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Reversed Micelle of Polybutadiene Living Anions in Cyclohexane

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ABSTRACT: Reversed micelles formed by living polybutadiene anions (LPB) with different molecular weights in cyclohexane were investigated by static and dynamic light scattering. The most plausible aggregation number was 4, and the lower limit of the association constant was estimated from the light-scattering results. Apparent hydrodynamic radii and second virial coefficients of the reversed micelles of the three LPB were favorably compared with those expected for four-arm star polydutadiene in cyclohexane. The lower limit of the true propagation reaction rate constant for free LPB was also determined from literature reaction rate and association constant estimated.

1. Introduction

Amphiphilic (ionic−nonionic) diblock copolymers are known to form spherical micelles with a core comprising insoluble chains and ionic coronal chains in dilute aqueous solutions, and their micellar structures (the aggregation number, micellar and core sizes, critical micelle concentration, and so on) have been most extensively investigated so far.[1−5] Those copolymers form also reversed micelles in organic solvents, and their structural studies have been made by several research groups,[6−9] although the investigation is less extensive than normal micelles formed in aqueous medium.

Polymer living anions consisting of a nonpolar main chain and a polar active end can be regarded as a *limiting case* of amphiphilic block copolymers. They form reversed micelles during the living anionic polymerization carried out in nonpolar solvents. Micellization plays an important role in polymerization reaction kinetics because only dissociated free living anions are believed to be active species for the propagation reaction (in particular for high-molecular-weight chains). Thus the precise aggregation number m, association constant K_m, and structure of the reversed micelle formed by polymer living anions are prerequisite to the precise control of the anionic polymerization.

The aggregation of polymer living anions in nonpolar solvents has been studied for a long time.[10−20] However, precise determinations of m and K_m have not been performed yet. The difficulty arises from the following reasons: (1) Because the extrapolation to the infinite dilution may change the degree of aggregation, m and K_m must be determined at finite concentrations (or as functions of the concentration). Thus we have to analyze micellar solution properties at finite concentrations by taking into account intermicellar interactions (e.g., the nonideality in thermodynamic properties), which affect appreciably the solution properties even in a considerably dilute region for good solvent systems. (2) Because polymer living anions are very sensitive to atmospheric moisture, available experimental methods for estimating m and K_m are limited. The methods utilized so far were mostly light scattering or small-angle neutron scattering, where test solutions were in sealed cells.

Recently, we[21] have investigated the reversed micelle of a living polybutadiene (LPB) anion sample in cyclohexane by static and dynamic light scattering and concluded that the main species of LPB anions in cyclohexane is a tetramer. The present study extended the previous work by using two more LPB samples with different molecular weights. Light-scattering data obtained in the present and previous studies were analyzed in terms of micellization theory, which takes into account effects of intermicellar interactions to determine K_m and micellar shape as well as the propagation reaction rate constant for free LPB anions.

Fetters et al.[22−24] studied the aggregation of living polymer anions in nonpolar solvents by small-angle neutron scattering and dynamic light scattering. They found a tiny amount of huge aggregates of living polymer anions with hundred nanometer sizes in the solutions, and this was confirmed in our previous study. Because the huge aggregates disappeared after living polymers were quenched, the formation of the huge aggregates should be related to the polar living end of the chain, but little about the formation mechanism of such large aggregates has been known yet. In the present study, we focused on the major component of the reversed micelle with a much smaller size.

2. Experimental

2.1. Preparation of Test Solutions. Two living polybutadiene (LPB) samples (LPB-35k and LPB-82k) and the corresponding quenched ones (QPB) (QPB-35k and QPB-82k) were used in this study. Their synthesis procedure was the same as that employed in our previous study.[21] After the propagation reaction had completed and the solvent was changed from benzene to cyclohexane, fractions of each LPB solution were split into light-scattering glass cells connected to the vacuum reaction flask through a fine glass filter. Given amounts of cyclohexane were distilled into respective cells to prepare LPB solutions of different concentrations. Then the cells were sealed off from the vacuum flask and subjected to light-scattering measurements. A part of LPB solutions were quenched with degassed methanol, and the QPB samples obtained were recovered by precipitation using a large excess of methanol and then dried in vacuum to use for sedimentation equilibrium measurements.

