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Aggregation Behavior of Functional Polymers in Solution

Yoichi Ogata

2015
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1 Introduction

1.1 Background

In chemical industry today, polymers play an important role in creating high-performance materials, which are essential for our life as well as metal and inorganic materials. Many chemical enterprises have been focusing on research and development (R&D) of novel polymer materials because the demand of polymer materials in a variety of fields is expected to increase progressively. Under the corporate identity “Materials Innovation,” we have also been developing a wide variety of polymer materials, i.e. elastomer, emulsion, display, electronic, optical and medical materials. Most of these polymer materials are solution products. Some of them have serious troubles due to aggregation, which is characteristic of polymers, while polymer aggregation in solution may also lead high performance of polymer materials.

In general, the origin and phenomenon of polymer aggregation are explained as follows: Polymer aggregation is caused by the short-range intra- and/or intermolecular interactions between segments constituting of polymers. Because polymer chains are isolated in dilute solution, effects of intermolecular forces are considered to be negligible. Thus, polymer chains in dilute solution do not penetrate into each other. As the concentration increases and the distance between the polymer chains become shorter, the effects of interchain forces become larger. Polymer coils finally start to entangle with each other to form “loose aggregates.” Further increase in the concentration gives large interpenetration of the polymer chains, resulting in the formation of “strong aggregates.” Then, polymer aggregation may be led by, for example, the change of temperature, concentration and pH, and the addition of electrolyte such as salt and surfactant.

Aggregation behavior of copolymers becomes increasingly complex owing to the interaction between dissimilar co-monomers. The size and structure of the aggregates from the copolymers vary according to the above-noted conditions. So far, there has been great interest in characteristic properties of aggregation from many copolymers, which are currently applied
to new fields such as self-assembly\textsuperscript{11}, nanowire\textsuperscript{12} and drug delivery system (DDS)\textsuperscript{13} by taking advantage of the particular aggregation. In some of these application fields, polymer products practically work as thin film. Aggregate parts are denser than non-aggregate parts. Then, thin films produced from the polymer solution including aggregates have necessarily dense and loose parts. The density inhomogeneity in thin film causes roughness of the surface of the film, and leads to product defects in the use of the films as optical and electric materials. Practically, convex defects are most often observed on the thin film made by spin-coating of the polymer solution containing aggregates. This is because small aggregates develop into large ones in polymer solution with increasing concentration drastically during volatilization of solvents in the spin-dry process.

Therefore, it is necessary for polymer solution products to detect aggregates at the stage of quality check (QC). In the QC, quality inspection for polymer products is practically carried out both for the solution and solid (thin film) of the products. The quality inspection items for solution products are usually checked off by generic analysis methods such as gel permeation chromatography (GPC) for molecular weight and molecular weight distribution, hot plate method for total solid content (TSC), viscometry for solution viscosity, Karl-Fischer reagent titration\textsuperscript{14} for water content in solution, and so on. Unfortunately, however, these methods are not suitable for the detection of aggregates in polymer solutions.

The static and dynamic light scattering (SLS and DLS) are powerful tools to detect aggregates in solution, as is well known. By SLS measurements, the weight-averaged molecular wight $M_w$, ($z$-averaged) mean-square radius of gyration $\langle S^2 \rangle$ as a measure of average chain dimensions of solutes (polymers and aggregates) in solution, and second virial coefficient $A_2$ are determined. The quantities $M_w$ and $\langle S^2 \rangle$ or the scattering intensity itself are sensitive to existence of large aggregates, although their amount is tiny, in solution. In the case of DLS measurements with the CONTIN analysis,\textsuperscript{15} the (effective) hydrodynamic radius $R_H$, which is defined from the translational diffusion coefficient $D$ by the Stokes-Einstein relation,\textsuperscript{16} and also the size ($R_H$) distribution of solutes in solution are determined. We have then already employed the LS technique to screen how much polymer solution products have aggregates causing the defects in the QC.

The LS is useful not only for the QC but also for the R&D of polymer materials. In the R&D, a primary purpose of investigating aggregation behavior of polymers in solution by the LS measurements is to verify whether polymer materials have required functionality or not, and to feed back to material design. Specifically, in the case of medical materials, the aggregation
and shape change of polymer chains themselves in aqueous solution is largely related to the functionality: release behavior of medicine included in polymer carriers such as micelle, vesicle and nanogel depends highly on the shape change of the carriers in aqueous solution, which may be caused by external stimuli, such as the temperature, pH jump, light emission, magnetic or electric field impression, and so on. The combination of SLS and DLS measurements may elucidate the above-mentioned shape change of the polymer chains and aggregates in solution.

Detailed in the following chapters, in this study, we investigated the aggregability of functional polymers, which are composed of polar and non-polar monomers, rigid and coiled monomers, and bulky and non-bulky monomers, by means of SLS and DLS. The purpose is to clarify the factor causing aggregation in order to inhibit and/or eradicate undesirable aggregability which triggers the defect trouble of polymer materials, and give unique aggregability which results in the required functionality to them. The consideration and conclusion for the analysis results are mainly based on the correlation between monomer and solvent polarity. This is because the guideline for monomer selection in manufacturing polymer materials and solvent selection in preparing solution products is essential in order to control aggregability of polymer materials, for example “aggregate-free” and “aggregate as molecularly-designed,” in accordance with the practical use. Therefore, we believe it is possible to develop high-quality polymer materials by demonstrating aggregation behavior of polymers in solution.

1.2 Outline

The plan of this thesis is as follows;

In Chapter 2, the aggregation behavior of cyclic saturated copolymers prepared from 8-methyl-8-methoxycarbonyltetracyclo[4.4.0.12,5.17,10]dodec-3-ene (MMT) with polar ester group and dicyclopentadiene (DCP) without polar group via ring-opening metathesis polymerization (ROMP) followed by hydrogenation was investigated by using SLS and DLS for toluene (TL)/cyclopentene (CPE), TL/cyclohexane (CHX), THF and dichloromethane (DCM) solutions. The comparison of monomer reactivity of DCP and MMT indicated that the copolymer had distribution of DCP composition in a macromolecule chain, which could provide the interesting aggregation behavior. DLS analysis revealed that the aggregation
degree of the copolymer decreased with increasing hydrophobicity of solvent, decreasing polymer concentration, decreasing molecular size of solvent, and increasing temperature. Based on these findings, the mechanism of aggregation behavior was clarified that the DCP-rich unit in a macromolecule might be acting as core to give the aggregation in poor solvent.

In Chapter 3, the aggregation behavior of hydrogenated polystyrene-\(b\)-poly(ethylene/butylene)-\(b\)-polystyrene triblock copolymer (SEBS copolymer) was studied by using SLS and DLS for CHX and \(N\)-methylpyrrolidone (NMP) solutions. From the values of \(<S^2>^{1/2}/R_H\) and solubility parameters, SEBS copolymer proved to exist as single chain close to random coil in nonpolar CHX, whereas aggregate into the core-shell micelle consisting of poly(ethylene/butylene) (PEB) core surrounded by polystyrene (PS) shell in polar NMP. The comparison with the aggregation behaviors in other solvents demonstrated that the aggregate compactness of the copolymer depended largely on solvent polarity, resulting in formation of the highly dense PEB core and the thick PS shell in high-polar NMP.

In Chapter 4, the aggregation behavior of poly(\(\gamma\)-benzyl-L-glutamate)-\(b\)-polyisoprene-\(b\)-poly (\(\gamma\)-benzyl-L-glutamate) (GIG copolymer) was examined by using SLS and DLS for \(N, N\)-dimethylformamide (DMF) solution and DMF/TL mixed solutions. GIG copolymer proved to aggregate in DMF and under DMF-rich condition, that is, high-polar region. The aggregate decreased in size, and completely disappeared under TL-rich condition, that is, low-polar region. The correlation between solubility parameter and aggregate size of GIG copolymer in the DMF/TL solution systems quantitatively demonstrated how strongly polarity caused by hydrogen bond made an impact on the aggregation behavior. Because the main driving force to the aggregation under DMF-rich condition originates with polyisoprene (PIP) blocks, the aggregate in DMF is considered to be a core-shell micelle consisting of flexible PIP core surrounded by rigid poly(\(\gamma\)-benzyl-L-glutamate) (PBLG) shell. The values of \(<S^2>^{1/2}/R_H\) revealed that a single chain of GIG copolymer had the form of rigid rod with flexibility, that is, once-broken rod, caused by the incorporation of a flexible PIP chain between two rigid PBLG rods in the DMF/TL solution system.

In Chapter 5, the aggregation behavior including dilute solution property and surface-activity of the amphiphilic random copolymer composed of 2-(acrylamido)-2-methylpropanesulfonic acid and tris(trimethylsiloxy)silylpropylmethacrylate (AMPS/TRIS copolymer) in aqueous solution were investigated by SLS and DLS, surface tension measurement, and transmission electron microscopy (TEM) for aqueous solution. The surface tension measurement made it
clear that AMPS/TRIS copolymer exhibited weaker surface-activity than a typical low-molecular weight surfactant sodium dodecyl sulfate in water, that is, there were no plateau of surface tension $\gamma$ versus concentration and no critical micelle concentration (CMC) in the whole concentration studied. SLS and DLS analyses, and TEM revealed that AMPS/TRIS copolymer self-associated into imperfect core-shell micelles having hydrophobic TRIS core surrounded by hydrophilic AMPS shell in water. AMPS shell was considered as a hard shell due to the stiffness of AMPS chain in water. TRIS chain could not densely aggregate in water due to the large steric hindrance between bulky trimethylsiloxy groups despite its hydrophobic nature, thereby providing TRIS core with less-dense structure. The balance between the spreading force of stiff AMPS chain and the cohesion force of bulky TRIS chain provides the driving force for forming the unique micelle having less-dense TRIS core and hard AMPS shell.

In Chapter 6, the aggregation behavior of the organic-soluble semi-aromatic polyimides, whose degrees of imidization range from 69 to 96 %, obtained using 4,4’-oxydianiline (ODA), 4,4’-diamino-3,3’diroyloxybiphenyl (DDO) and bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA) in NMP, NMP/cyclohexanone (CHN) and NMP/$\gamma$-butyrolactone (GBL) (BCDA-based polyimides) were studied by SLS and DLS. DLS analyses demonstrated the specific character unlike flexible polymers that the single BCDA-based polyimide chains first associate with each other to form small clusters in the dilute region, and then expand to large aggregates by the entanglements between the small clusters with an increasing concentration into the semi-dilute region. Given the semi-aromatic structure of BCDA-based polyimides weakening the charge-transfer (CT) interaction between the diamine and the dianhydride unit, it is concluded that the unique aggregation behavior of BCDA-based polyimides is dominated by the balance between the driving force for the “organic-solubility” given by both the increase in bulkiness and the decrease in the CT interaction, and that for the “organic-insolubility” derived from both the hydrogen-bonded interaction of the phenolic hydroxyl groups and the $\pi$-$\pi$ interaction of the phenyl rings.

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2 Aggregation Behavior of New Cyclic Saturated Copolymers Synthesized via Ring-opening Metathesis Polymerization

2.1 Introduction

We have been developing a hydrogenated cycloolefine polymer under the trade name of ARTON prepared from 8-methyl-8-methoxycarbonyltetracyclo[4.4.0.12,5.17,10]dodec-3-ene (MMT) by ring-opening metathesis polymerization (ROMP). ARTON has the quite high glass transition temperature of 171 °C and high transparency, and also shows low birefringence caused by the orientation of the main-chain with the bulky cyclic structure. Thus, ARTON has been used for various optical products, such as lens, disk, display, and so on. Copolymers of polar MMT and its non-polar analogue, dicyclopentadiene (DCP), may be considered to be useful for modification of the optical properties of ARTON.

