \rangle$ for BS-PM in this solvent may be described by the unperturbed wormlike chain model. The unperturbed mean-square radius of gyration $\langle S^2 \rangle_0$ of the wormlike chain is expressed as,[20]

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

The contour length L of the polymacromonomer molecule may be related to M_w by,[21]

$$L = M_w / M_L + \delta \tag{2}$$

Here, δ denotes the additional contour length of the polymacromonomer molecule by the side chains near the main chain ends, which apparently increase the length of the molecule.[21] Therefore, parameters to be assigned to draw a calculated line are λ^{-1}, M_L, and δ. However, since it is impossible to determine these three parameters uniquely from the data in Figure 3, we estimated M_L as follows. From the experimental results for PS-PM, the main-chain contour length per unit macromonomer residue h was close to the value when the main chain takes the extended conformation.[9-12] Therefore, we assumed that the main chain of BS-PM takes an extended

conformation of *cis*-1,4 connection and then obtained h as 0.44 nm. Divided this h by the macromonomer molecular weight, M_L was obtained to be 5200 nm^{-1}. With this value of M_L, the data for BS-PM in cyclohexane at 29.0 °C in Figure 3 were fitted by the calculated curve by changing λ^{-1}. The lower solid line in Figure 3 shows the calculated values with $\lambda^{-1} = 8.5$ nm, where δ was ignored for the preliminary fit. It is known that the effect of δ changes $\langle S^2 \rangle$ values to some extent when the length of the main chain is relatively short.[12] However, if we use the δ values determined by the analyses of $[\eta]$ (see below), the change of calculated $\langle S^2 \rangle$ values was less than 1 % in the molecular weight range studied. Thus, we ignored δ in the analyses of the present $\langle S^2 \rangle$ data. The effect of the chain diameter is also negligibly small in this molecular weight range.

For the data of cyclohexane solutions at 34.5 °C and toluene solutions, it may be mandatory to consider the intramolecular excluded-volume effect, which is represented by the radius expansion factor α_S. This factor may be calculated by the following modified Domb-Barret equation,[22,23]

$$
\begin{aligned}
\alpha_S{}^2 &= [1 + 10\tilde{z} + (70\pi/9 + 10/3)\tilde{z}^2 + 8\pi^{3/2}\tilde{z}^3]^{2/15} \\
&\times [0.933 + 0.067 \exp(-0.85\tilde{z} - 1.39\tilde{z}^2)]
\end{aligned}
\tag{3}
$$

Here, $\tilde{z}$ is the scaled excluded-volume parameter given by,[23]

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

In the above equation, $K(\lambda L)$ is a known function[23] and z is the original excluded-volume parameter defined by[24]

$$
z = \left(\frac{3}{2\pi} \right)^{3/2} (\lambda B)(\lambda L)^{1/2}
\tag{5}
$$

For cyclohexane solutions of PS-PM, it was shown that λ^{-1} is not sensitive to temperature in the range from 32 to 45 °C.[9] It is also expected that M_L is also insensitive to temperature. Therefore, we tried to fit the $\langle S^2 \rangle$ data for cyclohexane solutions at

34.5 °C by the calculated curve to determine B, with the fixed values of $M_L = 5200$ nm^{-1} and $\lambda^{-1} = 8.5$ nm for BS-PM in cyclohexane at 29.0 °C. The upper solid line in Figure 3 shows the calculated values from eqs 1 and 3 with $B = 0.5$ nm. It is known that λ^{-1} of PS-PM in toluene is different from that for the same polymer with the same side-chain length in cyclohexane .[9-12] Therefore, the data for toluene solutions were fitted by the calculated curve to determine both λ^{-1} and B, with M_L fixed at 5200 nm^{-1}. The lower solid line shows that the calculated curve with $\lambda^{-1} = 15$ nm and $B = 2.0$ nm closely fits the data points for the toluene solutions.

The results of light scattering measurements along with $[\eta]$ are summarized in Table 1.

