Characterization of Associating Polymers in Solution

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Introduction

Associating Polymers, bearing functional groups of strong attractive interactions, form macromolecular assemblies in solution or in bulk.[1] There are many types of architecture of macromolecular assemblies (cf. Figure 1). For associating polymers with a single attractive moiety per chain (e.g., diblock copolymers, polymer living anions, water-soluble polymers hydrophobically modified at one end), the architecture may be spherical (star-like), cylindrical, or bilayer. On the other hand, if the chain possesses a number of attractive moieties, its assembly may be a uni-core or multi-core flower. Multi-stranded helical polymers or mixtures of polyacid and polybase may form assemblies of their unique architecture.
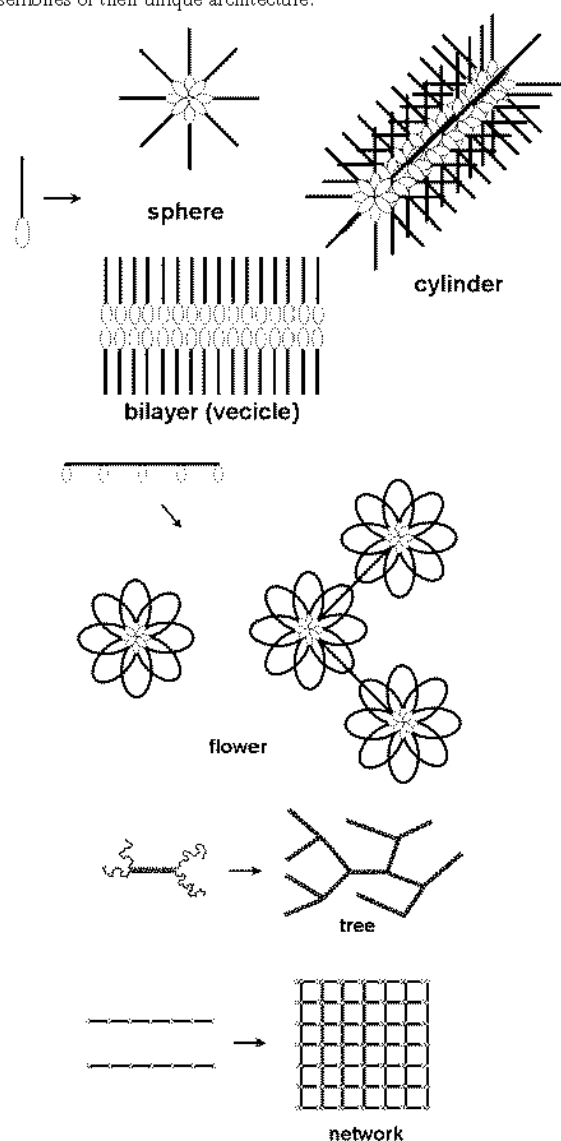

Figure 1. Various architecture of macromolecular assemblies

The macromolecular assemblies formed by associating polymers in solution can be characterized by (1) the architecture, (2) the size (i.e., the radius of gyration, intrinsic viscosity, or hydrodynamic radius), (3) the average aggregation number, (4) the distribution of the aggregation number, and (5) inter-assembly interaction. However, the determination of these characteristics is not necessarily an easy task in comparison with molecularly dispersed polymers. Difficulty comes from the concentration dependence of the degree of aggregation. The standard procedure of infinite dilution and also size exclusion chromatography does not necessarily provide right information of the assemblies at a given finite concentration. To make proper characterization, we have to consider in detail the association – dissociation equilibrium of associating polymers in solution.

The present paper deals with two examples of associating polymer systems: polymer living anions in an organic solvent and amphiphilic random copolymers in aqueous medium.

Reversed Micellization of Polybutadiene Living Anions[2]

In a non-polar solvent, the living polybutadiene anion (LPB) does not exist as a free anion but forms an ion pair with the counter ion. This was demonstrated by the normal second virial coefficients of LPB in cyclohexane. However, the ion pair at the LPB chain end possesses a large dipole moment, inducing the strong dipole-dipole interaction among LPB chain ends in non-polar solvents. This strong inter-chain interaction makes LPB chain ends associate each other to form a uni-core polymer micelle (a reversed micelle).

Samples. The anionic polymerization was made in high vacuum glass flasks/ampoules using *sec*-butyllithium as the initiator. Cyclohexane solutions of LPB thus prepared were transferred into light scattering cells directly connected to the polymerization flasks, diluted by suitable amounts of pure cyclohexane, and the cells were sealed off from the vacuum flask. Three different molecular weight LPB samples were used for light scattering measurements. Their weight average molecular weights M_1 after quenched by methanol were 9,600 (10k), 35,200 (30k), and 81,900 (80k).