The copolymer of polar MMT and non-polar DCP may form aggregates in solution even if ARTON (MMT homopolymer) itself is completely dissolved in tetrahydrofuran (THF) and dichloromethane (DCM), and also, in the mixed solvent of toluene (TL) and cyclopentene (CPE) and that of TL and cyclohexane (CHX). The aggregates must be removed in the industrial processing of optical materials like ARTON. For establishment of the copolymer of MMT and DCP as a new optical material, it is then necessary to examine whether the aggregates form in the solution of the copolymer or not. Further, if the aggregates are formed, we need to examine effects of solvent conditions on the size of the aggregates.

In this chapter, we then synthesize the copolymer of MMT and DCP by ROMP and carry out the static and dynamic light scattering (SLS and DLS) measurements for the copolymer in the solvents THF, DCM, TL/CPE, and TL/CHX with varying the polymer concentration and temperature.

2.2 Experimental
2.2.1 Materials

Toluene and DCP (Maruzen chemical) were dried over molecular sieves (type 4 A) under nitrogen. MMT (JSR) was freshly distilled before use. The other reagents were obtained commercially and used as received.

2.2.2 Syntheses of the Homopolymer and the Copolymer

In a 500 mL autoclave purged with dry nitrogen fitted with a stirrer were placed 25 g DCP (0.189 mol), 75 g MMT (0.323 mol), 150 g toluene and 7.31 g 1-hexene (0.0870 mol). The polymerization was initiated by the addition of triethyl aluminum (0.1536 mmol) and tungsten hexachloride (0.0256 mmol) to the stock solution at 105 °C while the mixture was vigorously stirred for 1 hour. The obtained toluene solution of the copolymer and 37.7 mg RuHCl(CO)(PPh₃)₃ as a hydrogenation catalyst were mixed in an autoclave under a dry atmosphere. Then, the dry nitrogen in the autoclave was replaced by dry hydrogen. The mixture was allowed to heat to the hydrogenation temperature during stirring. Hydrogenation was carried out at 160 °C for 3 hours under 10 MPa of H₂. The resulting viscous solution was poured into a large amount of methanol with vigorous stirring. The obtained white powder was dried at 100 °C under vacuum (yield = 96 %). The procedure for the homopolymer was carried out as well as the synthesis for the copolymer (Scheme 2.1).

Monomer reactivity ratio was determined by Fineman-Ross method as follows: Toluene/monomer feed ratio = 3, DCP/MMT wt% feed ratio in the range from 0.1, 0.3, 1, 3 and 9, initial temperature at 80, 105 and 130 °C, monomer/WCl₆ feed ratio = 30,000 and WCl₆/triethyl aluminum feed ratio = 6. The reaction solution was quenched by methanol within 10 sec because the monomer conversion should be depressed under 30 %. DCP and MMT units incorporated into the copolymer were calculated by each monomer conversion.

2.2.3 Characterization

¹H NMR spectra were obtained using a Bruker AVANCE 500 MHz instrument using CDCl₃ as a solvent. GC measurement was conducted to determine monomer conversion with a Shimazu GC-2014 TC-WAX I.D. (0.53 mm length 30 mdf 100 μm). Gel permeation chromatography (GPC) was performed in THF as an eluent using a TOSOH 8020 HPLC
Scheme 2.1. Syntheses of the homopolymer and copolymer.
system equipped with four TSKgel columns (TSKgel G7000HxL, TSKgel GMHxL, TSKgel GMHxL and TSKgel G2000xL) using RI detector and polystyrene calibration. Thermal analysis was performed on a Seiko instruments DSC 6200 at a heating rate of 20 K/min. A chlorobenzene solution with a concentration of $5 \times 10^{-3} \text{ g/cm}^3$ was prepared, and an intrinsic viscosity was measured under the condition of 30 °C using RIGOSHA & Co., Ltd, Automatic Viscometer VMC-222.

2.2.4 Preparation of Polymer Solution

Solutions for LS measurements were prepared by dissolving the appropriate amount of polymer in TL/CPE = 50/50 mixed solvent, TL/CHX = 50/50 mixed solvent, THF and dichloromethane (DCM) at seven concentrations of 0.2, 0.4, 0.6, 0.8, 5, 10 and 15 wt%. Solvents and polymer solutions were filtered through 0.2 and 0.5 μm PTFE filters, respectively, and measured directly into the scattering cell. The values of the refractive indexes $n_0$ at $\lambda_0 = 589 \text{ nm}$ of the homopolymer and the copolymer were 1.5120 and 1.5175, respectively. These values were close to that of TL (1.4960). Both polymers were not soluble in CHX and CPE. The measurements, therefore, in TL, CHX and CPE could not be carried out and the mixed solvents consisting of TL and CHX, and TL and CPE were used.

2.2.5 Dynamic Light Scattering (DLS)

DLS measurements were carried out to determine translation diffusion coefficient $D$ for four dilute solutions ($c = 0.2, 0.4, 0.6, 0.8 \text{ wt%}$) of the homopolymer and the copolymer at four scattering angles of 60°, 90°, 120° and 150° at 23 °C. In addition, we investigated the aggregation behavior of these two polymers in a dilute solution ($c = 0.8 \text{ wt%}$) and three semi-concentrated solutions ($c = 5, 10, 15 \text{ wt%}$) at a scattering angle of 60° at four temperatures of 23, 30, 40 and 50 °C. The measurements were made with an ALV/DLS/SLS-5000 light-scattering system, with a 22 mW He-Ne laser emitting vertically polarized light of 632.8 nm wavelength as the light source.

From the measurements, the normalized autocorrelation function $g_2(t)$ of scattered light intensity $I(t)$ at time $t$ was measured:
\[ g_2(t) = \frac{\langle I(0)I(t) \rangle}{\langle I(0) \rangle^2} \] (2.1)

\( g_2(t) \) is related to the normalized autocorrelation function \( g_1(t) \) of the electric field by Siegert’s relation:\(^3\)

\[ g_2(t) = 1 + \beta |g_1(t)|^2 \] (2.2)

where \( \beta \) is a spatial coherence factor dependent on the detection system. For polydisperse solutes, \( g_1(t) \) may be expressed by a continuous distribution function \( G(\Gamma) \) of the decay rate \( \Gamma \), which is the inverse of the decay time \( \tau \).

\[ g_1(t) = \int_0^\infty d\Gamma G(\Gamma) \exp(-\Gamma t) \] (2.3)

\( G(\Gamma) \) leading to \( \Gamma \) was determined by performing an inverse Laplace transform on eq. (2.3) from the data for \( g_2(t) \) because the samples used in this study were polydisperse. This method is CONTIN analysis,\(^4\) which is useful for analysis of more complicated data. Because \( D \) is related to \( \Gamma \) in eq. (2.4), \( D \) was determined by using \( \Gamma \).

\[ D = \lim_{q \to 0} \frac{\Gamma}{q^2} \] (2.4)

\( q \) is the magnitude of the scattering vector

\[ q = \frac{4\pi n_0}{\lambda_0} \sin \frac{\theta}{2} \] (2.5)

defined in terms of the solvent refractive index \( n_0 \), the wavelength in vacuum of the light used \( \lambda_0 \), and the scattering angle \( q \). For dilute solutions, \( D \) may be expanded as

\[ D = D_0 (1 + k_D c + \cdots) \] (2.6)

where \( D_0 \) is \( D \) at infinite dilution, and \( k_D \) is the diffusion second virial coefficient. The \( k_D \) could be a solubility index of polymers because \( k_D \) is related to the thermodynamic second
virial coefficient $A_2$.\(^5\) The slope of each line divided by $D_0$ gives us $k_D$ according to eq. (2.6). From $D_0$, the hydrodynamic radius $R_H$ is calculated by the Stokes-Einstein equation given in eq. (2.7), with $k_B$ Boltzmann constant, $T$ the sample temperature, and $\eta_0$ the solvent viscosity.

$$R_H = \frac{k_B T}{6\pi \eta_0 D_0} \quad (2.7)$$

For semi-dilute or concentrated solutions, two or more relaxation modes could be observed. These relaxation modes that involve the fast mode due to the motion of single polymer chain and the slow mode related to the motion of polymer aggregation in solution would be observed.\(^6,7\) Note that the intensity of the fast mode is proportional to the osmotic compressibility and is strongly dependent on the solvent quality, while the slow mode corresponding to the elastic modulus is rather invariant with the solvent quality.\(^8\) Unlike in the case of dilute solutions, correlation length $\xi$ is calculated by using $D$ on eq. (2.8):

$$\xi = \frac{k_B T}{6\pi \eta_0 D} \quad (2.8)$$

In a narrow sense, $\xi$ is not equal to $R_H$ by definition. However, note that both physical values are shown together as $R_H$ in the abscissa of some figures in order to compare the size of single polymer chain directly with that of aggregated polymer, and demonstrate the concentration dependence of polymer aggregation.

The refractive indices of the four solvents at 23 °C were determined with a Kyoto Electronics refractometer (model RA-500 N) to be 1.4558, 1.4547, 1.4057 and 1.4217, respectively. The densities of the four solvents at 23 °C were determined with a Kyoto Electronics density/specific gravity meter (model DA-505) to be 0.8141, 0.8131, 0.8842 and 1.3202 g/cm\(^3\), respectively. The viscosity of the four solvents at 23 °C were determined with a Toki Sangyo rotational viscometer (model RE-80L) to be 0.468, 0.611, 0.491 and 0.468 cP, respectively. Applying polymer solution viscosity to size analysis of aggregate polymer might make the analysis more complicated because the amount of aggregate polymer depends on solution system. Therefore solvent viscosity was not used for size analysis of only single polymer chain but also aggregate polymer in eqs. (2.7) and (2.8).

### 2.2.6 Static Light Scattering (SLS)
SLS measurements were carried out to determine the weight average molecular weight $M_w$ and $A_2$ for four dilute solutions ($c = 0.2, 0.4, 0.6, 0.8 \text{ wt\%}$) of the homopolymer and the copolymer in the scattering angle range $30$-$150^\circ$ at $10^\circ$ intervals at $23 \ ^\circ\text{C}$. The measurements were made with the same apparatus as DLS measurements. The values of $\partial n/\partial c$ for TL/CPE mixed solution, TL/CHX mixed solution, THF solution and DCM solution of the homopolymer at $23 \ ^\circ\text{C}$ were $0.0848$, $0.0980$, $0.1302$ and $0.1135 \text{ cm}^3/\text{g}$, respectively. Meanwhile, the values of $\partial n/\partial c$ for the four solutions of the copolymer at $23 \ ^\circ\text{C}$ were $0.0850$, $0.0938$, $0.1358$ and $0.1135 \text{ cm}^3/\text{g}$, respectively. $A_2$ was calculated from the slope of concentration dependence at $q = 0$ in a Berry plot:\(^9\)

$$
\left( \frac{Kc}{\Delta R_{\theta=0}} \right)^{1/2} = \frac{1}{M_w^{1/2}} (1 + A_2M_w c + \cdots)
$$

(2.9)

where $K$ is the optical constant

$$
K = \frac{4\pi^2 n_0}{N_A \lambda_0^4} \left( \frac{\partial n}{\partial c} \right)^2
$$

(2.10)

defined in terms of $n_0$, the Avogadro number $N_A$, $\lambda_0$ and the refractive index increment $\partial n/\partial c$.