⟨Table 1⟩

3.3. Intrinsic Viscosity

The intrinsic viscosities $[\eta]$ for BS-PM in toluene at 15.0 °C and in cyclohexane at 34.5 °C are double-logarithmically plotted against M_w in Figure 5. According to the theory for the touched-bead model of the wormlike chain, the unperturbed intrinsic viscosity $[\eta]_0$ is expressed as a function of λL and λd_b as,[23,25]

$$[\eta]_0 = f(\lambda L, \lambda d_b)/(\lambda^3 M) \tag{6}$$

Here, d_b is the diameter of the bead and $f(\lambda L, \lambda d_b)$ is a known function.[23,25] From the studies on PS-PM's, it was shown that the effect of side chains near the main chain end on the contour length is remarkable to $[\eta]$ of polymacromonomers.[11,12,21] We note that, in these studies, $[\eta]_0$ for the touched-bead chain with λd_b larger than 0.2 was regarded as that for the cylindrical chain with the cross-sectional diameter d equated to d_b. The excluded-volume effects are considered by multiplying $[\eta]_0$ by the intrinsic viscosity expansion factor α_η^3, which may be calculated from the

following modified Barrett equation,[23,26]

$$\alpha_\eta^3 = (1 + 3.8\tilde{z} + 1.9\tilde{z}^2)^{0.3} \tag{7}$$

In the analyses of the $[\eta]$ data, M_{L}, λ^{-1}, and B are assumed to be the same as those determined from $\langle S^2 \rangle$. The other parameters, d and δ, were determined by the curve-fitting procedure. The lower solid line in Figure 5 shows the calculated values with $d = 4.4$ nm and $\delta = 2.2$ nm along with $M_{\mathrm{L}} = 5200$ nm^{-1}, $\lambda^{-1} = 8.5$ nm, and $B = 0.5$ nm.

⟨Figure 5⟩

For $[\eta]$ of BS-PM in toluene, d and δ were also determined by the curve-fitting procedure with the other parameters fixed at those determined from $\langle S^2 \rangle$. The upper solid line for BS-PM in toluene at 15.0 °C was calculated with $d = 4.8$ nm, and $\delta = 2.2$ nm along with $M_{\mathrm{L}} = 5200$ nm, $\lambda^{-1} = 8.5$ nm, and $B = 2.0$ nm. The agreement between the theoretical and experimental values is satisfactory.

The d values for PS-PM with $n = 20$ in cyclohexane at 34.5 °C and in toluene at 15.0 °C are estimated from the previous results (see Figure 7 of Ref. 11) as 5.5 nm and 6.1 nm, respectively. These values are appreciably larger than those for BS-PM. This suggests that the side chain of BS-PM takes less extended conformation than PS-PM reflecting the lower side-chain density.

The scattering profiles (not shown here) obtained by the SAXS measurements were not well described by theoretical values for the cylindrical wormlike chain. Possibly, this may be due to the low side chain density, that makes the surface of the molecule irregular. Theoretical and computer simulation studies on the side chain conformation might be desirable to support this conclusion.

The molecular parameters thus obtained are summarized in Table 2.

⟨Table 2⟩

3.4. Chain Stiffness

Figure 6 shows λ^{-1} for BS-PM in toluene and cyclohexane plotted against n along with the values for PS-PM in these solvents. The figure indicates that the value of λ^{-1} for BS-PM in each solvent is smaller than that for PS-PM with the same n in the same solvent.

The stiffness parameter for PS-PM may be calculated by the following equation,[16]

$$\lambda^{-1} = \lambda_{\mathrm{b}}^{-1} + \lambda_{0}^{-1} \tag{8}$$

The values of $\lambda_{\mathrm{b}}^{-1}$ for toluene solutions may be calculated by the following first-order perturbation expression,[16]

$$\lambda_{\mathrm{b}}^{-1} = \frac{1}{8\pi} \left(\frac{n}{h}\right)^2 \beta_2 \tag{9}$$

where β_2 denotes the binary-cluster integral between side-chain segments. We note that this expression is similar to the equation derived by Subbotin et al.,[15] except the difference in the prefactor. To calculate $\lambda_{\mathrm{b}}^{-1}$ for PS-PM in toluene at 15.0 °C, we used the following parameter set; $\beta_2 = 3.4 \times 10^{-2}$ nm^3 known for polystyrene in toluene,[28] $h = 0.27$ nm for PS-PM.[9-12] The upper solid line in Figure 6 shows λ^{-1} for PS-PM in toluene calculated by eq 8 with $\lambda_0^{-1} = 12$ nm.[16]