2.2. Light-Scattering Measurements on LPB. Simultaneous measurements of static and dynamic light scattering were made on cyclohexane solutions of LPB-35k and LPB-82k at 25 °C in the same procedure as in the previous work.[21] Relaxation spectra $A(\tau)$

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Table 1. Molecular Characteristics of Quenched Polybutadiene (QPB) Samples

sample	$M_w/10^4$	A_2[a]	M_z/M_w	M_w/M_n[b]
QPB-82k	8.19	1.09	1.05	1.03
QPB-35k	3.52	1.35	1.03	1.03
QPB-10k	0.96[c]	1.60[c]		1.03

[a] In units of 10^{-3} cm^{3}mol g^{-2}. [b] Ratio of the weight- to the number-average molecular weights determined by size-exclusion chromatography. [c] Determined by light scattering.

of the intensity autocorrelation function, obtained by dynamic light scattering, were bimodal for both LPB samples, similar to that for the sample LPB-10k previously studied. This indicates the existence of large aggregates in the LPB solutions other than that of the main micellar component of smaller size.

Scattered intensities from the main micellar component of LPB were extracted from total intensities obtained by static light scattering using $A(\tau)$ obtained by the dynamic one.[21,25] In what follows, the mass concentration and the excess Rayleigh ratio of the main micellar component of LPB are written by c and R_θ (θ: the scattering angle), respectively. In all LPB solutions examined, the fraction of the large aggregate was verified to be negligibly small (cf. Supporting Information) so that c was approximated by the total polymer concentration. The previous result of the specific refractive index increment (0.108 g/cm^3) was used to calculate the optical constant K.

The first cumulant Γ of the main micellar component in each solution was also estimated from the fast-relaxation component in $A(\tau)$.[21,25] The apparent hydrodynamic radius $R_{H,app}$ was calculated using the equation[26]

$$\Gamma = \frac{k_BT(1-\bar{v}c)}{6\pi\eta_0}\frac{Kc}{R_0}\frac{M_w}{R_{H,app}}k^2 + O(k^4) \qquad (1)$$

where k_BT is the Boltzmann constant multiplied by the absolute temperature, $\bar{v}$ is the partial specific volume of the polymer, and η_0 is the solvent viscosity coefficient (= 0.893 mPa s).

2.3. Characterization of QPB. Sedimentation equilibrium measurements were made for dilute cyclohexane solutions of two QPB samples (QPB-35k and QPB-82k) at 25 °C using a Beckman–Coulter Optima XL-I ultracentrifuge. Aluminum 12 mm double-sector cells were used, and the height of the solution column was adjusted to ca.1.5 mm. Rotor speeds were chosen to be 21 000 rpm for sample QPB-35k and 16 000 rpm for sample QPB-82k. Detailed analysis of sedimentation equilibrium is shown in ref 27 and references therein.

Densitometry was made on cyclohexane solutions of QPB-35k using an oscillation U-tube densitometer (Anton-Paar, DMA5000), and $\bar{v}$, necessary for data analyses of sedimentation equilibrium (and also Γ in eq 1) was estimated to be 1.118 cm^3 g^{-1}. The specific refractive index increment $\partial n/\partial c$ at the wavelength 675 nm was estimated to be 0.103 cm^3 g^{-1} by extrapolation with the Couchy dispersion formula.

The weight-average and z-average molecular weights, M_w and M_z, as well as the second virial coefficient, A_2, obtained by sedimentation equilibrium for the two QPB samples, are listed in Table 1. Both samples of QPB as well as of LPB were named from the M_w values. Ratios of M_z to M_w for both QPB samples are close to unity, as expected for polybutadiene samples synthesized by living anionic polymerization. The results of A_2 are consistent with literature data[28,29] of polybutadiene in cyclohexane. In what follows, we denote M_w of the QPB samples as M_1 to distinguish from the molar mass of LPB samples in the micellar solution.

3. Results and Discussion

3.1. Light-Scattering Results of LPB. Figure 1 plots Kc/R_θ against k^2 for the major component of sample LPB-82k in cyclohexane. Although the data points are more or less scattered, no essential k^2 dependence of Kc/R_θ is observed for every c. From lines indicated, we have extrapolated Kc/R_θ to $\theta = 0$. The extrapolated values Kc/R_0, multiplied by the weight-average molecular weight M_1 of the corresponding QPB sample, are plotted against cM_1 in Figure 2. Previous results[21] of KcM_1/R_0 for sample LPB-10k are also shown in Figure 2. For all three LPB samples, data points obey slightly concave curves, and the intercepts of the curves seem to be less than unity, indicating that LPB forms aggregates in cyclohexane.