### 2.3 Results and Discussion

#### 2.3.1 Monomer Reactivity Ratio and Synthesis of the Copolymer

In order to investigate the copolymerization of MMT and DCP, the monomer reactivity ratio, i.e. $r_{DCP}/r_{MMT}$, was examined using Fineman-Ross method. The copolymerization of DCP and MMT was carried out in a temperature range from 80 to $130 \ ^\circ\text{C}$. As shown in Table 2.1, the monomer reactivity of DCP was higher than that of MMT in any condition. With increasing the reaction temperature, $r_{DCP}/r_{MMT}$ decreased to approximately 1. The copolymerization without quenching at a DCP/MMT feed ratio = 25/75 wt% conducted at $105 \ ^\circ\text{C}$ as a start temperature was completed in 60 sec. As a result, the internal final temperature of $140 \ ^\circ\text{C}$
Table 2.1. The monomer reactivity ratio of DCP and MMT

<table>
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<th>Reaction temp. / °C</th>
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<th>r_{MMT}</th>
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</table>
could be attained to give the copolymer in 96 % yield. Table 2.2 shows the copolymer composition obtained at the first stage and the final stage. Based on these findings, the reaction mechanism could be considered to be as follows: at the first stage, DCP is incorporated into the copolymer than the feed ratio. During the copolymerization, the internal temperature increased to give an ideal random copolymer, i.e. \( r_{\text{DCP}}/r_{\text{MMT}} = 1 \), may be obtained. At the final stage, on the other hand, MMT rich copolymer is obtained because reactive DCP is almost consumed. That is, the copolymer structure had a distribution of DCP unit in a macromolecule as shown in Scheme 2.2. This unique structure will provide an interesting aggregation behavior, which will be discussed in the next section.

Figure 2.1(a) shows \(^1\)H NMR spectra of the final product obtained at 105 °C as the initial temperature. The peaks at 5.30-5.80 ppm were assigned to vinyl protons of the copolymer main chain. In order to calculate the DCP unit incorporated into the copolymer, the integrated intensity of DCP’s single proton at 5.63 ppm (Hc) and MMT’s three protons at 3.68 ppm (He) were used for this purpose. The amount of DCP unit proved to be higher than the feed value because the monomer reactivity ratio of DCP was higher than that of MMT. Figure 2.1(b) displays \(^1\)H NMR spectra of the hydrogenated copolymer. In the hydrogenated copolymer, the vinyl protons disappeared, which demonstrated that the main-chain double bonds were perfectly hydrogenated.

### 2.3.2 Practical Properties of the Copolymer

Table 2.3 shows the practical properties of the copolymer. The incorporation of DCP unit of 27.2 wt% into the copolymer decreased the glass transition temperature from 171 to 148 °C, and improved antiwater absorption and toughness because flexible DCP unit without polar methyl ester group was incorporated into the polymer backbone. The amounts of water absorption of the homopolymer (0.4 %) and the copolymer (0.2 %) are very small compared with PMMA (1.93 %). Photoelastic coefficients of both polymers (3.0×10\(^{-13}\) cm\(^2\)/dyn) are much lower than that of polycarbonate (80×10\(^{-13}\) cm\(^2\)/dyn), which is often used as an optical material. These results indicate that the copolymer with high withdrawing strength as well as good heat resistance offers interesting possibility for applications in optics as a thin tough optical film.
Table 2.2. The copolymer composition of DCP and MMT

<table>
<thead>
<tr>
<th></th>
<th>Conversion / %</th>
<th>Copolymer Composition&lt;sup&gt;b&lt;/sup&gt; / wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DCP</td>
<td>MMT</td>
</tr>
<tr>
<td>First Stage</td>
<td>44.0</td>
<td>37.9</td>
</tr>
<tr>
<td>Final Stage</td>
<td>96.2</td>
<td>93.7</td>
</tr>
</tbody>
</table>

<sup>a</sup> Monomer feed ratio DCP/MMT = 25/75 (wt%) at 105 °C as an initial internal temperature.

<sup>b</sup> Calculated by monomer conversion using GC.
**Scheme 2.2.** Possible reaction mechanism of copolymer formation.
Figure 2.1. (a) $^1$H NMR spectrum of the copolymer before hydrogenation; (b) $^1$H NMR spectrum of the copolymer after hydrogenation.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Yield</th>
<th>Molecular weight</th>
<th>$M_w/M_n$</th>
<th>$\eta^c$</th>
<th>MMT/DCP unit$^d$</th>
<th>Degree of hydrogenation</th>
<th>$T_g^e$</th>
<th>Water Absorption$^f$</th>
<th>Film withdrawing strength$^g$</th>
<th>Photo elastic coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>homo polymer</td>
<td>94</td>
<td>139,000</td>
<td>42,900</td>
<td>3.2</td>
<td>0.78</td>
<td>100 / 0</td>
<td>&gt; 99.9</td>
<td>171</td>
<td>0.4</td>
<td>17</td>
</tr>
<tr>
<td>co polymer</td>
<td>96</td>
<td>53,400</td>
<td>27,100</td>
<td>4.1</td>
<td>0.65</td>
<td>75 / 25 / 73.5 / 27.2</td>
<td>&gt; 99.9</td>
<td>148</td>
<td>0.2</td>
<td>42</td>
</tr>
</tbody>
</table>

$^a$ Measured by SLS with THF solution.

$^b$ Measured by GPC using THF as eluent.

$^c$ Measured by intrinsic viscosity of 0.5 g/L in dichlorobenzene.

$^d$ Measured by $^1$H NMR spectroscopy in CDCl$_3$.

$^e$ Measured by DSC.

$^f$ According to ASTM D570; water immersion at 23 °C for 2 weeks.

$^g$ Measured by K7128 B.
2.3.3 Aggregation Behavior of the Hydrogenated Copolymer and Homopolymer

The copolymer had both hydrophobic DCP units and hydrophilic MMT units and a distribution of DCP units in a macromolecule as discussed in previous section; therefore, it is very interesting to investigate its solution properties in various solvents with the aid of DLS and SLS measurements and compare to the homopolymer.

Figure 2.2 depicts the DLS autocorrelation functions for the polar THF solutions of the homopolymer and the copolymer at concentrations of 10 wt%. Only one relaxation mode (fast mode) is observed for the homopolymer; however, two relaxation modes (fast and slow modes) were observed for the copolymer. In order to reveal these two relaxation modes, the $q^2$ dependences of $\Gamma$ for the THF solutions were examined as shown in Figure 2.3. $\Gamma$ of all relaxation modes in both polymers are proportional to $q^2$, indicating that they are diffusive. It can be concluded, therefore, that the fast mode in each polymer is attributed to the diffusive motion of each single polymer chain, while the slow mode in the copolymer is caused by aggregated polymer. It is conceivable to assume that the homopolymer is homogeneously dissolved, while the copolymer is heterogeneously dissolved in THF, resulting in the polymer aggregation.

The effects of both solvent polarity and temperature on the aggregation of the copolymer were investigated to clarify whether the selective depressions of the aggregation occurred or not. Figure 2.4 shows the decay rate distribution functions for the TL/CPE mixed solutions, the TL/CHX mixed solutions, the THF solutions and the DCM solutions. No polymer aggregates are detected in any of the four 15 wt% solutions of the homopolymer (Figure 2.4(a)) as well as the TL/CPE solution of the copolymer. The aggregates, however, are detected in the TL/CHX mixed solution, the THF solution and the DCM solution of the copolymer (Figure 2.4(b)). It is worth noting that the aggregate peak for the TL/CHX mixed solution of the copolymer ranges from 50 nm to 1 µm, while the peaks for the THF solution as polar solvent and the DCM solution as polar solvent of the copolymer range from 30 nm to about 100 µm (Figure 2.4(c)). These results indicate that the degree of aggregation of the copolymer increases with solvent polarity. Figure 2.5 displays the concentration dependence of the aggregate formation in the THF solution of the copolymer. It is interesting that the aggregate peak of the copolymer increases with concentration because solubility of the copolymer in high polar solvent decreases due to the low water absorption. This trend is also
Figure 2.2. Normalized autocorrelation functions of homopolymer and copolymer in THF solution with a concentration of 10 wt% at 23 °C and at $\theta = 60^\circ$. 
Figure 2.3. Scattering vector dependence of the decay rates of homopolymer and copolymer in THF solution with a concentration of 10 wt% at 23 °C.
Figure 2.4. (a) Decay rate distribution function versus the hydrodynamic radius of homopolymer in different four solutions with a concentration of 15 wt% at 23 °C and at $\theta = 60^\circ$; (b) decay rate distribution function versus the hydrodynamic radius of copolymer in different four solutions with a concentration of 15 wt% at 23 °C and at $\theta = 60^\circ$; (c) enlarged view of (b) in the hydrodynamic radius range from 10 to 10,000 nm.
Figure 2.5. Concentration dependence of the decay rate distribution function versus the hydrodynamic radius of copolymer in THF solution at 23 °C and at $\theta = 60^\circ$. 
identified in the TL/CHX mixed solution and the DCM solution of the copolymer. Figure 2.6 and 2.7 depict the temperature dependences of the aggregate formation in the TL/CHX mixed solution (Figure 2.6) and THF solution (Figure 2.7) of the copolymer, respectively. With increasing temperature from 23 to 50 °C, the aggregate size decreased in the TL/CHX mixed solution as hydrophobic solvent, while no change was observed in the THF solution as polar solvent. In order to discuss the relations between the aggregate formation and the solubility of these two polymers, the dielectric constants 3 of the four solvents, the second virial coefficients \( A_2 \) and the diffusive second virial coefficients \( k_D \) are listed in Table 2.4. Note that \( A_2 \) and \( k_D \) are due to single mode because the copolymer was not also confirmed to aggregate in dilute solutions.

As for the copolymer, the peak area ratios of the polymer aggregation increase, and \( A_2 \) and \( k_D \) corresponding to the polymer solubility decrease with increasing solvent polarity. Because the fast mode detected by DLS is strongly dependent on the solvent properties, \( k_D \) changes more significantly than \( A_2 \) on increasing the solvent polarity. Meanwhile, as for the homopolymer, no polymer aggregates are formed, and \( A_2 \) and \( k_D \) increase with increasing the solvent polarity. Based on these findings, it is concluded that in polar solvents such as THF and DCM, hydrophobic DCP-rich units in a macromolecule may aggregate with DCP as the core unit. It is also interesting to compare the result of the TL/CPE mixed solution with that of the TL/CHX mixed solution. Although both CPE and CHX are cyclic hydrocarbon solvents, the polymer aggregation behaviors in these two mixed solutions with the addition of TL are different from each other. The polymer aggregate is not formed in the TL/CPE mixed solution but is formed in the TL/CHX mixed solution. CPE, which has smaller size than CHX, may penetrate into the polymer and depress aggregate formation.

### 2.4 Conclusion

New cyclic saturated homopolymer and copolymer were prepared from MMT and DCP via ROMP. Kinetic studies indicate that a copolymer has distribution of DCP unit in a macromolecule. The distribution causes the copolymer to aggregate with DCP as the core unit in polar solvents such as THF and DCM; on the other hand, using TL/CPE mixed solvent or TL/CHX mixed solvent with an elevated heating temperature can prevent aggregation.
Figure 2.6. Temperature dependence of the decay rate distribution function versus the hydrodynamic radius of copolymer in TL/CHX mixed solution with a concentration of 15 wt% at $\theta = 60^\circ$. 