For cyclohexane solutions, $\lambda_{\mathrm{b}}^{-1}$ may be calculated from the following equation,[16]

$$\lambda_{\mathrm{b}}^{-1} = 0.02334 \left(\frac{n}{b}\right)^2 \frac{\beta_3}{h^3} \tag{10}$$

Here, b is the Gaussian segment length of the side chains and β_3 means the ternary-cluster integral among side-chain segments. The following parameters were used to calculate $\lambda_{\mathrm{b}}^{-1}$ for PS-PM in cyclohexane at 34.5 °C; $b = 0.74$ nm known for polystyrene,[27] $\beta_3 = 4 \times 10^{-3}$ nm^6 determined from the third virial coefficients of polystyrene in cyclohexane at 34.5 °C.[29] The lower solid line in Figure 6 represents the calculated values from eq 8 with $\lambda_0^{-1} = 8$ nm.[16]

We may calculate λ_b^{-1} for BS-PM by the same equations. Applying $h = 0.44$ nm and $n = 20$, we obtain $\lambda_b^{-1} = 2.8$ nm and 0.8 nm for BS-PM in toluene at 15.0 °C and in cyclohexane at 34.5 °C, respectively. These values are considerably smaller than the calculated values of λ_b^{-1} for PS-PM with the same n; 8.0 nm and 3.9 nm in toluene and cyclohexane, respectively. This is because eqs 9 and 10 predict λ_b^{-1} inversely proportional to h^2 and h^3, respectively.

From the values of λ_b^{-1} calculated above, we obtain 5.5 nm and 3.0 nm for the differences of λ_b^{-1} between PS-PM and BS-PM with $n = 20$ in toluene and cyclohexane, respectively. On the other hand, the differences between experimental values of λ^{-1} for BS-PM and PS-PM are 8.0 nm and 4.5 nm in toluene and cyclohexane, respectively, which are appreciably larger than the above values. Therefore, the differences in λ^{-1} between PS-PM and BS-PM do not originate only from the difference in λ_b^{-1}, *i.e.* the contributions of interactions among side chains, but also from the difference in λ_0^{-1}. The differences in λ_0^{-1} between BS-PM and PS-PM may be ascribed to the larger steric hindrance among side chains of PS-PM than that of BS-PM, because of the bulky phenyl groups and smaller side-chain spacing of PS-PM.

4. Conclusion

Here, we demonstrated that the stiffness parameters of BS-PM with $n = 20$ in toluene and cyclohexane are smaller than those for PS-PM with the same n. This qualitatively agrees with the prediction of the first-order perturbation theory, which considers two- and three-segment interactions among side-chains for good and theta solvent systems, respectively. However, the difference between experimental values of λ^{-1} for BS-PM and PS-PM in each of toluene and cyclohexane solutions is larger than that predicted by the corresponding theory. This suggests that the difference of λ^{-1} comes not only from the segmental interactions but also from the

steric hindrance among side chains.

Acknowledgment

References

(1) Wintermantel M, Schmidt M, Tsukahara Y, Kajiwara K, Kohjiya S. Macromol Rapid Commun 1994;15:279-84.

(2) Nemoto N, Nagai M, Koike A, Okada S. Macromolecules 1995;28:3854-9.

(3) Wintermantel M, Gerle M, Fischer K, Schmidt M, Wataoka I, Urakawa H, Kajiwara K, Tsukahara Y. Macromolecules 1996;29:978-83.

(4) Ito K, Kawaguchi S. Adv Polym Sci 1999;142:129-78.

(5) Rathgeber S, Pakula T, Wilk A, Matyjaszewski K, Beers KL. J Chem Phys 2005;122:124904.

(6) Zhang B, Grohn F, Pedersen JS, Fischer K, Schmidt M. Macromolecules 2006;39:8440-50.