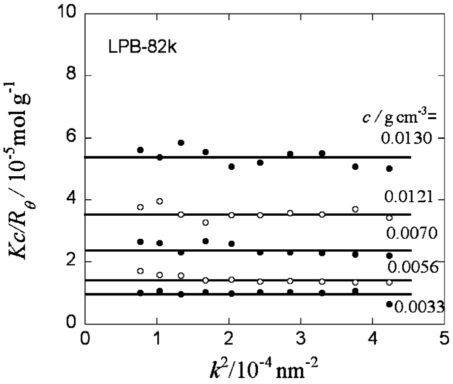

Figure 1. Angular dependencies of Kc/R_θ for sample LPB-82k in cyclohexane at 25 °C.

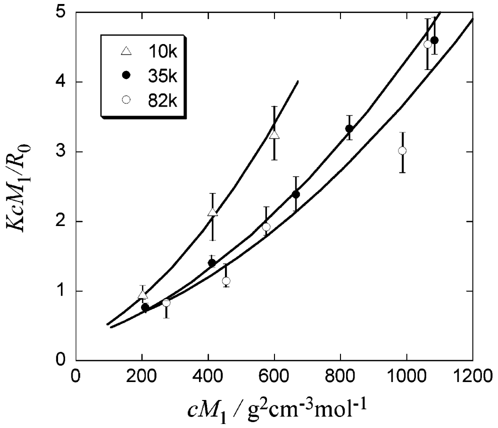

Figure 2. Plots of KcM_1/R_0 vs cM_1 for three LPB samples in cyclohexane.

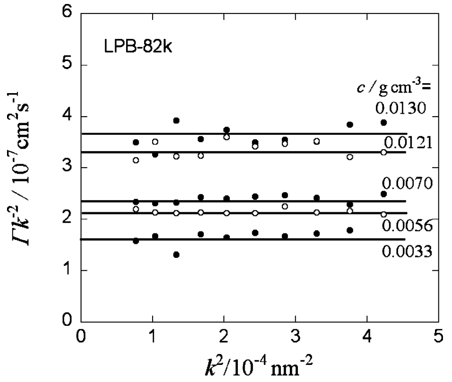

Figure 3. First cumulant Γ divided by k^2 for sample LPB-82k in cyclohexane.

Figure 3 illustrates the first cumulant Γ divided by k^2 for the main micellar component in solutions of sample LPB-82k. The data points of Γ/k^2 for every solution almost obey a horizontal line, and from this and Kc/R_0 determined in Figure 1, we have estimated $R_{H,app}/M_w$ using eq 1. As shown in Figure 4, $R_{H,app}/M_w$ are strongly increasing functions of c for all three samples, probably due to the hydrodynamic interaction among micelles.

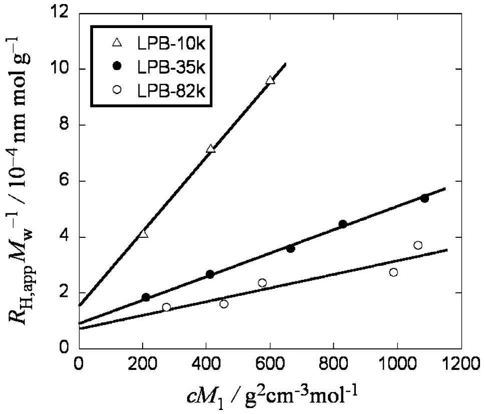

Figure 4. Plots of $R_{H,app}/M_w$ vs cM_1 for three LPB samples in cyclohexane; solid curve, theoretical values calculated by eqs 11 and 12.

3.2. Association−Dissociation Equilibrium in Micellar Solutions. In a nonpolar solvent, a great majority of the living polybutadiene anion does not exist as a free anion but forms an ion pair with the counterion (Li^+). This was demonstrated by normal concentration dependencies of Kc/R_0 shown in Figure 2. However, the Li−C bond at the LPB chain end should be polarized to give a strong dipole−dipole interaction among LPB chain ends in the nonpolar solvent (or some quantum mechanical calculation[30] even suggesting a multivalent C-metal bridge between allyl alkali metals). These strong interchain interactions make LPB chain ends associate each other to form a unicore reversed polymer micelle.

