ORIGINAL ARTICLE

Second and third virial coefficients of low-molecular-weight polyisoprene in 1,4-dioxane

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Light-scattering measurements were carried out on polyisoprene (PI) samples with weight-averaged molecular weights (M_w s) ranging from 1.1×10^3 to 2.7×10^4 in 1,4-dioxane at and near the theta point, 35.3 °C, which is defined as the temperature at which the second virial coefficient A_2 for sufficiently high M_w (larger than 1×10^4) vanishes. It was found that A_2 at the theta point decreases with decreasing M_w for $M_w < 1 \times 10^4$. This was explained by the effects of both the three-segment interaction and the side-chain end. The binary-cluster integral for the side-chain-end segment and the PI segment was negative, revealing the attractive interactions between them. The third virial coefficient increased with decreasing M_w . This was also attributed to the side-chain-end effect.

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INTRODUCTION

The theta point is defined as the solvent condition in which the second virial coefficient, A_2 , for a solute polymer with sufficiently high-molecular weight becomes zero. However, when the molecular weight becomes low, the A_2 values of certain polymers deviate from zero even at the theta point.^{1–5} The first report of such a behavior was given by Huber and Stockmayer¹ for polystyrene (PS) in cyclohexane (CH), whose A_2 at the theta temperature, Θ , became positive and increased with decreasing molecular weight, M . They ascribed this to the interactions among three segments. However, Yamakawa⁶ noted the importance of the chain-end effect on A_2 for low-molecular-weight polymers in theta solvents. Later, Yamakawa and Yoshizaki⁷ conducted a theoretical study for wormlike chains with the effects of both the chain-end and the three-segment interactions to explain the experimental data for several polymers in theta solvents. Mizuno *et al.*⁸ demonstrated that the A_2 of low-molecular-weight PS in CH at Θ remarkably depends on the chain-end structure; although A_2 for PS with a butyl end (butyl-PS) in CH was positive and increased with decreasing temperature, A_2 for PS with a benzyl end (benzyl-PS) became negative and decreased with decreasing temperature. With the aid of the theory of Yamakawa and Yoshizaki,⁷ they concluded that the positive A_2 for the former PS was mostly from the chain-end effect and that the negative A_2 for the latter system was due to the three-segment interactions.

The behavior of A_2 for linear polymers is reflected in the A_2 of branched polymers, including star^{9–11} and brush-like polymers such as polymacromonomers (PMs). The theta temperature of PS polymacromonomer (PS PM) with a benzyl group at each end (benzyl-PS PM) in CH agrees with that of linear PS.^{12–15} However,

the A_2 of PS PM with a butyl group at each side-chain end (butyl-PS PM) in CH is almost independent of temperature and is positive even at temperatures more than 20 °C lower than the theta temperature of linear PS.^{16,17} This has been ascribed to the repulsive interaction between the PS segment and the side-chain-end segment, which is the reflection of the positive A_2 for butyl-PS in this solvent at Θ . A PM having a polyisoprene (PI) backbone and PS side chains with a benzyl end (PI-PS PM) showed similar behavior; the A_2 in CH was positive at Θ for linear PS but became zero approximately 15 °C lower than Θ .¹⁸ While the positive A_2 of butyl-PS PM at Θ was attributed to the interaction between the chain-end segment and the PS segment, that of PI-PS PM was considered to be due to the interaction between the main-chain (PI) segment and the PS segment.

Recently, we studied a PM having a PS main-chain and PI side chains with a butyl end (PI PM).¹⁹ The A_2 of this polymer in 1,4-dioxane was positive at Θ for linear PI, decreased with decreasing temperature, and vanished at a temperature approximately 4 °C lower than Θ for linear PI. This may be attributed to the effect of the interaction between the PI segment and the side-chain-end segment or that between the PI segment and the main-chain (PS) segment. To determine which interaction is dominant for PI PM in 1,4-dioxane, it is important to study the A_2 of linear PI in this solvent.