(7) Nakamura Y, Norisuye T. Brush-Like Polymers. In: Borsali R, Pecora R editors. Soft-Matter Characterization. Berlin: Springer; 2008 [chater 5].

(8) Kikuchi M, Lien L T N, Narumi A, Jinbo Y, Izumi Y, Nagai K, Kawaguchi S. Macromolecules 2008;41:6564-72.

(9) Terao K, Takeo Y, Tazaki M, Nakamura Y, Norisuye, T. Polym J 1999;31:193-8.

(10) Terao K, Nakamura Y, Norisuye, T. Macromolecules 1999;32:711-6.

(11) Hokajo T, Nakamura Y, Norisuye T. Polym J 2001;33:481-5.

(12) Sugiyama M, Nakamura Y, Norisuye T. Polym. J. 2008;40:109-15.

(13) Frederckson GH. Macromolecules 1993;26:2825-31.

(14) Zhulina EB, Vilgis TA. Macromolecules 1995;28:1008-15.

(15) Subbotin A, Saariaho M, Ikkala O, ten Brinke G. Macromolecules 2000;33:3447-52.

(16) Nakamura Y, Norisuye T. Polym J 2001;33:874-8.

(17) Takenaka K, Hirao A, Nakahama S. Macromol Chem Phys 1995;196:1687-96.

(18) Nunomoto S, Yamashita Y. J Org Chem 1979;44:4788-91.

(19) Berry GC., J Chem Phys 1966;44,4550-64.

(20) Benoit H, Doty P. J Phys Chem 1953;57:958-63.

(21) Terao, K.; Nakamura, Y.; Norisuye, T. Macromolecules 1999;32:3690-4.

(22) Domb C, Barrett AJ. Polymer 1976;17:179-84.

(23) Yamakawa H. Helical Wormlike Chains in Polymer Solutions. Berlin: Springer; 1997.

(24) Yamakawa H. Modern Theory of Polymer Solutions. New York: Harper & Row; 1971.

(25) Yoshizaki T, Nitta I, Yamakawa H. Macromolecules 1988;21:165-71.

(26) Barrett AJ. Macromolecules 1984;17:1561-5.

(27) Miyaki Y, Einaga Y, Fujita H. Macromolecules 1978;11:1180-6.

(28) Abe F, Einaga Y, Yoshizaki T, Yamakawa H. Macromolecules 1993;26:1884-90.

(29) Nakamura Y, Norisuye T, Teramoto A. Macromolecules 1991;24:4904-8.

Table 1. Properties of PS-PM polymacromonomer samples in cyclohexane (CH) at 34.5 °C and toluene (Tol) at 15.0 °C

Solvent	Sample	$M_{\mathrm{w}}/10^5$	$\langle S^2 \rangle^{1/2}$(nm)	$10^5 A_2$(cm³ mol g⁻²)	$[\eta]$ (cm³/g)
	BS1	5.95	16.3	6.9	27.0
	BS2	5.30	15.1	6.7	24.9
Tol	BS3	3.98	12.4	7.8	20.9
	BS4	3.18	—	—	17.8
	BS5	2.65	—	—	16.0
	BS1	5.76 (5.72)[a]	12.0 (11.7)[a]	1.2 (0.0)[a]	16.2
	BS2	5.44 (5.32)[a]	11.7 (11.3)[a]	1.1 (0.0)[a]	15.6
CH	BS3	4.11 (4.03)[a]	10.2 (10.2)[a]	1.1 (0.0)[a]	13.7
	BS4	3.18[b]	—	—	12.4
	BS5	2.65[b]	7.4[c]	—	—

[a]values at 29.0°C [b]values in toluene [c]from SAXS measurements

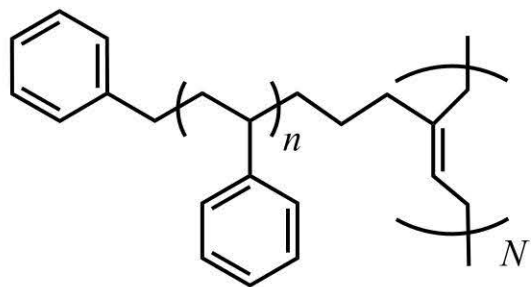Table 2. Molecular parameters for BS-PM polymacromonomers