Let us consider a dilute solution containing free chains and reversed micelles with different aggregation numbers and refer to the component of the aggregation number m as m-mer, including unimer with $m = 1$. When the solution is in an association−dissociation equilibrium, we define the (apparent) association constant by

$$K_m \equiv C_m/C_1^{\,m} \tag{2}$$

where C_m and C_1 are the molar concentrations of m-mer and unimer, respectively, in the solution. This constant K_m is determined by the equilibrium condition $\mu_m = m\mu_1$, where μ_m and μ_1 are the chemical potentials of m-mer and unimer, respectively.

The chemical potential μ_m can be written within the third virial approximation as[31]

$$\frac{\mu_m}{RT} = \frac{\mu_m^\circ}{RT} + \ln\left(\frac{c_m}{M_m}\right) + 2M_m\sum_{k\geq 1} A_{mk}c_k + \frac{3}{2}M_m\sum_{k,l\geq 1} A_{mkl}c_kc_l \tag{3}$$

where μ_m°, c_m, and M_m are the internal free energy (or the standard chemical potential), the mass concentration, and molar mass of the m-mer, respectively, A_{mk} and A_{mkl} are the second and third virial coefficients among the components indicated by the subscripts, respectively, and k_BT is the Boltzmann constant multiplied by the absolute temperature. The summation on the right-hand side is taken over all polymer components existing in the solution. By inserting this equation into the above equilibrium condition, we have the following relation

$$K_m = 10^3\left\{\exp\left[-\epsilon_m - 3\ln 10 + M_1(A_{11} - A_{mm})c + \frac{1}{2}M_1(A_{111} - A_{mmm})c^2\right]\right\}^m \tag{4}$$

where

$$\epsilon_m \equiv \frac{(\mu_m^\circ/m) - \mu_1^\circ}{RT} \tag{5}$$

and c is the total polymer mass concentration. Deriving eq 4, we have replaced A_{mk} and A_{mkl} among different components by the arithmetic averages of the homogeneous components. While K_m was assumed to be constant in the previous work,[21] eq 4 indicates that K_m is not a constant but depends on c due to nonideality of the solution.

In eq 4, ϵ_m is the key parameter determining the micellar size distribution. For spherical micelles, ϵ_m may be expressed in the form $\epsilon_m m = -\delta m + \sigma m^2 + 4\pi R_c^2\gamma$.[32−34] Here, δ is the free energy gain when a solvophobic group enters in the micelle core from the solvent, σ is the free energy due to interaction between two solvophilic chains in the micelle, and the third term is the interfacial free energy of the micelle core (R_c: the radius of the micellar core; γ: the interfacial tension). This expression of ϵ_m is rewritten as

$$\epsilon_m = \sigma m_0\left(\frac{m}{m_0} + \frac{m_0}{m} - 2\right) + \epsilon_0 \qquad (m \geq 2) \tag{6}$$

where m_0 is the aggregation number that minimizes ϵ_m, and ϵ_0 is the minimum value of ϵ_m at $m = m_0$. From the definition (cf. eq 5), $\epsilon_1 = 0$, and then $K_1 = 1$.

The weight fraction w_m of m-mer in the total polymer is calculated by

$$w_m = mK_m w_1^{\,m} C_0^{\,m-1} \tag{7}$$

where C_0 is the molar concentration of the total polymer chains in the solution ($= 1000\ c/M_1$). The weight fraction w_1 of unimer is determined from the normalization condition: $\sum_{m\geq 1} w_m = 1$.

Light-scattering theory[35] gives us the following excess Rayleigh ratio R_0 at the zero scattering angle under the third virial approximation:

$$\frac{KcM_1}{R_0} = \frac{1}{m_w} + 2A_{2,z}(M_1c) + \left[\frac{2A_{3,z} + A_{3,w}}{M_1} - m_w\left(\overline{A_2^{\,2}}_z - A_{2,z}^{\,2}\right)\right](M_1c)^2 \tag{8}$$

where m_w is the weight-average aggregation number, and $A_{2,z}$, $\overline{A_2^{\,2}}_z$, $A_{3,z}$ and $A_{3,w}$ are average second and third virial coefficients defined by

$$\begin{cases} A_{2,z} \equiv m_w^{\,-1}\sum\limits_{m\geq 1} mw_mA_{mm}, & \overline{A_2^{\,2}}_z \equiv m_w^{\,-1}\sum\limits_{m\geq 1} mw_mA_{mm}^{\,2} \\ A_{3,z} \equiv m_w^{\,-1}\sum\limits_{m\geq 1} mw_mA_{mmm}, & A_{3,w} \equiv \sum\limits_{m\geq 1} w_mA_{mmm} \end{cases} \tag{9}$$

with the second virial coefficient A_{mm} and the third virial coefficient A_{mmm} of m-mer (eq 8 was derived with the same approximation for A_{mk} and A_{mkl} as used in eq 4). Using eq 7 for w_m, we can calculate the averaged quantities as well as m_w appearing in eq 8.