Copolymer 15 % TL/CHX solution
Figure 2.7. Temperature dependence of the decay rate distribution function versus the hydrodynamic radius of copolymer in THF mixed solution with a concentration of 15 wt% at $\theta = 60^\circ$. 
Table 2.4. The relations between aggregation and solubility of homopolymer and copolymer

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\varepsilon$</th>
<th>Peak area of aggregation$^a$</th>
<th>$10^4 A_2^a$ cm$^3$mol$^{-2}$</th>
<th>$k_D^a$ cm$^3$g$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TL/CPE =50/50</td>
<td>2.23$^b$</td>
<td>0.0 / 0.0</td>
<td>7.3 / 12.0</td>
<td>20.8 / 33.4</td>
</tr>
<tr>
<td>TL/CHX=50/50</td>
<td>2.20$^c$</td>
<td>0.0 / 7.2</td>
<td>8.1 / 12.0</td>
<td>20.2 / 30.0</td>
</tr>
<tr>
<td>THF</td>
<td>7.52$^d$</td>
<td>0.0 / 12.4</td>
<td>9.6 / 8.1</td>
<td>55.4 / 13.5</td>
</tr>
<tr>
<td>DCM</td>
<td>8.93$^d$</td>
<td>0.0 / 18.5</td>
<td>10.3 / 6.0</td>
<td>60.7 / 1.3</td>
</tr>
</tbody>
</table>

$^a$ Listed in the order corresponding to homopolymer/copolymer.
$^b$ The average value of TL (2.38)$^{10}$ and CPE (2.08)$^{10}$
$^c$ The average value of TL (2.38)$^{10}$ and CHX (2.02)$^{10}$
$^d$ The value of literature.$^{10}$

28
References

3 Aggregation Behavior of Polystyrene-\textit{b}-poly(ethylene/butylene)-\textit{b}-polystyrene Triblock Copolymer in \textit{N}-Methylpyrroldione

3.1 Introduction

In general, conventional polymer binders for the cathode of lithium-ion battery, which are necessarily used to bind the active material (lithium cobaltate) with the current collector (aluminum), cover up to 70 % of the surface of the active materials and work inevitably as electrical resistances.\textsuperscript{1} Then, the battery efficiency is worsened, to some extent, by the binders.\textsuperscript{2-4} It is desired to develop a new polymer binder such that a necessary amount of the binders and the coverage of the surface of the active materials are decreased, called the “spot-binding” binder.

We have been applying hydrogenated polystyrene-\textit{b}-poly(ethylene/butylene)-\textit{b}-polystyrene (SEBS copolymer) for the cathode binder of lithium-ion battery.\textsuperscript{5} SEBS copolymer is a versatile triblock copolymer, and form aggregates in several solvents, for example, tetrahydrofuran (THF),\textsuperscript{6} 4-methyl-2-pantanone,\textsuperscript{7} \textit{n}-octane,\textsuperscript{8} and \textit{n}-octane/4-methyl-2-pantanone.\textsuperscript{9,10} SEBS copolymer is synthesized in non-polar cyclohexane (CHX), followed by it being dissolved in polar \textit{N}-methylpyrroldione (NMP), which is a dispersant for polyvinylidene fluoride (PVDF) most widely used for the cathode binder at present. The CHX solution is very viscous, suggesting that the copolymer has a widespread form and achieves no “spot-binding” in non-polar CHX. On the other hand, the NMP solution is not viscous, suggesting that the copolymer has dispersion morphology and achieve “spot-binding” in polar NMP. Ovejero et al. have reported that non-polar solvents, i.e. CHX, cyclopentane and methylcyclohexane, are good solvents for the copolymer, suggesting that polar solvents could be poor choices.\textsuperscript{11} Therefore, if SEBS copolymer forms the compact aggregates in polar NMP, SEBS copolymer may work as the spot-binding binder, providing excellent battery properties.

In this chapter, we then carry out static and dynamic light scattering (SLS and DLS)
measurements for SEBS copolymer in NMP and also in CHX, and examine effects of the polarity of solvents on the aggregation behavior of the copolymer.

3.2 Experimental

3.2.1 Materials

CHX, n-hexane, and THF were obtained commercially and purified by distillation for use as polymerization solvents. SEBS copolymer with a styrene content of 49 wt% was synthesized via living anionic polymerization. After a certain amount of styrene (Wako Pure Chemical Industries) and CHX/n-hexane/THF = 90/10/3 (v/v/v) mixed solvent were charged into 50 L autoclave, the polymerization was initiated by addition of n-butyllithium (Asia Lithium) under adiabatic condition at 50 °C. The system was cooled to 30 °C after the completion of polymerization of styrene, followed by addition of a certain amount of butadiene (JSR). The polymerization of butadiene was also carried out under adiabatic condition. After completion of polymerization proceeded by second addition of a certain of styrene, the mixture was heated up to 90 °C. Finally, hydrogenation was carried out by addition of hydrogenation catalyst composed of titanocene compound at hydrogen pressure 1.0 MPa for 2 hours as described in a patent. The characterization results for the copolymer by gel permeation chromatography (GPC) are given in Table 3.1. The GPC characterization was performed in THF as an eluent at 40 °C using a TOSOH GPC instrument (model HLC-8120GPC) equipped with a TOSOH column (model TSK-GEL GMHXL) using RI detector and PS calibration.

3.2.2 Preparation of Polymer Solutions

Solutions for SLS measurement were prepared by dissolving the appropriate amount of SEBS copolymer in CHX and NMP at four concentrations of 0.2, 0.4, 0.6, and 0.8 wt%. Solutions for DLS measurement were prepared by dissolving the copolymer into the two solvents at four concentrations of 0.2, 0.4, 0.6, and 1.0 wt% in the same manner as the preparation for SLS. Solvents and polymer solutions were filtered through 0.2 and 0.5 μm PTFE filters, respectively, and measured directly into the scattering cell.
Table 3.1. Characterization results of GPC for SEBS copolymer

<table>
<thead>
<tr>
<th>$M_w$ / gmol$^{-1}$</th>
<th>$M_n$ / gmol$^{-1}$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>93,000</td>
<td>82,100</td>
<td>1.13</td>
</tr>
</tbody>
</table>
3.2.3 Static Light Scattering (SLS)

SLS measurements were carried out to determine mean-square radius of gyration $<S^2>$, second virial coefficient $A_2$ and weight-average molecular weight $M_w$ for four dilute solutions ($c = 0.2, 0.4, 0.6, 0.8$ wt%) of SEBS copolymer in the scattering angle range $30-150^\circ$ at $10^\circ$ intervals at $23^\circ$C. The measurements were made with an ALV/DLS/SLS-5000 light scattering system, with a $22$ mW He-Ne laser emitting vertically polarized light of $632.8$ nm wavelength as the light source. The detail of measurement principle and analysis method using a Berry plot$^{13}$ of SLS is described in Chapter 2. The refractive indexes of CHX and NMP at $\lambda_0 = 589$ nm and $23^\circ$C were determined with a Kyoto Electronics refractometer (model RA-500N) to be $1.4243$ and $1.4694$, respectively. The densities of the two solvents at $23^\circ$C were determined with a Kyoto Electronics density/specific gravity meter (model DA-505) to be $0.7757$ and $1.0310$ g/cm$^3$, respectively. The values of $\partial n/\partial c$ for the CHX solution and the NMP solution of the copolymer at $23^\circ$C were $0.1251$ and $0.0488$ cm$^3$/g, respectively.

3.2.4 Dynamic Light Scattering (DLS)

DLS measurements were carried out to determine translational diffusion coefficient $D$ for three dilute solutions ($c = 0.2, 0.4, 0.6$ wt%) of SEBS copolymer at four scattering angles of $60^\circ, 90^\circ, 120^\circ$, and $150^\circ$ at $23^\circ$C. Additionally, diffusion second virial coefficient $k_D$ and hydrodynamic radius $R_H$ were calculated, respectively. We also investigated the aggregation behavior of the copolymer in a dilute solution ($c = 1.0$ wt%) at $23^\circ$C and at $\theta = 60^\circ$. The measurements were made with the same apparatus as SLS measurements. The detail of measurement principle using Siegert’s relation$^{14}$ and analysis method using CONTIN analysis$^{15}$ of DLS is described in Chapter 2. Note that $k_D$ could be a solubility index of polymers because $k_D$ is related to $A_2$. The viscosities of the two solvents at $23^\circ$C were determined with a Toki Sangyo rotational viscometer (model RE-80L) to be $0.916$ and $1.757$ cP, respectively.

3.2.5 Calculation of Solubility Parameter

Calculation of solubility parameter was carried out to predict the compatibilities of CHX, NMP and the two polymer components, PS and poly(ethylene/butylene) (PEB), composing
SEBS copolymer. First, Hansen solubility parameter, which is divided into three components, dispersion $\delta_d$, polarity $\delta_p$, and hydrogen bond $\delta_h$ terms, was calculated by using the calculation method of Krevelen with group contribution method.\textsuperscript{17} The three components are defined in terms of cohesion energy $E_{coh}$, atom group parameter $F_i$ of $E_{coh}$, and molar molecular volume $V$.

$$
\delta_d = \frac{\sum F_{di}}{V}, \quad \delta_p = \sqrt{\frac{\sum F_{pi}^2}{V}}, \quad \delta_h = \sqrt{\frac{\sum F_{hi}}{V}} \quad (3.1)
$$

Next, Hildebrand solubility parameter $\delta$ was calculated by using Hansen solubility parameter because both solubility parameters have the relationship as follows:

$$
\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3.2)
$$

Note that solubility parameters of the copolymer were calculated by the summation of each solubility parameter multiplied with each component ratio (molar ratio) of PS and PEB in the copolymer.

### 3.3 Results and Discussion

#### 3.3.1 Dilute Solution Properties of SEBS Copolymer

Figure 3.1 shows the Berry plots in SLS for the CHX solution and the NMP solution of SEBS copolymer. As listed in Table 3.2, it is interesting to note that $M_w$ in the NMP solution (6.21×10$^6$ g/mol) is much larger than that in the CHX solution (9.5×10$^4$ g/mol), although $<S^2>^{1/2}$ in the NMP solution (15.1 nm) is smaller than that in the CHX solution (23.4 nm). The large difference between both $M_w$ values suggests that the copolymer exists as single chain in CHX, whereas aggregates in NMP. Additionally, compared second virial coefficient $A_2$ in the CHX solution (1.61 cm$^3$mol/g$^2$) with that in the NMP solution (0.05 cm$^3$mol/g$^2$), it is concluded that non-polar CHX is a better solvent than polar NMP for the copolymer, agreeing with the conclusion in the report by Ovejero et al.\textsuperscript{11}
**Figure 3.1.** Berry plots in SLS for SEBS copolymer in CHX solution and NMP solution.
Table 3.2. Characterization results of SLS and DLS for SEBS copolymer

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$M_w$</th>
<th>$\langle S^2 \rangle^{1/2}$</th>
<th>$10^4 A_2$</th>
<th>$R_h$</th>
<th>$k_D$</th>
<th>$\rho$</th>
<th>$d$</th>
<th>$N_{agg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHX</td>
<td>95,000</td>
<td>23.4</td>
<td>1.61</td>
<td>9.8</td>
<td>95.5</td>
<td>2.3</td>
<td>0.04</td>
<td>-</td>
</tr>
<tr>
<td>NMP</td>
<td>6,210,000</td>
<td>15.1</td>
<td>0.05</td>
<td>27.4</td>
<td>15.3</td>
<td>0.55</td>
<td>0.12</td>
<td>65</td>
</tr>
</tbody>
</table>
Figure 3.2 shows the decay rate distribution functions in DLS for the CHX solution and the NMP solution of SEBS copolymer at a concentration of 1 wt%. Although the NMP solution had a single peak alone, whose peak top was located at $R_H \sim 20$ nm, the CHX solution had small and large peaks, whose peak tops were located at $R_H \sim 7$ and 100 nm, respectively. It is considered that the small peak is attributed to single polymer chain (fast mode), whereas the large peak is caused by aggregated polymer (slow mode). Note that the amount of aggregated polymer in the CHX solution should be in minute amounts given the relationship that scattered light intensity is proportional to the sextuplicate value of $R_H$, and the two peaks ratio, small/large $\sim 0.5/1.0$, in the CHX solution. Thus, the large peak represents only a very small amount of aggregated polymer even its area looks large. In CHX, in other words, most of the copolymer exists as single chain in the dilute region up to 1 wt%. That is why translational diffusion coefficient $D$ of fast mode alone was plotted to determine $R_H$ in the CHX solution as shown in Figure 3.3, which shows the concentration dependences of $D$ in DLS for the CHX solution and the NMP solution of the copolymer. The data points for both samples are seen to follow a straight line, and thus $k_D$ were accurately determined from its ordinate intercept and slope.