Light Scattering Results. Figure 2 shows light scattering results of three LPB samples in cyclohexane, where K is the optical constant, c the polymer mass concentration, and R_0 the excess Rayleigh ratio at the zero scattering angle. Data points for each sample almost follow a straight line, and simple extrapolations to the zero concentration give us an aggregation number of ca. 3 to 4 for every sample.
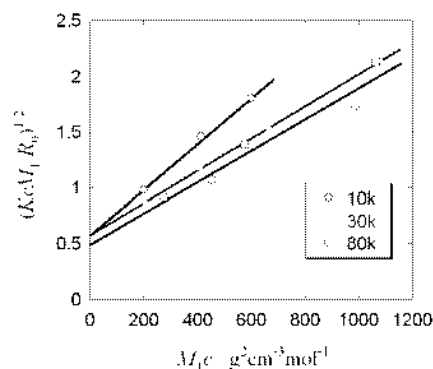

Figure 2. Light scattering results of three polybutadiene living anion samples in cyclohexane.

The above light scattering results should be analyzed by the theory of association-dissociation equilibrium described in the following theoretical section. For star micelles, the intermicellar interaction can be specified by eqs 7 and 8 within the third virial approximation, where α, A_{11}, and A_{111} for linear polybutadiene are known. The association constant K_m is calculated by eq 2. Assuming that the aggregation number m is monodisperse, we have searched for a m value leading to the best fit of our light scattering results. Figure 3 shows the fitting result, from which we have concluded that m of LPB in cyclohexane is 4. Although we have chosen ε_m to be 14 in Figure 3, similar fitting was also observed for $\varepsilon_m > 14$

If only the dissociated LPB participates in the propagation reaction, kinetic data of living anionic polymerization must be analyzed along with the knowledge of the association–dissociation equilibrium. The true rate constant k_p of the propagation reaction for the dissociated LPB was estimated to be 135 $M^{-1}s^{-1}$ at $\varepsilon_m = 14$ (when $\varepsilon_m > 14$, we obtain larger k_p). This rate constant is larger than that for radical polymerization (24 $M^{-1}s^{-1}$).
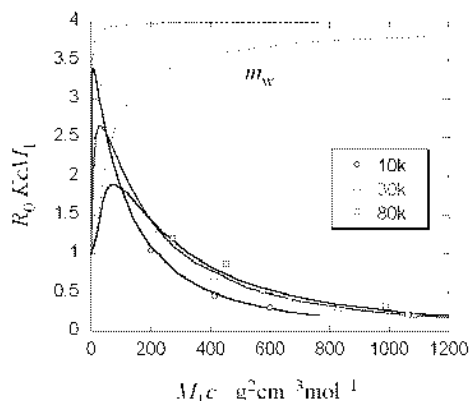
Figure 3. Comparison of light scattering results of three LPB samples with eq 5 for $m = 4$ and $\varepsilon_m = 14$.

Micellar Structure of Amphiphilic Statistical Copolymers

As indicated in Figure 1, amphiphilic statistical copolymers composing of hydrophobic and electrolyte monomer units are expected to form flower micelles in aqueous media by strong intra- and intermolecular hydrophobic interactions, but their micellar structure is affected also by intra- and intermolecular electrostatic interactions.[3]

We have recently studied the micellar structure of statistical copolymers of N-acryloyl-amino acid sodium salt and N-dodecylmethacrylamide (see the right scheme) where we chose glycine (Gly; R = H), valine (Val; R = CH(CH₃)₂), and isoleucine (Llu; R = CH(CH₃)(C₂H₅)) as amino acid residues.

Figure 4 shows the degree of polymerization $N_{0,w}$ dependence of the hydrodynamic radius R_H for three kinds of the copolymers ($x = 0.2 - 0.4$) as well as the corresponding homopolymers without dodecyl groups (C12). While the dependencies for the copolymers and homopolymers is almost independent of the kind of amino acid residues and also of x for the copolymers, R_H values of the copolymers are much smaller than those of the homopolymers at same $N_{0,w}$. The red curve in the figure indicates theoretical values for the flower micelle model with a minimum loop size determined by the chain stiffness. The agreement with the data points demonstrates the flower micellar architecture for the amphiphilic copolymer aggregates.
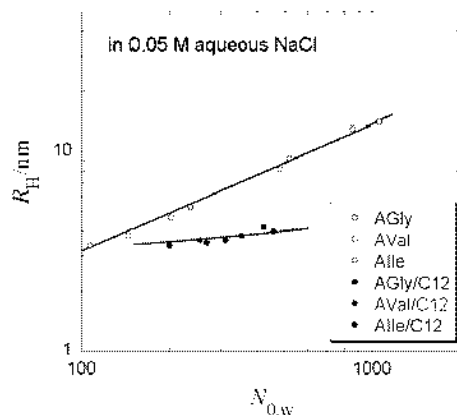

Figure 4. Degree of polymerization dependence of the hydrodynamic radius R_H for amphiphilic polyelectrolytes and homo-polyelectrolytes.