The third virial coefficients, A_3 , for linear flexible polymers in theta solvents are known to be positive.^{20–25} This is considered to be from the effect of the three-segment interaction.^{26–28} Nakamura *et al.*²⁰ showed that the A_3 of linear PS in CH at Θ is almost independent of M for $M > 2 \times 10^4$. This behavior of A_3 is consistent with the prediction of the zeroth-order perturbation theory,^{26–28} which enables us to estimate the value of the ternary-cluster integral

among polymer segments. Yamakawa *et al.*²² studied A_3 for low-molecular-weight butyl-PS and poly(methyl methacrylate) in theta solvents and found that A_3 increases with decreasing M . They ascribed this to the chain-end effect. Mizuno *et al.*⁸ studied the A_3 of low-molecular-weight benzyl-PS in CH at Θ and demonstrated that it is larger than that for butyl-PS in the same solvent.

Although A_3 data for polymers synthesized from vinyl monomers have been well studied, there are few data for the A_3 values of other type of polymers. Here, we performed a light-scattering study of the A_2 and A_3 of linear PI in 1,4-dioxane to clarify the segmental interactions among PI and the chain-end segments.

EXPERIMENTAL PROCEDURE

Polymer samples

Three PI samples, P5896-IP, P7621-IP and P4964-IP, were purchased from Polymer Source (Montreal, QC, Canada) and are designated here as I1, I3 and I10, respectively. By $^1\text{H-NMR}$ measurements of I1, a secondary butyl group at one of the chain ends was detected. The measurement also showed that the contents of *cis*-1,4 and *trans*-1,4 and 3,4 microstructures were 66, 27 and 7%, respectively. In addition to these samples, two PI samples, I7 and I27, were synthesized by the anionic polymerization of isoprene in hexane with *sec*-butyllithium as the initiator. The contents of the microstructures of these samples agreed within the experimental error with those for the purchased samples. Gel-permeation chromatography was performed on these samples to estimate the weight-to-number average molecular weight ratios, M_w/M_n .

Preparation of solutions

The polymer samples were preserved as frozen benzene solutions with approximately 0.1% dibutylhydroxytoluene. These samples were re-precipitated into methanol and dried under vacuum for more than a week. The solvent, 1,4-dioxane, was distilled after refluxing over sodium metal for ~ 4 h. The solutions for the light-scattering measurements were prepared by mixing the PI sample and a solvent containing 0.05 % (w/w) dibutylhydroxytoluene and stirred for a week under room temperature. These solutions were optically clarified by passing through a polytetrafluoroethylene filter with 0.1 μm pores. The polymer mass concentration, c , was calculated by multiplying the weight fraction w of the polymer by the solution density ρ , which was calculated by

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

Here, ρ_0 is the density of the solvent and $\bar{v}$ is the specific volume of the solute. The latter quantity for I27 was determined from the ρ measured by a densitometer DMA5000 (Anton Paar, Graz, Austria) at 32, 35 and 38 °C and was found to be expressed by the following equation:

$$\bar{v} = 1.47 \times 10^{-3} T(^{\circ}\text{C}) + 1.080 \quad (\text{cm}^3 \text{g}^{-1})$$

Light-scattering measurement

Light-scattering measurements were made by a Fica 50 light-scattering photometer (Fica, Saint Denis, France) with a 435.8 nm wavelength at scattering angles θ ranging from 30 to 142.5° at 35.3 °C for I1, I3, I7 and I10, and at 31, 33, 34.5, 36 and 38 °C for I27. From six to eight solutions with different concentrations were prepared and measured to obtain the reduced scattering intensity R_θ at θ . Berry's square-root plots²⁹ were employed to obtain Kc/R_θ extrapolated to $\theta \rightarrow 0$. The refractive index increment $\partial n/\partial c$ included in the scattering constant K at 435.8 nm for I27 was measured by a Shultz-Cantow type differential refractometer, DR-1 (Shimadzu, Kyoto, Japan), at 32, 35 and 38 °C. In this temperature range, $\partial n/\partial c$ was expressed by the following equation:

$$\partial n/\partial c = 1.15 \times 10^{-4} T(^{\circ}\text{C}) + 0.1120 \quad (\text{cm}^3 \text{g}^{-1})$$