As summarized in Table 3.2, it is interesting to note that $R_H$ in the NMP solution (27.4 nm) is much larger than that in the CHX solution (9.8 nm), although $<S^2>^{1/2}$ in the NMP solution (15.1 nm) is smaller than that in the CHX solution (23.4 nm). This suggests that conformations of both a single polymer chain in the CHX solution and an aggregated polymer in the NMP solution differ greatly from each other. Additionally, compared $k_D$ in the CHX solution (95.5 cm$^3$/g) with that in the NMP solution (15.3 cm$^3$/g), the magnitude relationship between both $k_D$ values proved to be the same as that of $A_2$ in both solutions. This indicates that the copolymer has much better solubility in non-polar CHX than in polar NMP, agreeing with the conclusion in the report by Ovejero et al.$^{11}$ From these results, therefore, it is concluded that SEBS copolymer exists as single chain because of the high solubility in CHX, whereas the copolymer aggregates due to the low solubility in NMP. This is why molecular weight of the copolymer in the CHX solution is much smaller than that in the NMP solution.

3.3.2 Aggregation Behavior of SEBS Copolymer

The dimensionless parameter $\rho$ defined as the ratio of $<S^2>^{1/2}/R_H$ is commonly used to
Figure 3.2. Decay rate distribution function versus hydrodynamic radius of SEBS copolymer in CHX solution and NMP solution with a concentration of 1 wt% at 23 °C and at $\theta = 60^\circ$. 
Figure 3.3. Concentration dependence of $D$ in DLS for SEBS copolymer in CHX solution (fast mode) and NMP solution.
examine polymer conformation in solution. Polymer conformation changes from a rigid rod \((\rho = \infty)\) to a hard sphere \((\rho = 0.775)\) through a random coil \((\rho = 1.2-1.5)\).\(^{18}\) For a nondraining core-shell micelle, \(\rho\) is less than 0.775 if the core is denser than the shell. On the basis of these values, it may be considered that SEBS copolymer in CHX has the form of flexible rod because of the value of \(\rho = 2.3\) listed in Table 3.2. Note that, however, this value was overestimated due to the slow mode, whose peak was larger than the fast mode peak in the CHX solution at a concentration of 1 wt% in DLS as shown in Figure 3.2. Scattered light of the CHX solution in SLS should include the slow mode even in the dilute region up to 1 wt%. Thus, \(\langle S^2 \rangle^{1/2}\) of a single polymer chain due to the fast mode alone should be less than 23.4 nm, leading to the \(\rho\) value below 2.3. This means that the copolymer in CHX has the form close to random coil. In NMP, on the other hand, it is considered that the copolymer aggregates into the core-shell micelle, in which the core is much denser than the shell according to the value of \(\rho = 0.55\).

According to the Hildebrand and the Hansen solubility parameters of CHX, NMP and the two polymer components summarized in Table 3.3, non-polar CHX \((16.8 \text{ (MPa)}^{1/2})\) is confirmed to be a common better solvent for both PS \((17.7 \text{ (MPa)}^{1/2})\) and PEB \((16.1 \text{ (MPa)}^{1/2})\) components than polar NMP \((23.0 \text{ (MPa)}^{1/2})\), which could be a common poor solvent for them. To be more precise, PS solubility to NMP is higher than PEB solubility because PS is slightly closer to NMP than PEB with respect to Hildebrand solubility parameter. In Hansen solubility parameter, both polarity \((\delta_p = 12.3 \text{ (MPa)}^{1/2})\) and hydrogen-bond \((\delta_h = 7.2 \text{ (MPa)}^{1/2})\) terms of NMP are much larger than those of CHX \((\delta_p = \delta_h = 0.0 \text{ (MPa)}^{1/2})\), involving in the difference of dielectric constant between NMP \((\varepsilon = 32.2)\) and CHX \((\varepsilon = 2.0)\).\(^{19}\) Therefore, it is concluded that the core and the shell of the core-shell micelle formed of SEBS copolymer in NMP is PEB and PS component, respectively. The driving force for the aggregation into the core-shell micelle would be the slight difference of solubility to NMP between both non-polar polymer components.

Generally, small-angle neutron scattering (SANS) is needed to determine the core radius \(R_c\) and the shell thickness \(\Delta R (= R - R_c)\) of the core-shell micelle with a radius \(R\). In this study, however, we tried to calculate \(R_c\) and \(\Delta R\) using both LS data and the relation expression, which has been formulated by Tu et al.\(^{20}\) on the basis of the model used by Noolandi and Hong\(^{21}\) and Leibler et al.\(^{22}\) In this model, it is assumed that the core and the shell have different, but uniform densities.
Table 3.3. Solubility parameters of the materials used in this study

<table>
<thead>
<tr>
<th>Solubility parameter</th>
<th>CHX</th>
<th>NMP</th>
<th>PS</th>
<th>PEB</th>
<th>SEBS*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_d$ (MPa)$^{1/2}$</td>
<td>16.8</td>
<td>18.0</td>
<td>17.7</td>
<td>16.1</td>
<td>16.8</td>
</tr>
<tr>
<td>$\delta_p$ (MPa)$^{1/2}$</td>
<td>0.0</td>
<td>12.3</td>
<td>1.1</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>$\delta_h$ (MPa)$^{1/2}$</td>
<td>0.0</td>
<td>7.2</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>$\delta$ (MPa)$^{1/2}$</td>
<td>16.8</td>
<td>23.0</td>
<td>17.7</td>
<td>16.1</td>
<td>16.8</td>
</tr>
</tbody>
</table>

* $\delta_{SEBS} = 0.437$ (molar ratio) $\times \delta_{PS} + 0.563$ (molar ratio) $\times \delta_{PEB}$
where $A$ is the ratio of $M_c/M_s$ obtained from the masses of the core $M_c$ and the shell $M_s$, and $x$ is the ratio of $R_c/R$. Note that $M_c/M_s$ equals to the constant mass ratio of the insoluble parts (PEB) and soluble parts (PS), independent of the actual density distributions of the core and the shell. Therefore, we determined $x = 0.164$ with $\rho = 0.55$ according to eq. (3.3), and finally obtained $R_c = 4.5$ nm and $\Delta R = 22.9$ nm because of $R_c = R_H x$ and $\Delta R = R_H (1 - x)$ by replacing $R$ with $R_H$. From the above-mentioned discussion using solubility parameters and the values of both $R_c$ and $\Delta R$, the core-shell micelle formed of the copolymer in NMP could be illustrated as shown in Scheme 3.1. Note that this micelle conformation in NMP is based on the coarse graining model with the assumption that both the core and the shell have each uniform density. In other words, this model micelle is different from an actual micelle in a narrow sense. An actual micelle could have the mixing part composed of both the core and the shell with each nonuniform density. Therefore, we would like to limit ourselves to the rough consideration that an actual valid core radius is possibly larger than $R_c = 4.5$ nm.

### 3.3.3 Correlation Between Solvent Polarity and Aggregation Behavior

Aggregation number $N_{agg}$ is an important parameter to describe the characteristic of an aggregated polymer. From the weight-average molecular weight of a single polymer chain $M_{w, single}$ in the CHX solution and that of a core-shell micelle $M_{w, mic}$ in the NMP solution, the $N_{agg}$ value of the core-shell micelle of SEBS copolymer was determined to be 65 by using the following equation.

$$N_{agg} = \frac{M_{w, mic}}{M_{w, single}}$$  \hspace{1cm} (3.4)

Additionally, average chain densities $d$ of a single polymer chain in CHX and a core-shell micelle formed in NMP were determined to be 0.04 and 0.12 $g/cm^3$, respectively, from each $M_w$ and $R_H$ in the two solutions by using the following equation.
Scheme 3.1. Difference between conformations of SEBS copolymer in CHX and NMP.
When compared these values of $N_{agg} = 65$ and $d = 0.12 \text{ g/cm}^3$ for the core-shell micelle formed in polar NMP with those of $N_{agg} = 12$ and $d = 0.079 \text{ g/cm}^3$ for the micelle formed in non-polar $n$-octane, it is suggested that the copolymer forms a more compact aggregate in polar solvents than in non-polar solvents according to the difference of dielectric constant between NMP ($\varepsilon = 32.2$) and $n$-octane ($\varepsilon = 1.94$). Note that $n$-octane is a selective solvent for PEB, i.e. PS forms core and PEB forms shell in $n$-octane unlike in NMP. This component difference of the copolymer micelles between $n$-octane and NMP should be due to the effect of solvent polarity.

To investigate the correlation between solvent polarity and aggregation behavior of SEBS copolymer in detail, $\rho$ values for the copolymer in two solvents, i.e. THF and 4-methyl-2-pentanone, along with those in CHX and NMP were plotted against $\delta$ in Figure 3.4. The $\rho$ values in THF (1.0) and 4-methyl-2-pentanone (0.67) were cited from the reports by Wu et al. and Villacampa et al., respectively. Note that these styrene contents of the copolymers cited as the comparison data of $\rho$ values are 30-32 wt% which are different from the styrene content (49 wt%) of SEBS copolymer used in this study. If these copolymers had the same styrene content as that of SEBS copolymer, PS shell of the aggregate and/or micelle in the two polar solvents would be larger than each original conformation. Accordingly, these $\rho$ values in the two solvents would be less than each value cited, indicating that they are slightly close to the $\rho$ value (0.55) in NMP. That is why we consider that these $\rho$ values are good reference data to discuss the aggregation behavior of the copolymer in polar solvents. On the other hand, the $\delta$ values of THF and 4-methyl-2-pentanone were determined to be 18.0 and 18.5 (MPa)$^{1/2}$, respectively, by means of the same method as the calculations for those of CHX (16.8 (MPa)$^{1/2}$) and NMP (23.0 (MPa)$^{1/2}$). A solid line shows the $\delta$ dependence of $\rho$ in the three solvents other than CHX. A dash line indicates the $\delta$ value of the copolymer (16.9 (MPa)$^{1/2}$). It is interesting to note that $\rho$ decreases with increasing $\delta$ ranging from 18.0 to 23.0 (MPa)$^{1/2}$, meaning that the aggregate compactness depends largely on solvent polarity. Therefore, it is concluded that the increase in solvent polarity leads to the decrease in solubility of SEBS copolymer with the two non-polar polymer components, PS and PEB, resulting in formation of the core-shell micelle with the highly dense PEB core and the thick PS shell in polar NMP.
Figure 3.4. Plots of $\rho$ against $\delta$ for SEBS copolymer in several solvents: ○, CHX and NMP (present data); △, THF (Wu et al.); ◇, 4-methyl-2-pentanone (Villacampa et al.).
In addition, $\rho$ determined to be 2.3 in CHX was expected to have a value ranging from 1.2 to 1.5 by extrapolation of the solid line to $\delta = 16.8$ (MPa)$^{1/2}$. Accordingly, $\rho$ in CHX was confirmed again to be overestimated due to the slow mode. Given that the above-mentioned discussion for the $\rho$ value in the CHX solution, and the experimental result says that CHX is a better solvent than NMP for SEBS copolymer, it is concluded that the copolymer in CHX has the form close to random coil as shown in Scheme 3.1. As concluded above, SEBS copolymer forms the core-shell micelle in NMP, which could achieve “spot binding” in binding both active material and current collector. The copolymer in NMP is expected to provide excellent properties as a cathode binder of lithium-ion battery.

### 3.4 Conclusion

SEBS copolymer consisting of non-polar polymer components of PS (49 wt%) and PEB (51 wt%) exists as single chain close to random coil with the high solubility in non-polar CHX. In polar NMP, the copolymer aggregates into the core-shell micelle, consisting of PEB core surrounded by PS shell, due to the low solubility caused by the difference of polarity between the two polymer components and NMP. The core-shell micelle formed in NMP is composed of 65 polymer chains, having three times larger average chain density ($d = 0.12$ g/cm$^3$) than a single polymer chain ($d = 0.04$ g/cm$^3$) in CHX. The aggregate compactness of the copolymer depends largely on solvent polarity, resulting in formation of the highly dense PEB core ($R_c = 4.5$ nm) and the thick PS shell ($\Delta R = 22.9$ nm) in high-polar NMP. The particular core-shell micelle could provide excellent properties as a cathode binder of lithium-ion battery.