3.3. Comparison between Theory and Experiment. Now we compare eq 8 with the experimental results of KcM_1/R_0 for LPB micellar solutions shown in Figure 2 to determine parameters characterizing the association−dissociation equilibrium. Equation 8 contains five unknown parameters: m_0, σ, ϵ_0,

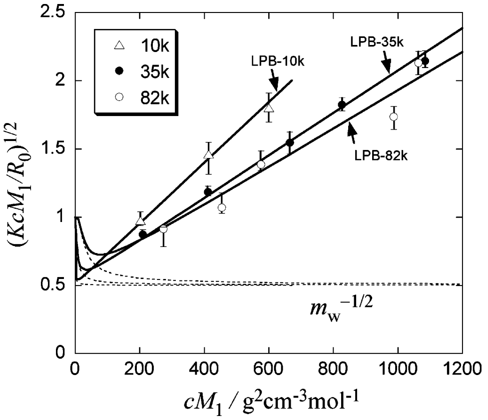

Figure 5. Comparison between theory and experiment in the plot of $(KcM_1/R_0)^{1/2}$ against cM_1; solid curves, theoretical values calculated by eq 8.

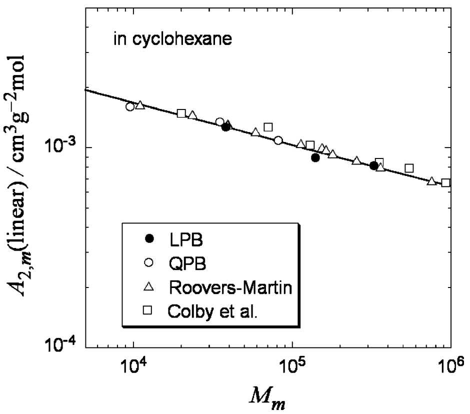

Figure 6. Second virial coefficients $A_{2,m}$(linear) used to calculate the theoretical curves in Figure 5, compared with A_2 for QPB in the same solvent condition obtained in the present study and by Roovers and Martin[28] and Colby et al.[29]

A_{mm}, and A_{mmm}. Among them, the virial coefficients for the LPB star micelle can be calculated from the corresponding coefficients $A_{2,m}$ (linear) and $A_{3,m}$ (linear) for the linear chain with the molar mass mM_1 using relations $A_{mm} = g_{A2,m}A_{2,m}$ (linear) and $A_{mmm} = g_{A3,m}A_{3,m}$(linear). From literature data,[36−38] we have the following empirical equations of the g-factors for flexible star polymers in good solvents: $g_{A2,m} = 1 - 0.04(m - 2)$ and $g_{A3,m} = 1 - 0.08(m - 2)$. Furthermore, we can write $A_{3,m}$(linear) $= \gamma A_{2,m}(\text{linear})^2 M_m$, where γ is empirically known to be 0.3 for linear flexible polymers in good solvents.[39]

It was difficult to uniquely determine the remaining parameters m_0, σ, and ϵ_0 characterizing ϵ_m in eq 6 from the results in Figure 2. Here σ was assumed to be so large that the aggregation number of the LPB star micelle is practically monodisperse ($m = m_0$). A best fit to the experimental $(KcM_1/R_0)^{1/2}$ for LPB micellar solutions was obtained when m_0 was chosen to be 4 for all three LPB samples.[40] Figure 5 demonstrates the fitting results, where $A_{2,m}$(linear) values chosen are favorably compared with literature data[28,29] for linear polybutadiene in cyclohexane in Figure 6. Although we chose ϵ_0 to be −14 in Figure 5,[41] we can obtain similar good fits for $\epsilon_0 \leq -14$ and also by using smaller σ corresponding to the case of polydisperse aggregation numbers, although not shown. In the previous study,[21] Kc/R_0 data for LPB-10k was fitted by using $K_4 = 10^{13}$ M^{-3}, which corresponds to $\epsilon_0 = -12.5$ at $c = 0.04$ g/cm^3 (the middle concentration of light-scattering measurements made for sample LPB-10k). This ϵ_0 value was too large to fit light-scattering data for LPB-82k.