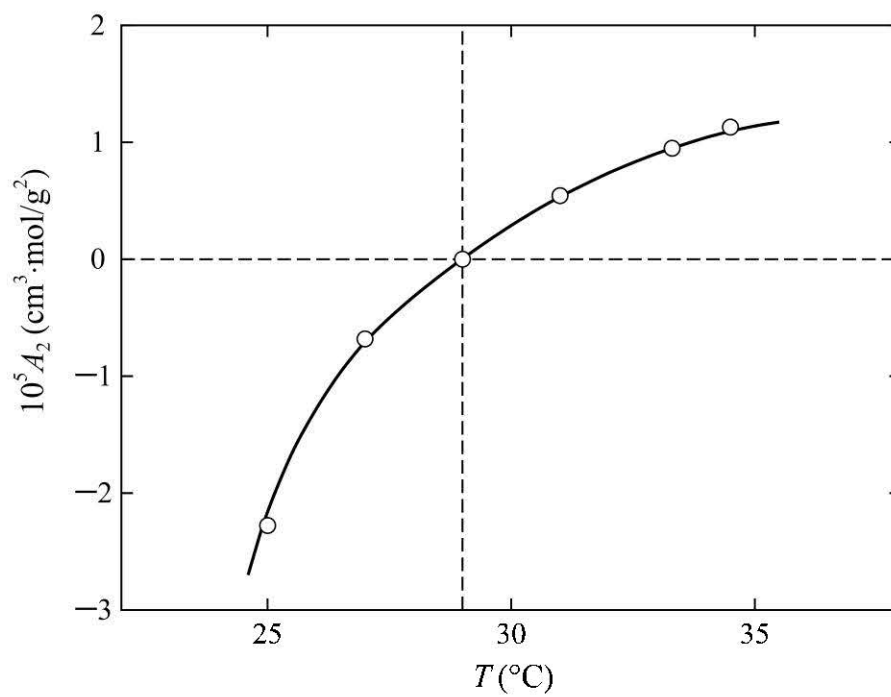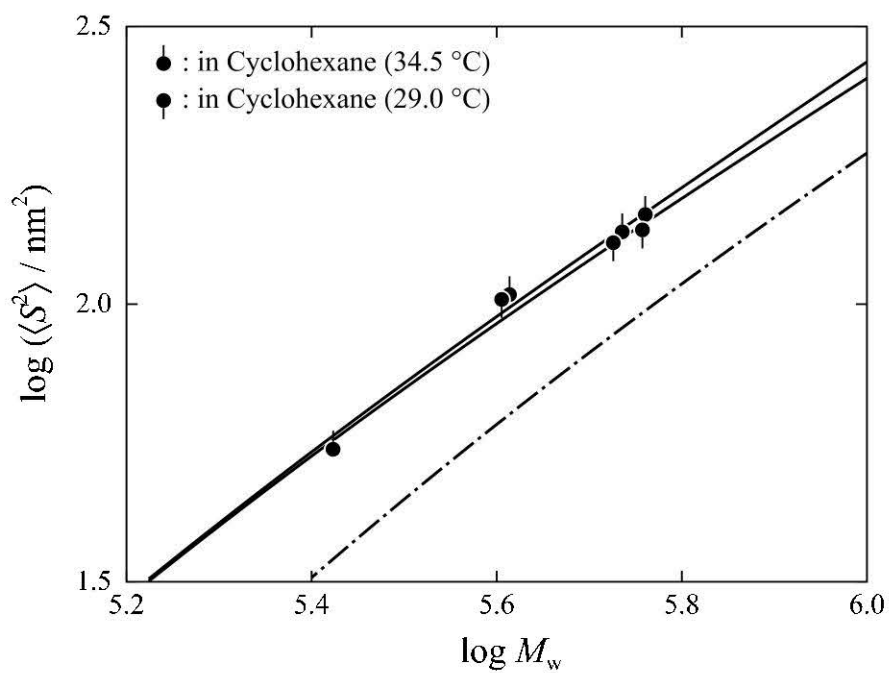| Solvent	Temp.(°C)	M_{L} (nm⁻¹)	λ^{-1}(nm)	B (nm)	d (nm)	δ (nm)
Tol	15.0	5200	16	2.0	4.8	2.2
CH	29.0	5200	8.5	0.0	—	—
	34.5	5200	8.5	0.5	4.4	2.2