For the scattering data for I1, I3, I7 and I27, the Bawn plot,³⁰ $S(c_i, c_j)$ vs $c_i + c_j$, was employed, where c_i and c_j are different concentrations and $S(c_i, c_j)$ is defined by³¹

$$S(c_i, c_j) = \frac{(Kc/R_\theta)_{c=c_j} - (Kc/R_\theta)_{c=c_i}}{c_j - c_i} = A_2 + A_3(c_i + c_j) + \dots \quad (1)$$

Figure 1 Bawn plots for polyisoprene in 1,4-dioxane at 35.3 °C for I1, I3 and I7 and at 36.0 °C for I27.

Table 1 Properties of polyisoprene samples in 1,4-dioxane at 35.3 °C

Sample	$10^{-3}M_w$	M_w/M_n^a	$10^4 A_2$ ($\text{cm}^3 \text{mol g}^{-2}$)	$10^3 A_3$ ($\text{cm}^6 \text{mol g}^{-3}$)
I1	1.06	1.1 ₀	−8.6	4.4
I3	3.07	1.0 ₇	−2.5	1.9
I7	7.13	1.0 ₅	−0.4	1.1
I10	10.5	1.0 ₂	0.0	—
I27	27.1	1.0 ₁	0.0 ^b	0.8 ^b

^aFrom gel-permeation chromatography.

^bInterpolated values.

Here, $(Kc/R_\theta)_{c=c_i}$ indicates (Kc/R_θ) at $c = c_i$. The Bawn plots for I1, I3 and I7 at 35.3 °C and for I27 at 36.0 °C in 1,4-dioxane are shown in Figure 1. Each plot can be represented by a straight line, whose intercept at $c_i + c_j = 0$ and slope give A_2 and A_3 , respectively. The weight-averaged molecular weight M_w for each of these samples was determined by averaging the apparent weight-averaged molecular weight defined by $(Kc/R_\theta - 2A_2c - 3A_3c^2)^{-1}$ at different concentrations. The conventional square-root plot was used to determine the A_2 for the solution of I10.

The results of the light-scattering measurements are summarized in Table 1.

RESULTS AND DISCUSSION

Second virial coefficient

The temperature dependence of A_2 for I27 is shown in Figure 2. The figure indicates that A_2 vanishes at 35.3 °C. This temperature is close to the theta temperature of 34.7 °C reported by Tsunashima *et al.*³² for

linear PI in 1,4-dioxane but rather higher than that of 34.1 °C reported by Hadjichristidis and Roovers.³³ The contents of the *cis*-1,4 structure in the samples used by Hadjichristidis and Roovers and by Tsunashima *et al.* were equal (70%). Therefore, the difference in the theta temperatures is likely not due to differences in the contents of the microstructures. Rather, it might be due to the different contents of dibutylhydroxytoluene in the solvent; 0.02% for Hadjichristidis and Roovers and 0.05% for Tsunashima *et al.* In the following, we use 35.3 °C as the theta temperature for PI in 1,4-dioxane.

Figure 3 shows the plots of A_2 at 35.3 °C against $\log M_w$. The unfilled circles show that A_2 for PI in 1,4-dioxane becomes negative and decreases with decreasing M_w . The filled and unfilled squares show the values for butyl-PS³ and benzyl-PS,⁸ respectively, in CH at 34.5 °C (theta temperature). The figure shows that the A_2 values for the former PS become positive and increase with decreasing M_w , while those for the latter PS become negative and decrease with

decreasing M_w . It was shown that the chain-end effect is dominant on A_2 for the former PS and that the three-segment interaction is essential to A_2 for the latter PS. The behavior of A_2 for PI in 1,4-dioxane is close to that for the latter PS, suggesting that the three-segment interaction has an important effect on A_2 for PI.