The hydrodynamic radius R_H for LPB micellar solutions is given by

$$\frac{R_H}{M_w} = \left[\frac{w_1 M_1}{R_{H,1}} + \frac{w_m M_m}{g_{H,m} R_{H,m}\,(\text{linear})}\right]^{-1} \tag{10}$$

where $R_{H,1}$ and $R_{H,m}$(linear) are hydrodynamic radii of unimer and the PB linear chain with the molecular weight of m-mer, respectively, and $g_{H,m}$ is the g-factor with respect to R_H for the m-arm star polymer. For linear polybutadiene in cyclohexane (at 25 °C), literature gives us the following empirical equation: [28]

$$R_{H,m}\,(\text{linear}) = 1.5 \times 10^{-2}\, M_m^{\;0.57}\ \text{nm} \tag{11}$$

On the other hand, it is known that, for four-arm star flexible polymers in good solvents, $g_{H,4} = 0.93$.[36]

The apparent hydrodynamic radius $R_{H,app}$ is affected by the intermolecular hydrodynamic interaction. Referring to the Huggins equation for viscosities of dilute polymer solutions[42] (eq A1 in the Appendix), we may express $R_{H,app}$ in dilute polymer solutions by[26]

$$R_{H,app} = R_H(1 + k'_H c/c^*) \tag{12}$$

where k'_H and c^* are the strength of the intermolecular hydrodynamic interaction and the overlap concentration, respectively, corresponding to the Huggins constant k' and the reciprocal of the intrinsic viscosity $[\eta]$ in eq A1; R_H is calculated by eq 10. It is convenient to estimate c^* in eq 12 from

$$c^* = 3M_w/4\pi N_A R_H^{\;3} \tag{13}$$

where N_A is the Avogadro constant.

Solid curves in Figure 4 indicate theoretical values of R_H/M_w calculated by eqs 10−13 using $k'_H = 6.8$, 5.7, and 6.3, respectively, for LPB-10k, LPB-35k, and LPB-82k. (The weight fractions w_1 and w_m in eq 10 were calculated in the same way as in Figure 5.) These k'_H values are within the normal range of k'_H for flexible polymers in good solvents (cf. Figure 8 in Appendix). The favorable fitting of $R_{H,app}$ demonstrates that LPB exists as a four-arm star micelle in cyclohexane.

3.4. Rate Constant of the Propagation Reaction in Living Anionic Polymerization. On the assumption that only free LPB (unimer) is the active species for the propagation reaction, the propagation rate is calculated by

$$-\frac{\mathrm{d}\ln[\mathrm{M}]}{\mathrm{d}t} = k_{p,app}C_0 = k_p w_1 C_0 \tag{14}$$

where [M] is the molar concentration of the monomer butadiene, C_0 is the total molar concentration of LPB (i.e., the molar concentration of the initiator), $k_{p,app}$ is the apparent propagation rate constant, k_p is the *true* rate constant of the free LPB, and w_1 is the weight fraction of the free LPB calculated from K_m given by eq 4 with the parameters determined above from light-scattering results.

The propagation reaction rate of LPB in cyclohexane was measured many years ago by Spirin et al.[10] and Johnson and Worsfold.[14] Their results are presented in Figure 7 by filled and unfilled circles. The apparent rate constant $k_{p,app}$, calculated from these data with eq 14, was not constant but dependent on C_0 in the form $9.4 \times 10^{-3} C_0^{\;-0.8}$ M$^{-0.2}$ s^{-1}. On the other hand, taking into account the association of LPB, we have three curves shown in Figure 7 for M_1 of the three LPB samples, drawn by

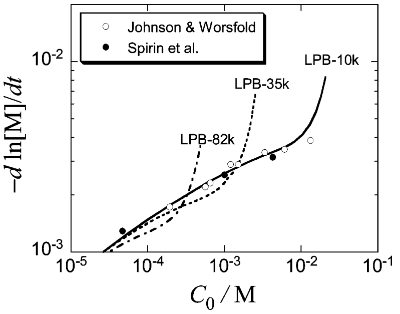

Figure 7. Propagation reaction rate of LPB in cyclohexane determined by Johnson and Worsfold[14] and Spirin et al.;[10] solid, dashed, and dot−dash curves, theoretical values calculated by eq 14 for samples LPB-10k, 35k, and 82k, respectively.