(a) PS-PM
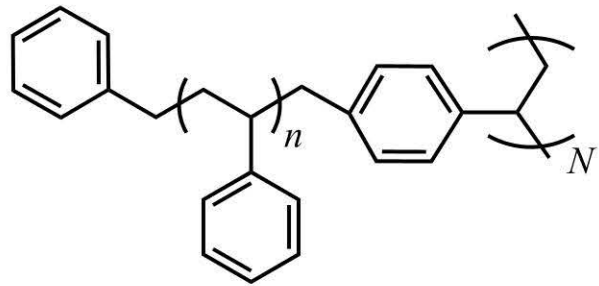
(b) BS-PM

**Figure 1.** Chemical structures of polystyrene polymacromonomer (a) and BS-polymacromonomer (b).

Figure 2. Temperature dependence of the second virial coefficient for BS2 in cyclohexane.

Figure 3. Molecular weight dependence of the mean-square radius of gyration for BS-PM in cyclohexane at 34.5 °C (pip up) and 29.0 °C (pip down). The dot-dashed line represents the values for PS-PM with $n = 20$ in the same solvent. The solid lines show the calculated values for the wormlike chain model.
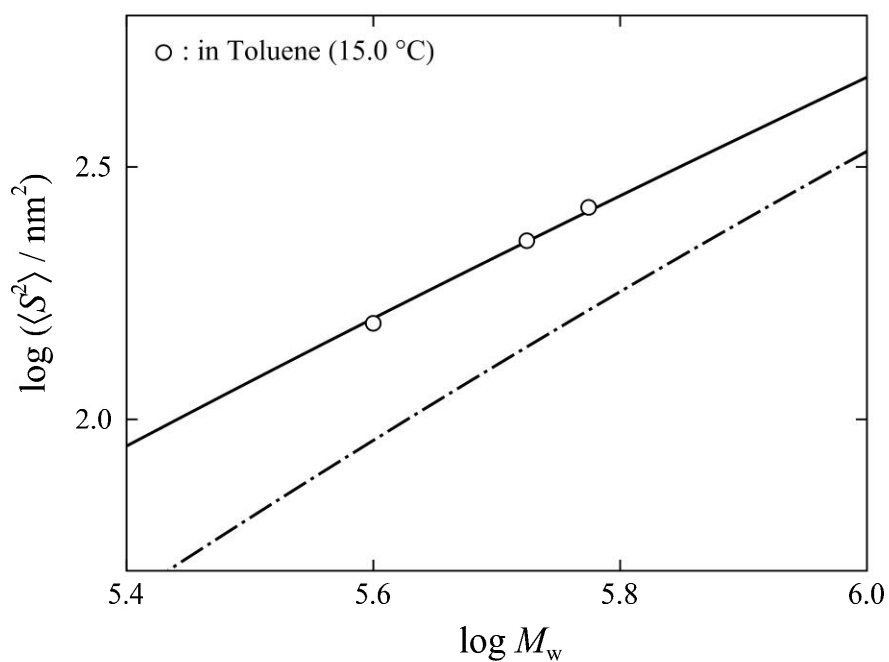
Figure 4. Molecular weight dependence of the mean-square radius of gyration for BS-PM in toluene at 15.0 °C. The dot-dashed line represents the values for