### References

4 Aggregation Behavior of Poly(γ-benzyl-L-glutamate)-b-polyisoprene-b-poly(γ-benzyl-L-glutamate) Rod-Coil-Rod Triblock Copolymer in N,N-Dimethylformamide

4.1 Introduction

Poly(γ-benzyl-L-glutamate) (PBLG) is a rod-like polypeptide which forms two secondary structures: α-helices stabilized by intramolecular hydrogen bonds and β-sheets stabilized by intermolecular hydrogen bonds.\(^1\) Various kinds of block copolymers composed of PBLG block(s) along with PBLG itself have been widely studied in this decade for medical applications because of their excellent biocompatibility.\(^2\)\(^-\)\(^7\)

We have been developing PBLG-b-polyisoprene-b-PBLG (GIG copolymer),\(^8\) which has been already shown to have a good affinity for tissue and blood,\(^9\) as a biomaterial. In solution, PBLG maintains α-helix, that is, rod-like conformation,\(^10\)\(^,\)\(^11\) whereas polyisoprene (PIP) has the form of random coil.\(^12\)\(^,\)\(^13\) Thus, GIG copolymer may be described as a once-broken rod\(^14\) because the middle block (PIP) is intolerant of helix formation and so acts as a flexible joint portion of PBLG rods. PBLG is soluble in polar solvents, but is hard to dissolve into non-polar solvents\(^10\), whereas PIP is soluble in non-polar solvents, but is hard to dissolve into polar solvents. Given the solubility difference between the two polymers to solvents, GIG may form aggregates of the core–shell structure with the PIP core and the PBLG shell in polar solvents. Although such unique properties of GIG copolymer may seem to affect, to large extent, properties of the GIG-based biomaterials, few studies of the solution properties or aggregation behavior of the copolymer have been reported.\(^14\)

In this chapter, we then carry out static and dynamic light scattering (SLS and DLS) measurements for GIG copolymer in the mixed solvents of (polar) dimethyformamide (DMF) and (non-polar) toluene with varying the solvent composition, and examine effects of the solvent composition on the aggregation behavior of the copolymer.
4.2 Experimental

4.2.1 Materials

Dichloromethane, diethyl ether, methanol, \( n \)-hexane, and \( n \)-butyl ammonium were obtained commercially, and were used without purification for the polymerization. \( \gamma \)-Benzyl-L-glutamate \( N \)-carboxyanhydride (\( \gamma \)-BLG-NCA) was purchased from CHUO KASEIHIN. Amine-terminated polyisoprene (AT-PIP) was synthesized by the same manner as a patent.\(^8\)

4.2.2 Synthesis of PBLG

In a 100 mL round-bottom flask flushed with dry nitrogen and fitted with a stirrer were placed \( \gamma \)-BLG-NCA and dichloromethane. The polymerization was initiated by the addition of \( n \)-butyl ammonium at room temperature (r.t.) with the ratio of monomer to initiator (\( n \)-butyl ammonium), \( M_0/I_0 = 50.1 \). After kept on stirring at r.t. for 4 hours, the polymerization was terminated by pouring the reaction solution into excess of diethyl ether. Finally, solid PBLG was obtained by drying. The characterization result for the polymer by gel permeation chromatography (GPC) is given in Table 4.1. The GPC characterization was performed in \( N, N \)-dimethylformamide (DMF) as an eluent with lithium bromide (LiBr) at 35 °C using a Shimazu GPC instrument (SIL-120A) equipped with two TOSOH columns (TSKgel \( \alpha \)-2500), RI detector, and polystyrene calibration.

4.2.3 Synthesis of GIG Copolymer

GIG copolymer was synthesized as described in the patent.\(^8\) The detailed synthesis method is as follows. In a 100 mL round-bottom flask purged with dry nitrogen and fitted with a stirrer were placed \( \gamma \)-BLG-NCA and dichloromethane. The polymerization was initiated by the addition of AT-PIP at r.t. with the ratio of monomer (\( \gamma \)-BLG-NCA) to initiator (AT-PIP), \( M_0/I_0 = 100.7 \). After kept on stirring at r.t. for 4 hours, the polymerization was terminated by pouring the reaction solution into excess of methanol. The polymer was redissolved into dichloromethane followed by reprecipitation using \( n \)-hexane. After drying, we obtained two kinds of GIG copolymers with different monomer composition, which proved to be PBLG/PIP/PBLG=21.3/57.4/21.3 (GIG copolymer 1) and 29.8/40.4/29.8 (GIG copolymer 2)
Table 4.1. Characterization results of GPC for PBLG and GIG copolymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>PBLG/PIP/PBLG / mol%</th>
<th>$M_w^a /$ gmol$^{-1}$</th>
<th>$M_n^a /$ gmol$^{-1}$</th>
<th>$M_w / M_n^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBLG</td>
<td>50/0/50</td>
<td>12,500</td>
<td>8,900</td>
<td>1.41</td>
</tr>
<tr>
<td>GIG copolymer 1</td>
<td>21.3/57.4/21.3</td>
<td>64,200</td>
<td>24,200</td>
<td>2.65</td>
</tr>
<tr>
<td>GIG copolymer 2</td>
<td>29.8/40.4/29.8</td>
<td>94,900</td>
<td>39,600</td>
<td>2.39</td>
</tr>
</tbody>
</table>

$^a$ Measured using DMF for PBLG and chloroform for GIG copolymers as eluent, and calibration with polystyrene.
(mol%) by NMR measurements as shown in Scheme 4.1. The microstructure of AT-PIP was also found to be a mixture of 1,4-/1,2-/3,4-type in a ratio of 33.9/5.9/60.2 (mol%). Note that the molecular structure of 1,4-type PIP was described as an example of PIP blocks as a matter of convenience in Scheme 4.1. The characterization results for the copolymers by GPC are also listed in Table 4.1. The GPC characterization was performed in chloroform as an eluent at 35 °C using a Waters GPC instrument (model 2695) equipped with two TOSOH columns (TSKgel Multipore HXL-M and TSKguardcolumn MP(XL)), RI detector, and polystyrene calibration.

4.2.4 Preparation of Polymer Solutions

PBLG solutions for light scattering (LS) measurements were prepared by dissolving the appropriate amount of the polymer into DMF/toluene = 100/0, 30/70 (wt%) at a concentration of 1.0 wt%. GIG copolymer solutions for LS measurements were prepared by dissolving the appropriate amount of the copolymer into DMF/toluene = 100/0, 90/10, 70/30, 50/50 (wt%) at a concentration of 1.0 wt% and DMF/toluene = 30/70 at four concentrations of 0.8, 1.0, 1.2, and 1.5 wt%. Solvents and polymer solutions were filtered through 0.2 and 0.5 μm PTFE filters, respectively, and measured directly into the scattering cell.

4.2.5 Dynamic Light Scattering (DLS)

DLS measurements were carried out to investigate the aggregation behavior of PBLG in dilute DMF solution and dilute DMF/toluene = 30/70 solution, and GIG copolymers in dilute DMF/toluene = 100/0, 90/10, 70/30, 50/50, 30/70 solutions at a concentration of 1.0 wt% at a scattering angle of 60° at 23 °C. We also determined translational diffusion coefficient $D$ for three dilute DMF/toluene = 30/70 solutions of GIG copolymer ($c = 1.0, 1.2, 1.5$ wt%) at five scattering angles of 30°, 60°, 90°, 120°, and 150° at 23 °C. Additionally, diffusion second virial coefficient $k_D$ and hydrodynamic radius $R_H$ were calculated, respectively. The measurements were made with an ALV/DLS/SLS-5000 light-scattering system, with a 22 meW He-Ne laser emitting vertically polarized light of 632.8 nm wavelength as the light source. The detail of measurement principle using Siegert’s relation$^{15}$ and analysis method using CONTIN analysis$^{16}$ of DLS is described in Chapter 2. Note that $k_D$ could be a solubility index of polymers because $k_D$ is related to second virial coefficient $A_2$. The refractive
GIG copolymer 1: $m/n/m = 21.3/57.4/21.3$ (mol%)
GIG copolymer 2: $m/n/m = 29.8/40.4/29.8$ (mol%)

**Scheme 4.1.** Chemical structure of GIG copolymers.
indexes of DMF, toluene, and the mixed solvents, DMF/toluene = 90/10, 70/30, 50/50, 30/70, at $\lambda_0 = 589$ nm at 23 °C were determined with a Kyoto Electronics refractometer (model RA-500N). The densities of DMF and the mixed solvents at 23 °C were determined with a Kyoto Electronics density/specific gravity meter (model DA-505). The viscosities of DMF and the mixed solvents at 23 °C were determined with a Toki Sangyo rotational viscometer (model RE-80L).

4.2.6 Static Light Scattering (SLS)

SLS measurements were carried out to determine mean-square radius of gyration $<S^2>$, second virial coefficient $A_2$ and weight-average molecular weight $M_w$ for four dilute DMF/toluene = 30/70 solutions of GIG copolymer ($c = 0.8, 1.0, 1.2, 1.5$ wt%) in the scattering angle range 30°-150° with 10° intervals at 23 °C. The measurements were made with the same apparatus as DLS measurements. The detail of measurement principle and analysis method using a Berry plot of SLS is described in Chapter 2. The $\partial n/\partial c$ for the DMF/toluene solution of the copolymer at 23 °C was 0.0632 cm³/g.

4.2.7 Calculation of Solubility Parameter

Calculation of solubility parameter for the solvents used in both LS measurements was carried out to find out the main factor for the aggregation of GIG copolymer. Hansen solubility parameter, which is divided into three components, i.e., dispersion $\delta_d$, polarity $\delta_p$, and hydrogen bond $\delta_h$ terms, was calculated by using the calculation method of Krevelen with group contribution method. The three components are defined in terms of the cohesion energy $E_{coh}$, the atom group parameter $F_i$ of $E_{coh}$ and molar molecular volume $V$.

$$\delta_d = \frac{\sum F_{di}}{V}, \quad \delta_p = \sqrt{\frac{\sum F_{pi}^2}{V}}, \quad \delta_h = \sqrt{\frac{\sum E_{hi}}{V}}$$ (4.1)

Solubility parameters of the DMF/toluene mixed solvents were calculated by the summation of each solubility parameter multiplied with each mixture ratio (molar ratio) of DMF and toluene.
4.3 Results and Discussion

4.3.1 Aggregation Behavior of GIG Copolymer

Figure 4.1 shows the decay rate distribution function for the DMF solution of GIG copolymer 2 with a concentration of 1.0 wt% at 23 °C and at θ = 60° in DLS. Note that \( R_H \) is used instead of \( \tau \) for the horizontal axes in all of the figures displaying decay rate distribution function to compare the size of single polymer chain directly with that of aggregated polymer. Because all of the solutions measured in DLS to give decay rate distribution functions have the equal concentration of 1.0 wt%, we considered the comparison of both sizes using \( R_H \) to be preferable to make both interpretation and consideration easy for all of the data. The copolymer in DMF had two peaks with each peak top at around \( R_H = 7 \) and 200 nm, respectively. The smaller peak is attributed to a fast mode, whereas the larger peak is due to a slow mode. This consideration would be further developed on the basis of Figure 4.2, which shows the \( q^2 \)-dependence of \( \Gamma \) for the DMF solution of GIG copolymer 2 with a concentration of 1.0 wt% at 23 °C. \( \Gamma \) of both relaxation modes for the DMF solution are proportional to \( q^2 \), indicating that they are diffusive. It can be concluded, therefore, that the fast mode is ascribed to the diffusive motion of single polymer chains, whereas the slow mode is caused by the diffusive motion of aggregated polymers. Note that the main component in the DMF solution should not be aggregates but should be single chain given the relationship that scattered light intensity is proportional to the sextuplicate value of \( R_H \), and the two peaks ratio, small/large = 0.3/1.0.