eq 14 with $k_P = 133$ M^{-1} s^{-1} (and $\epsilon_0 = -14$). At sufficiently low C_0, the reaction rate is independent of M_1, but with increasing C_0, the nonideality terms in K_m leads to unique M_1 dependence of the reaction rate. The molecular weight dependence of the propagation reaction rate in the living anionic polymerization was observed for polyisoprene and polybutadiene living anions by Bywater and Worsfold,[43] Madani et al.,[44] and Niu et al.[45]

The theoretical solid curve for $M_1 = 9600$ almost fits to experimental data points over a whole C_0 range investigated, although literature[10,14] reporting the propagation rate of LPB did not specify M_1 at kinetic measurements. If ϵ_0 is chosen to be less than −14, the rate constant k_P must be increased from 133 M^{-1} s^{-1} to fit to the experimental data. Thus this k_P value is its lower limit, which is larger than the lower limit (35 M^{-1} s^{-1}) previously determined[21] using the lower K_4 value mentioned above. It is noted that k_P of the free LPB is larger than that at the radical polymerization ($\approx$ 20 M^{-1} s^{-1})[46] and thus that the reactivity of the LPB anion is higher than that of the polybutadiene radical.

3.5. Comparison with the Micellization Behavior of Diblock Copolymers. As mentioned in the Introduction, living polymer anions can be regarded as the limiting case of amphiphilic diblock copolymers with the degree of polymerization of the polar block to be unity. We here briefly compare the aggregation number of the LPB micelles estimated with those of spherical or starlike micelles of normal diblock copolymers and low-molar-mass surfactants reported so far.

The block chain length dependence of the aggregation number m for spherical micelles formed by amphiphilic diblock copolymers and small molecular amphiphiles in organic or aqueous medium has been extensively studied so far.[1−6] Förster et al.[6] proposed a general equation for this dependence, given by

$$m = 36\pi(\upsilon_{0,c}/b_0^{\,3})^2 N_{0,c}^{\,2} N_{0,s}^{\,-0.8} \tag{15}$$

where $N_{0,c}$ and $N_{0,s}$ are the degrees of polymerization of block chains forming the core and shell (or corona), respectively, and $\upsilon_{0,c}$ is the volume of the monomer unit of the core-forming block; the definition of b_0 is given later. This relation was originally proposed for the strongly segregating limit model of block copolymers but found to be valid for many macromolecular and small molecular amphiphiles. It can be semiempirically derived as follows. If the core is not swollen by the solvent, we have the relation $(4\pi/3)R_c^{\,3} = mN_{0,c}\upsilon_{0,c}$, where R_c is the radius of the spherical core. This R_c is also related to the distance b between junction points of nearest-neighbor block copolymer chains on the core interface by $4\pi R_c^{\,2} = mb^2$. These two equations yield

$$m = \frac{36\pi N_{0,c}^{\,2} \upsilon_{0,c}^{\,2}}{b^6} \tag{16}$$

In this equation, b is the key parameter, relating not only to the packing density of block chains in the core but also to the grafting density of coronal chains on the spherical core surface. There are many theoretical predictions about this parameter,[41] but Förster et al.[6] adopted the empirical equation

$$b = b_0 N_{0,c}^{\,0} N_{0,s}^{\,\epsilon} \tag{17}$$

with $\epsilon = 2/15$ and the adjustable parameter b_0 (b at $N_{0,s} = 1$) and obtained eq 15. This equation indicates that coronal chains determine b, corresponding to the high grafting density case of coronal chains. Förster et al. demonstrated that eq 15 successfully describes experimental m for spherical micelles formed by polystyrene-*block*-poly(4-vinylpyridine) (in toluene)[6] and by polystyrene-*block*-poly(methacrylic acid) (in a water−dioxane mixture)[1] with $N_{0,s}$ and $N_{0,c}$ ranging from 59 to 960 and from 25 to 1290, respectively.

As mentioned above, m ($= m_0$) is 4 for all three LPB samples with $N_{0,s} = 180-1520$, which does not agree with eq 15. The $N_{0,s}$ independence of m indicates that b is not determined by the coronal polybutadiene chain but by the polar end of LPB. A quantum mechanical calculation[30] for allyllithium proposed a dimer model through strong interactions of two lithium cations with C_1 and C_3 atoms in two C_3H_5 anions. If this dimer further self-associates to form a tetramer in cyclohexane, the bulkiness of the polar core rather than the coronal chains may determine b. Of course, the bulkiness of coronal chains increases with $N_{0,s}$. Therefore, it is possible that m depends on $N_{0,s}$ beyond the $N_{0,s}$ range examined in this study.