Yamakawa and Yoshizaki⁷ considered the contribution of the three-segment interaction to A_2 for wormlike chains. According to their theory, this contribution can be expressed as:

$$A_2^{(0)} = -\frac{N_A \lambda^2 L^2}{M^2} \left(\frac{3}{2\pi a^2} \right)^{3/2} \beta_3 [I(\infty) - I(\lambda L)] \quad (2)$$

Here, N_A , L , a and β_3 are the Avogadro constant, the contour length of the chain, the segment length and the ternary-cluster integral, respectively, and $I(\lambda L)$ is a known function of λL (Equation 36 of ref. 7). The stiffness parameter, λ^{-1} , of PI was estimated as 1.0 nm from the known equation for $\langle S^2 \rangle$ in 1,4-dioxane at 34.5 °C:³²

$$\langle S^2 \rangle^{1/2} = 3.35 \times 10^{-2} M_w^{1/2} \quad (\text{nm})$$

with the relation $\langle S^2 \rangle = L/(6\lambda)$ for infinitely long wormlike chains. Here, L was calculated from $L = M_w/M_L$ using the molecular weight for the unit contour length, M_L , which was estimated to be 150 nm⁻¹ from M_0/a with the molecular weight of the isoprene monomer, M_0 . Taking a monomer as a segment, a was estimated to be 0.46 nm from the contents of the microstructures and the molecular model for the PI chain.

With $\beta_3 = 1.6 \times 10^{-3} \text{ nm}^6$ estimated from the A_3 values (see the next section), we obtained the dashed line in Figure 3. However, the line deviates from the data points, especially at low M_w . This deviation implies the necessity of considering the chain-end effect. The contribution of this effect can be expressed by the following equation,⁶

$$A_2^{(E)} = a_1/M \quad (3)$$

if the term of the order of M^{-2} is ignored. Here, a_1 is a constant, which is represented by⁶

$$a_1 = 2N_A \beta_{01}/M_0 \quad (4)$$

where β_{01} denotes the average of the two excess binary integrals; one is for the segment in the middle of the PI chain (PI segment) and the segment at one of the chain ends, and the other is for the PI segment and the segment at the other chain end. The solid line in Figure 3 shows the calculated value of $A_2^{(0)} + A_2^{(E)}$ with $a_1 = -0.5 \text{ cm}^3 \text{ mol}^{-1}$. This line comes close to the experimental values, indicating that the interaction between the chain-end segment and the PI segment is essential. From the above a_1 , we obtained $-2.8 \times 10^{-2} \text{ nm}^3$ for β_{01} .

Because the negative β_{01} shows that an attractive interaction occurs between the chain ends and the PI unit, it can be concluded that an attractive interaction also occurs between the PI segment and the side-chain-end segment of PI PM. However, if we consider only this interaction, the A_2 of PI PM in 1,4-dioxane would become negative at 35.3 °C, contrary to the experimental observation. Therefore, the positive A_2 of PI PM in this solvent indicates the presence of repulsive interactions between the PS main chain and the middle of the PI side chain.

The PI chain consists of three different microstructures, *cis*-1,4 and *trans*-1,4 and 3,4 additions. Therefore, the cluster integrals obtained can be regarded as averaged values over the different segments with these microstructures. For PI samples with different contents of the microstructures, the cluster integrals must be different.

Figure 2 Temperature dependence of the second virial coefficient of the polyisoprene sample I27 in 1,4-dioxane.