PS-PM with $n = 20$ in the same solvent. The solid line shows the calculated values for the wormlike chain model.
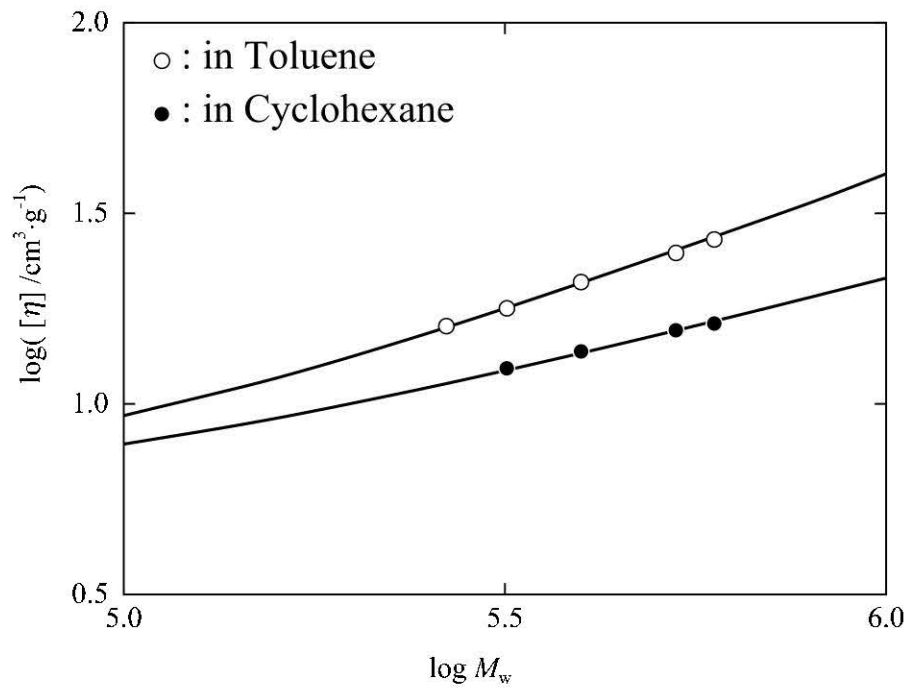
Figure 5. Molecular weight dependence of the intrinsic viscosity for BS-PM in toluene at 15.0 °C and cyclohexane at 34.5 °C. The solid lines show the calculated values for the wormlike chain model.
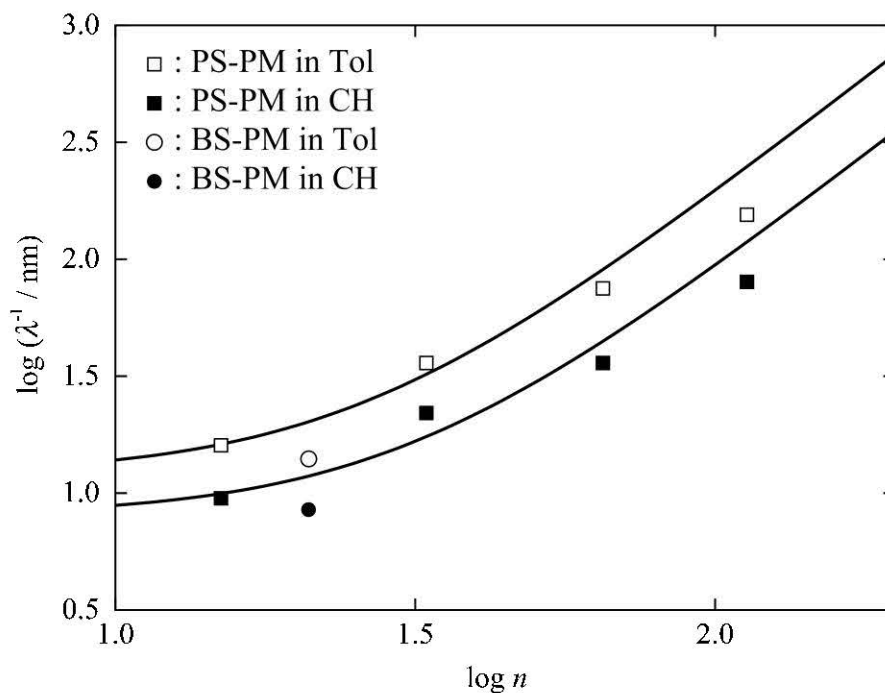
Figure 6. Comparison of the stiffness parameter of BS-PM (circles) with those for PS-PM (squares) plotted against the degree of polymerization of side chain. The unfilled and filled symbols indicate the values for toluene (at 15.0 °C) and cyclohexane (at 34.5 °C) solutions, respectively. The solid lines represent the calculated values from eq 8 for PS-PM.