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Appendix. Strength of the Intermolecular Hydrodynamic Interaction in the Apparent Hydrodynamic Radius.

The concentration c dependence of the specific viscosity η_{sp} of dilute polymer solutions is usually expressed in terms of the Huggins equation

$$\eta_{sp}/c = [\eta](1 + k'[\eta]c) \tag{A1}$$

with the intrinsic viscosity $[\eta]$ and the Huggins constant k'. It is known that, for molecularly dispersed polymer solutions, k' ranges from 0.3 to 0.6, irrespective of the polymer molecular weight and kinds of polymer and solvent. Bauer et al.[47] demonstrated that k' of star polymers is also within this range unless the number of arms exceeds ten.

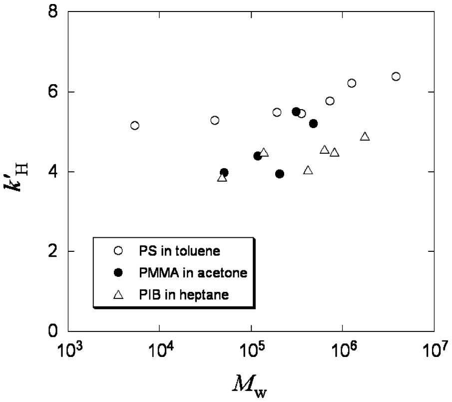

Figure 8. Strength of the intermolecular hydrodynamic interaction in the apparent hydrodynamic radius for flexible polymer−good solvent systems, polystyrene (PS) in toluene,[49,50] poly(methyl methacrylate) (PMMA) in acetone,[51,52] and polyisobutylene (PIB) in heptane.[53,54]

On the other hand, the c dependence of the diffusion coefficient D of polymers in dilute solutions is conventionally represented by the equation

$$D = D_0(1 + k_D c) \tag{A2}$$

where D_0 is D at infinite dilution and k_D is the concentration coefficient. In contrast with the Huggins constant k', k_D is affected not only by the intermolecular hydrodynamic interaction but also by the thermodynamic interaction and moreover depends on the polymer molecular weight. (The polymer solution viscosity is not affected by the thermodynamic interaction.[48]) Therefore k_D cannot be regarded as a *universal* constant.

To take out the thermodynamic interaction effect from D, the apparent hydrodynamic radius $R_{H,app}$ is defined by eq 1 in the text, where KcM_w/R_0 on the right-hand side is the factor with respect to this effect. Using the relation of $R_{H,app}$ to D and eq A2, we can write the c dependence of $R_{H,app}$ as $R_{H,app} = R_H[1 + (2A_2M_w - k_D - \bar{v})c]$ (the last term $\bar{v}c$ is related to the effect of the solvent backflow accompanied by the translational diffusion). Comparing this equation with eq 12 in the text, we have the relation

$$k'_H = (2A_2M_w - k_D - \bar{v})c^* \tag{A3}$$

This k'_H may be regarded as a universal constant, corresponding to the Huggins constant k' in eq A1. In fact, as shown in Figure 8, k'_H calculated from literature data[49−54] for some typical flexible polymers in good solvents mostly range from 4 to 6, almost irrespective of the kind of polymers and molecular weight. The k'_H values are one order of magnitude larger than the Huggins constant (0.3−0.6) for the polymer solution viscosity. This is due not only to use of eq 13 for c^* (instead of $c^* = 1/[\eta]$) but also to different effectiveness of the hydrodynamic interaction on the translational and rotational motions of polymer chains.[26]

Supporting Information Available: Characteristics of a tiny amount of huge aggregates of LPB detected by light scattering. This material is available free of charge via the Internet at http://pubs.acs.org.

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(40) We could not exclude the possibility of the coexsistence of the dimer and tetramer, because the static and dynamic light-scattering results were fitted by use of the dimer−tetramer equilibrium model as good, as demonstrated in Figures 5 and 4. If this is the case, we must replace the term "unimer" by "dimer" to make the same argument in the Discussion section.
(41) From $\epsilon_0 = -14$, we can calculate the free energy of aggregation $\Delta G^\circ \equiv \mu_m^\circ - m\mu_1^\circ = m\epsilon_0 RT$ to be −140 kJ/mol (−33 kcal/mol). This result is comparable to the heat of aggregation (= −37 kcal/mol) obtained by Morton and Fetters[13] for the polyisoprene anion in *n*-hexane.
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