Figure 3 Molecular weight dependence of the second virial coefficient of linear polyisoprene in 1,4-dioxane at 35.3 °C (circles). The filled and unfilled squares represent the data for butyl-polystyrene (PS) and benzyl-PS, respectively, in cyclohexane at 34.5 °C. The dashed line represents the values calculated by equation 2, and the thick solid line represents the values calculated by equations 2 and 3.

Figure 4 Temperature dependence of the third virial coefficient of the polyisoprene sample I27 in 1,4-dioxane. The solid line is a guide to the eye.

Third virial coefficient

The temperature dependence of A_3 for I27 is shown in Figure 4. The A_3 values are almost independent of temperature, T , being similar to other polymers with low-molecular weights in theta solvents.^{8,20,21,34,35}

The molecular weight dependence of A_3 at 35.3 °C is illustrated in Figure 5. It shows that A_3 sharply increases with decreasing M_w . This behavior of the A_3 value is similar to that of the values for butyl-PS²² and benzyl-PS⁸ in CH at 34.5 °C (filled and unfilled squares, respectively), for which the chain-end effect is known to be essential.

By the binary-cluster approximation, the A_3 at the theta point vanishes along with A_2 . However, if the effect from the three-segment interaction is not negligible, it has a finite value. The contribution of this effect to A_3 may be represented by the following zeroth-order approximation:^{26,27}

$$A_3^{(0)} = \frac{N_A^2 n^3}{3M^3} \beta_3 \quad (5)$$

Here, n denotes the number of segments in a chain. Because n is proportional to M , $A_3^{(0)}$ does not depend on M .

If the chain-end effect as well as the effect of the three-segment interaction are not negligible, A_3 may be expressed as the sum of $A_3^{(0)}$ and the following term:²²

$$A_3^{(E)} = \frac{2N_A^2}{n} \left(\frac{n}{M}\right)^3 \beta_{001} \quad (6)$$

where β_{001} denotes the averaged excess ternary-cluster integral concerning the interaction among a segment of one of the chain ends and two middle PI segments. The above equation shows that the absolute value of $A_3^{(E)}$ increases with decreasing M by M^{-1} . The solid line in Figure 5 shows the calculated values from equations 5 and 6 using $\beta_{001} = 2.3 \times 10^{-2}$ and $\beta_3 = 1.6 \times 10^{-3} \text{ nm}^6$. It closely fits the data points, showing that the effects of both the three-segment interaction and of the chain end are essential to explain the A_3 of the low-molecular-weight PI. The above value of β_{001} is between the values of butyl-end ($1.2 \times 10^{-2} \text{ nm}^6$)³ and benzyl-end ($3.7 \times 10^{-2} \text{ nm}^6$)⁸ PS.

The present data show that β_{001} is positive when β_{01} is negative. This result may be understood from the analogy of the second and

Figure 5 Molecular weight dependence of the third virial coefficient of linear polyisoprene in 1,4-dioxane at 35.3 °C. The symbols are the same as those in Figure 3. The solid line represents the calculated values from equations 5 and 6.

third virial coefficients (B_2 and B_3 , respectively) for rigid sphere molecules with the Lennard–Jones (LJ) potential,³⁶ for which B_3 is positive when B_2 is negative below the Boyle point.

CONCLUSIONS

The present study showed that the A_2 of PI in 1,4-dioxane at the theta point becomes negative and decreases with decreasing molecular weight. This was attributed to the three-segment interaction and the attractive interactions between PI segment and chain-end segment with negative β_{01} . From this result, we concluded that the positive A_2 of PI PM in 1,4-dioxane at 35.3 °C is due to the repulsion between the PS main-chain segment and the PI segment in the middle of the side chain. The present data also showed that the chain-end effect is essential to the A_3 of PI in 1,4-dioxane. The obtained β_{001} for PI was positive. This was explained by the analogy of rigid sphere molecules with the LJ potential, for which B_3 is positive when B_2 is negative below the Boyle point.

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