Figure 4.3 shows the decay rate distribution functions for the four solutions, whose solvent compositions are (a) DMF = 100, (b) DMF/toluene = 90/10, (c) DMF/toluene = 70/30, and (d) DMF/toluene = 50/50 (wt%), of GIG copolymer 2 with a concentration of 1.0 wt% at 23 °C and at \( \theta = 60° \) in DLS. As the toluene content increased, the smaller peak due to single polymer chains increased, whereas the larger peak due to aggregated polymers decreased. Ultimately, no aggregate was observed at the toluene content of 50 wt%. In these solution systems, the addition of toluene corresponds to the decrease in solvent polarity. Actually, it was confirmed that the copolymer homogeneously dissolved in the given low-polar region, leading to disappearance of the aggregates. As previously noted, polar solvents are good solvents for PBLG, but are poor solvents for PIP. On the other hand, nonpolar solvents are poor solvents for PBLG, but are good solvents for PIP. Given the difference in solubility
Figure 4.1. Decay rate distribution function versus the hydrodynamic radius of GIG copolymer 2 in DMF with a concentration of 1.0 wt % at 23 °C and at $\theta = 60 ^\circ$.
Figure 4.2. Scattering vector dependence of the decay rates of GIG copolymer 2 in DMF with a concentration of 1.0 wt% at 23 °C.
Figure 4.3. Decay rate distribution function versus the hydrodynamic radius of GIG copolymer 2 in the four solvents, that is, (a) DMF = 100, (b) DMF/Toluene = 90/10, (c) DMF/Toluene = 70/30, and (d) DMF/Toluene = 50/50, with a concentration of 1.0 wt % at 23 °C and at \( \theta = 60^\circ \).
between PBLG and PIP to solvents, it is considered that the aggregation of the copolymer in DMF is caused by the difference in solubility between both polymer blocks to DMF. This would be supported by the consideration for Figure 4.4, which shows the decay rate distribution functions for the DMF/toluene = 50/50 and 30/70 solutions of GIG copolymer 1 with a concentration of 1.0 wt% at 23 °C and at \( \theta = 60^\circ \) in DLS. It is interesting to note that GIG copolymer 1 aggregates in DMF/toluene = 50/50, in which GIG copolymer 2 has no aggregation. Ultimately, GIG copolymer 1 had no aggregation in DMF/toluene = 30/70. These results indicate that a large amount of good solvents for PIP blocks are necessary to redissolve the aggregates of the copolymer having much PIP blocks than GIG copolymer 2.

In order to quantitatively investigate the correlation between solubility and aggregation behavior of GIG copolymer in detail, solubility parameter was used. According to the solubility parameter dependence of the aggregation peak ratio of GIG copolymer 2 shown in Figure 4.5, both polarity \( \delta_p \) and hydrogen bond \( \delta_h \) terms proved to make an impact more largely on the aggregation behavior than dispersion \( \delta_d \) terms. Note that the aggregation peak ratio corresponds to the relative scattered light intensity obtained from the aggregates alone because the total scattered light intensity obtained from both the single chains and the aggregates has been normalized to be 100 \%. Because scattered light intensity is generally proportional to the square of the mass of scattering objects, the number of the aggregates should be too small compared to that of single chain. Accordingly, we considered correlating the number of the aggregates with solubility parameter to be hard to interpret the correlation results due to the small change of the number of the aggregates in varying solubility parameter. That is why the aggregation peak ratio was used to investigate the correlation between solubility and aggregation behavior in this study. These results mean that both polarity and hydrogen bond dominate the solubility in the aggregation system of the copolymer, suggesting that polarity depends highly on hydrogen bonds. Therefore, it is conceivable to assume that polarity caused by hydrogen bond controls the aggregation behavior. In order to examine the polarity effect to the aggregation of the copolymer in DMF/toluene solution systems, the apparent hydrodynamic radii \( R_{\text{Happ}} \) of both a single chain and an aggregate of GIG copolymer 2 in each solution system with a concentration of 1.0 wt% were plotted against \( \delta_p \) alone in Figure 4.6. The single chains had no size change over the whole polar region examined, whereas the aggregates monotonically grew as the solvent polarity increased. These results define that the aggregate growth depends highly on the specific factor of polarity, suggesting that the main driving force to the aggregation in DMF is the polarity
Figure 4.4. Decay rate distribution function versus the hydrodynamic radius of GIG copolymer 1 in DMF/toluene = 50/50 and 30/70 with a concentration of 1.0 wt % at 23 °C and at $\theta = 60^\circ$. 
Figure 4.5. Solubility parameter dependence of the aggregation peak ratio of GIG copolymer 2.
Figure 4.6. Solubility parameter dependence of the apparent hydrodynamic radius for a single polymer and an aggregated polymer of GIG copolymer 2 with a concentration of 1.0 wt %.
difference between both polymer blocks.

From all of the results shown so far, our understanding for the aggregation behavior of GIG copolymer in DMF is as follows. It is known that dilute PBLG/DMF solution system at r.t. has only isotropic phase\textsuperscript{13,20,21} and semidilute PBLG/toluene solution system has gelation above crossover concentration $c^*$.\textsuperscript{22} Compared actual concentration $c$ (1.0 wt% $= 8.9 \times 10^{-3}$ g/cm\(^3\)) of the DMF/toluene $= 30/70$ solution of GIG copolymer 1 with $c^*$ (5.5$ \times 10^{-2}$ g/cm\(^3\)) of the solution determined by using the following equation,

$$c^* = \frac{3M_w}{4\pi N_A R_H^3}$$ \hspace{1cm} (4.2)

it is obvious that the actual solution concentration is in dilute region according to $c/c^* < 0.2$. Besides, PBLG actually dissolved well in both DMF and DMF/toluene $= 30/70$ without aggregates at r.t. as shown in Figure 4.7. Note that the difference of each peak width may be due to the difference in existence form of PBLG between in the DMF solution and in the DMF/toluene mixed solution. Perhaps, rod form of PBLG may also slightly change due to the polarity difference between both solutions. Given these findings, PBLG blocks of GIG copolymer should not aggregate or gelate in the DMF solution and the whole DMF/toluene solution systems examined. On the other hand, we confirmed that PIP (AT-PIP) does not dissolve in DMF at all, but dissolve in toluene. Note that LS measurements for a toluene solution of PIP were impossible because the refractive index of PIP ($n = 1.521$) is almost equal to that of toluene ($n = 1.496$). Thus, only PIP blocks of the copolymer would strongly aggregate when the copolymer is present in DMF. In other words, the above-mentioned main driving force to the aggregation in DMF should originate with PIP blocks of the copolymer.

As described in Scheme 4.2, therefore, it is concluded that GIG copolymer in DMF aggregates into a core-shell micelle consisting of flexible PIP core surrounded by rigid PBLG shell.

Given the change of the aggregate size shown in Figure 4.6, it is considered that the core-shell micelle would loosen into many single chains, and completely disappear as the solvent composition is close to toluene-rich, that is, low-polar region. As stated in introduction, a single polymer chain of the copolymer would have the form of once-broken rod. By the way, Huo et al.\textsuperscript{23} has already reported a similar study using a rod-coil-rod triblock copolymer, that is, oligo($p$-phenyleneethynylene)-$b$-polystyrene-$b$-oligo($p$-phenylene
Figure 4.7. Decay rate distribution function versus the hydrodynamic radius of PBLG in DMF and DMF/toluene = 30/70 with a concentration of 1.0 wt % at 23 °C and at θ = 60 °.
ethynylene), as this study. In particular, they also formed an interesting aggregate (core-shell micelle) consisting of rigid oligo(p-phenyleneethynylene) (OPE) core surrounded by flexible polystyrene (PS) shell in toluene/hexane mixed solutions. The micelle had both core and shell components in opposition to the core-shell micelle of GIG copolymer shown in Scheme 4.2. Their interesting micelle structure would also be due to the polarity difference between the two polymer components, that is, OPE and PS, to solvents as in the case of this study.

### 4.3.2 Single Chain Behavior of GIG Copolymer

Actually, in our previous research, we have already confirmed that single chain behavior in dilute solution is closely involved in aggregation behavior of a copolymer with specific molecular structures in both semidilute and concentrated regions. In particular, the copolymer had higher values of both $A_2$ and $k_D$ in some dilute solution systems than other dilute solution systems when the copolymer more largely aggregated in the latter semidilute and concentrated solution systems than the former semidilute and concentrated solution systems. Thus, dilute solution property should also control the aggregation behavior in dilute solution. The combination of DLS and SLS characterizations for the dilute DMF/toluene solution of GIG copolymer could give us an opportunity to investigate its single chain behavior. For both LS characterizations, we considered that GIG copolymer 1 was preferable to verify the solubility effect to the aggregation behavior since GIG copolymer 1 aggregated in the wide polarity region compared to GIG copolymer 2. We compared the LS characterization results of GIG copolymer 1 with those of PBLG and PIP to discuss the difference in polymer conformation among them.

Figure 4.8 shows the molecular weight dependence of $R_H$ of GIG copolymer 1 in DMF/toluene = 30/70 at 23 °C, PBLG in DMF at 25 °C, PIP in CHX at 25 °C, and PIP in 1,4-dioxane at 34.7 °C ($\Theta$). Although the copolymer was expected to show some kind of interesting single chain behavior due to the specific molecular structure, no notable change was observed with respect to the size of single polymer chain. Given the molecular weight dependence of each $R_H$ for both PBLG and PIP, the copolymer proved to have almost equal $R_H$ of the two polymers at the molecular weight ranging from 50,000 to 60,000 in each solution system. On the other hand, an interesting difference among GIG copolymer 1, PBLG, and PIP was found in Figure 4.9, which shows the molecular weight dependence of $k_D$ of GIG copolymer 1 in DMF/toluene = 30/70 at 23 °C, PBLG in DMF at 25 °C, and PIP in CHX at
Scheme 4.2. Aggregation behavior of GIG copolymer in DMF/toluene solution systems.
Figure 4.8. Double-logarithmic plots of the hydrodynamic radius against the weight-average molecular weight of GIG copolymer 1 in DMF/toluene = 30/70 at 23 °C, PBLG in DMF at 25 °C, PIP in CHX at 25 °C, and PIP in 1,4-dioxane at 34.7 °C (Θ).
Figure 4.9. Logarithmic plots of the diffusion second virial coefficient against the weight-average molecular weight of GIG copolymer 1 in DMF/toluene = 30/70 at 23 °C, PBLG in DMF at 25 °C,25 and PIP in CHX at 25 °C.12
The copolymer was found to have almost equal $k_D$ of PBLG in DMF at 25 °C although their conformations differed from each other. This result may mean that the contribution of “rod behavior” of two rigid PBLG rods is much larger than that of “coil behavior” of flexible PIP chain with respect to solubility of the copolymer. Besides, this result could agree with the above-mentioned consideration that the main driving force to the aggregation in DMF is the polarity (solubility) difference between both polymer blocks. In detail, decrease in solubility of PIP blocks with increasing solvent polarity could probably cause the aggregation into the specific core-shell micelle.