Theoretical

Association–Dissociation Equilibrium. In associating polymer solutions, the chemical potential μ_m of m-mer is written in general as

$$\frac{\mu_m}{RT} = \frac{\mu_m^o}{RT} + \ln\left(\frac{c_m}{M_m}\right) + 2M_m\sum_{k\geq1}A_{mk}c_k + \frac{3}{2}M_m\sum_{k,l\geq1}A_{mkl}c_kc_l \quad (1)$$

in the third virial approximation. Here, μ_m^o, c_m, and M_m are the internal free energy, mass concentration, and molar mass of m-mer, respectively, and A_{mk} and A_{mkl} are the second and third virial coefficients among the components indicated by the subscripts, respectively (RT: the gas constant multiplied by the absolute temperature).

The association constant K_m defined by C_m/C_1^m ($C_m = 1000c_m/M_m$: the molar concentration) is derived from eq 1 to be

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

where $\varepsilon_m = (\mu_m^o/m - \mu_1^o)/RT$ and the virial coefficients have been approximated by the arithmetic average of those for the homogeneous species. In this equation, ε_m is the key parameter determining the micellar size distribution. For spherical micelles, ε_m consists of (1) the free energy gain when solvophobic groups enter in the micelle core from the solvent, (2) the free energy due to interaction among solvophilic chains in the micelle, and (3) the interfacial free energy of the micelle core, but it is more convenient to express as

$$\varepsilon_m = \sigma m_0\left(\frac{m}{m_0} + \frac{m_0}{m} - 2\right) + \varepsilon_0 \quad (m \geq 2) \quad (3)$$

where σ is the free energy due to interaction between two solvophilic chains in the micelle and ε_0 is the minimum value of ε_m at $m = m_0$. The weight fraction w_m of m-mer in the total polymer is calculated by

$$w_m = mK_mw_1^m(1000c/M_1)^{m-1} \quad (4)$$

and w_1 is determined from the normalization condition $\sum_{m\geq1}w_m = 1$.

Light Scattering. Using eq 1, we can calculate the excess Rayleigh ratio R_0 at the zero scattering angle in the form

$$\frac{KcM_1}{R_0} = \frac{1}{m_w} + 2A_{2,z}(M_1c) + \left[\frac{2A_{3,z} + A_{3,w}}{M_1} - m_w\left(\overline{A_{2,z}^2} - A_{2,z}^2\right)\right](M_1c)^2 \quad (5)$$

with the weight average aggregation number m_w and various average second third virial coefficients defined by

$$\begin{cases} A_{2,z} \equiv m_w^{-1}\sum_{m\geq1}mw_mA_{mm}, & \overline{A_{2,z}^2} \equiv m_w^{-1}\sum_{m\geq1}mw_mA_{mm}^2 \\ A_{3,z} \equiv m_w^{-1}\sum_{m\geq1}mw_mA_{mmm}, & A_{3,w} \equiv \sum_{m\geq1}w_mA_{mmm} \end{cases} \quad (6)$$

The averages can be done with w_m given by eq 4.

In the calculation of eqs 2 and 5, expressions of A_{mm} and A_{mmm} are necessary. The expressions are dependent on the architecture of the aggregate. For star-like micelles,

$$A_{mm} = g_{A2,m}m^{-\alpha}A_{11}, \quad A_{mmm} = g_{A3,m}m^{1-2\alpha}A_{111}^2 \quad (7)$$

where $-\alpha$ is the exponent of the molecular weight dependence of A_{11} (for the linear chain), and $g_{A2,m}$ and $g_{A2,m}$ are the g-factors with respect to A2 and A3. Empirically, we know

$$g_{A2,m} \cong 1 - 0.04(m-2), \quad g_{A3,m} \cong 1 - 0.08(m-2) \quad (8)$$

for m-arm star flexible polymers in good solvents.

Conclusions

The characterization method for associating polymer solutions was briefly reviewed. The method has not yet established in comparison with the characterization method for molecularly dispersed polymers in solution. However, the two examples of associating polymer systems, living polybutadiene anions and amphiphilic statistical copolymers mentioned above, were successfully characterized on the basis of suitable model and theory.

References

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[3] A. Hashidzume, A. Kawaguchi, A. Tagawa, K. Hyoda, and T. Sato Macromolecules 2006, 39, 1135.