As for the conformation of single polymer chain, an interesting finding was obtained as shown in Table 4.2, which summarizes both LS characterization results for the DMF/toluene = 30/70 solution of GIG copolymer 1. Note that we could not determine $\rho$, defined as the ratio of $<S^2>^{1/2}/R_H$, of this sample because the scattered light intensity was not enough to determine $<S^2>^{1/2}$ in SLS. We used the measurement limit value for $<S^2>^{1/2}$ of 15 nm$^{26}$ to consider the $\rho$ value to be less than 2.0. According to the report by Schmidt, $^{25}$ $\rho$ value of PBLG in DMF is in the range between 2.4 and 2.9 at $M_w$ = 73,000-560,000. Besides, Kubota et al. $^{27}$ has reported that those values are 2.88 and 2.94 at $M_w$ = 299,000 and 372,000, respectively. These $\rho$ data of PBLG indicate that PBLG definitely has the form of rigid rod in DMF. Therefore, from the comparison between the $\rho$ value of less than 2.0 for GIG copolymer 1 having $M_w$ = 55,700 in DMF/toluene = 30/70 and that of 2.4 for PBLG having $M_w$ = 73,000 in DMF, $^{25}$ it is confirmed that GIG copolymer has the form of rigid rod with flexibility, that is, once-broken rod, in the DMF/toluene solution system. This special conformation of the copolymer differing from PBLG should be due to the incorporation of a flexible PIP chain between two rigid PBLG rods.

### 4.4 Conclusion

GIG copolymer aggregates in DMF due to the presence of both high-polar PBLG and low-polar PIP blocks. The correlation between solubility parameter and aggregate size of GIG copolymer in the DMF/toluene solution systems quantitatively demonstrated how strongly polarity caused by hydrogen bond made an impact on the aggregation behavior. Aggregate growth depends highly on the specific factor of polarity, suggesting that the main driving force to the aggregation in DMF is the polarity difference between both polymer blocks.
Table 4.2. Characterization results of SLS and DLS for GIG copolymer 1 in DMF/toluene = 30/70 solution

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$</th>
<th>$&lt;S^2&gt;^{1/2}$</th>
<th>$10^4A_2$</th>
<th>$R_H$</th>
<th>$k_D$</th>
<th>$\rho^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>gmol$^{-1}$</td>
<td>nm</td>
<td>cm$^3$mol$^{-2}$</td>
<td>Nm</td>
<td>cm$^3$g$^{-1}$</td>
<td>-</td>
</tr>
<tr>
<td>GIG copolymer 1</td>
<td>55,700</td>
<td>$&lt;15^b$</td>
<td>1.14</td>
<td>7.4</td>
<td>5.1</td>
<td>$&lt;2.0$</td>
</tr>
</tbody>
</table>

$^a \rho = <S^2>^{1/2}/R_H$

$^b$ Calculated using the measurement limit value for $<S^2>^{1/2}$ of 15 nm.
Because the main driving force to the aggregation in DMF originates with PIP blocks, the aggregate is considered to be a core-shell micelle consisting of flexible PIP core surrounded by rigid PBLG shell. In the DMF/toluene solution system in which GIG copolymer has no aggregation, the copolymer has no notable change with respect to the size of single polymer chain in the comparison among PBLG/DMF, PIP/CHX, and PIP/1,4-dioxane (Θ) solution systems at a equal molecular weight. The contribution of “rod behavior” of two rigid PBLG rods is larger than that of “coil behavior” of flexible PIP chain with respect to solubility of GIG copolymer. In the DMF/toluene solution system, a single chain of GIG copolymer has the form of rigid rod with flexibility, that is, once-broken rod, caused by the incorporation of a flexible PIP chain between two rigid PBLG rods.

References

5 Aggregation Behavior of Amphiphilic Random Copolymer of 2-(Acrylamido)-2-methylpropanesulfonic Acid and Tris(trimethylsiloxy)silylpropylmethacrylate in Aqueous Solution

5.1 Introduction

Perfluorinated polymers have been notable as an electrode binder of polymer electrolyte membrane (PEM) in proton exchange membrane fuel cell (PEFC) because of their advantages in chemical and thermal stability, high proton conductivity under the water-rich condition, and so on. Nevertheless, the perfluorinated polymers have several shortcomings for practical use, for example, high costs of synthesis and processing (and also recycling), low proton conductivity under the water-poor condition. Ordinary hydrocarbon polymer working as well as the perfluorinated polymers with low costs in practical purposes is desired.

We have then been developing an amphiphilic random copolymer composed of 2-(acrylamide)-2-methylpropanesulfonic acid (AMPS) and tris(trimethylsiloxy)silylpropylmethacrylate (TRIS) as an electrode binder of PEM in PEFC. It is known that AMPS has high proton conductivity due to the sulfonic acid group and AMPS copolymers with several hydrophobic co-monomers self-associate into interesting micellar aggregates. We consider that the aggregation induced by the amphiphilic structure of AMPS/TRIS copolymer might provide the excellent binder performances. This suggests that the polymer solution property is highly involved in the binder performances. Therefore, it is very significant to investigate the aggregation behavior of AMPS/TRIS copolymer to elucidate the molecular mechanism leading to the excellent binder performances.

In this chapter, we then carry out static and dynamic light scattering (SLS and DLS) measurements, surface tension measurements, and transmission electron microscopy (TEM) for AMPS/TRIS copolymer in the aqueous solution, and examine effects of the amphiphilic structure on the aggregation behavior of the copolymer.
5.2 Experimental

5.2.1 Sample Preparation

AMPS/TRIS copolymer was prepared as directed in the patent. Methanol was obtained commercially and purified by distillation for use as the polymerization solvent. In a roundbottom flask purged with dry nitrogen fitted with a stirrer were placed AMPS (TOA GOSEI), TRIS, whose trade name is X-22-2404 (Shin-Etsu Chemical), methanol, and purified water. The feed ratio of comonomers was AMPS/TRIS = 90/10 (wt%), and the mixing ratio of solvents was methanol/water = 97.7/2.3 (wt%). The polymerization was initiated at 50 °C by the addition of azobis(isobutyronitrile) with 0.4 wt% feed on the total weight of the two monomers at S/M = 15. Note that S/M is the weight ratio between solvent and monomer. The polymerization was terminated by water-cooling at 60 °C for 4 hours. The polymer solution was poured into another round-bottom flask filled with purified water, followed by reduced-pressure distillation to replace solvents from methanol to water. The product was purified by dialysis against purified water and then used to prepare a homogeneous clear aqueous solution of AMPS/TRIS copolymer with a concentration of 5 wt% by adding appropriate purified water. As for the robustness of the ester group in TRIS unit, it is considered that the ester group is stable at room temperature (r.t.) unless the AMPS/TRIS copolymer is left in the aqueous solution for a long term because its molecular weight had no change between before and after a series of the characterizations. In addition, it is interesting that AMPS/TRIS copolymer gelated by heating although further detailed investigation was not made in this study.

Polymer solutions for light scattering measurements were prepared by diluting the earlier-obtained polymer solution directly with purified water at five concentrations of 0.4, 0.5, 0.6, 0.8, and 1 wt%. Solvents and polymer solutions were filtered through 0.2 and 0.5 μm PTFE filters, respectively, and measured directly into the scattering cell.

5.2.2 Characterization

Elemental analysis was performed with a Perkin Elmer 2400 Series II CHNS/O elemental analyzer. For the sample of the elemental analysis, the aqueous polymer solution was dried to solid at r.t. under vacuum over night. Gel permeation chromatography (GPC) was performed
in the mixed solvent of water/sodium sulfate (Na$_2$SO$_4$)/acetonitrile = 69.7/0.5/29.8 (wt%) as an eluent using a TOSOH HLC-8220 GPC apparent equipped with three TSKgel columns (TSKgel G3000PW×L and TSKgel GMPW×L×2) using RI detector and sodium polystyrene sulfonate (NaPSS) calibration at 40 °C. It is considered that AMPS/TRIS copolymer is molecularly dispersed in the eluent because GPC curve did not reveal the presence of high-molecular weight composition, that is, aggregates. Fourier transform infrared spectroscopy (FTIR) was made with a HORIBA FT-720 FREEXACT Fourier transform infrared spectrometer. After drying the aqueous polymer solution to solid to prepare a sample for FTIR, the solid polymer was milled with potassium bromide (KBr) to form a very fine powder. This powder was then compressed into a thin pellet that can be analyzed. $^1$H NMR spectrum was recorded with a JEOL JNM-ECX400P (400 MHz) instrument using deuterated water ($D_2$O) as a solvent.

As shown in Table 5.1 and Scheme 5.1, both elemental analysis and GPC resulted in the found ratio of AMPS/TRIS = 58/42 (wt%), $M_w = 9,700$ and $M_w/M_n = 1.24$.

### 5.2.3 Static Light Scattering (SLS)

SLS measurements were performed to determine mean-square radius of gyration <$S^2>$, second virial coefficient $A_2$ and weight-average molecular weight $M_w$ for four dilute solutions of AMPS/TRIS copolymer ($c = 0.4, 0.6, 0.8, \text{and } 1 \text{ wt%}$) in the scattering angle range 30-150° at 10° intervals at 23 °C. The measurements were made with an ALV/DLS/SLS-5000 light-scattering system, with a 22 mW He-Ne laser emitting vertically polarized light of 632.8 nm wavelength as the light source. The detail of measurement principle and analysis method using a Berry plot$^{22}$ of SLS is described in Chapter 2. The refractive index of water at $\lambda_0 = 589$ nm and 23 °C was determined with a Kyoto Electronics refractometer (model RA-500N) to be 1.3327. The density of water at 23 °C was determined with a Kyoto Electronics density/specific gravity meter (model DA-505) to be 0.9975 g/cm³. The $\partial n/\partial c$ for the aqueous solution of AMPS/TRIS copolymer at 23 °C was determined to be 0.1452 cm³/g from the slope of the concentration dependence of $n$ measured by the above-mentioned refractometer.

### 5.2.4 Dynamic Light Scattering (DLS)

DLS measurements were performed to determine translational diffusion coefficient $D$ for
Table 5.1. Characterization results of elemental analysis and GPC for AMPS/TRIS copolymer

<table>
<thead>
<tr>
<th>Sample</th>
<th>AMPS/TRIS unit</th>
<th>Molecular weight</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed / wt%</td>
<td>Found(^a) / wt%</td>
<td>$M_w$(^b) / gmol(^{-1})</td>
</tr>
<tr>
<td>AMPS/TRIS copolymer</td>
<td>90/10</td>
<td>58/42</td>
<td>9,700</td>
</tr>
</tbody>
</table>

\(^a\) Determined by elemental analysis for sulfur.

\(^b\) Measured by GPC using water/Na\(_2\)SO\(_4\)/ACN = 69.7/0.5/29.8 (wt\%) as an eluent with NaPSS calibration.
Scheme 5.1. Molecular structure of AMPS/TRIS copolymer.
three dilute solutions of AMPS/TRIS copolymer \((c = 0.4, 0.6, \text{ and } 0.8 \text{ wt\%})\) at four scattering angles of 60°, 90°, 120°, and 150° at 23 °C. Additionally, diffusion second virial coefficient \(k_D\) and hydrodynamic radius \(R_H\) were calculated, respectively. We also investigated the aggregation behavior of the copolymer at a concentration of 0.5 wt% at 23 °C and at \(\theta = 60°\). The measurements were made with the same apparatus as SLS measurements. The detail of measurement principle using Siegert’s relation\(^{23}\) and analysis method using CONTIN analysis\(^{24}\) of DLS is described in Chapter 2. Note that \(k_D\) could be a solubility index of polymers because \(k_D\) is related to \(A_2\).\(^{25}\) The viscosity of water at 23 °C was determined with a Toki Sangyo rotational viscometer (model RE-80L) to be 0.932 cP.

### 5.2.5 Surface Tension

Surface tension was measured to study the surface activity of AMPS/TRIS copolymer using a BYK Gardner dynometer plus at r.t.. Aqueous polymer stock solutions with three concentrations of 1, 0.1, and 0.01 wt% (10, 1, and 0.1 g/L) were prepared by diluting the above-obtained polymer solution directly with purified water. The final concentrations of the aqueous polymer solutions varied from 0.001 to 1 wt% (from 0.01 to 10 g/L).

### 5.2.6 Transmission Electron Microscopy

TEM was used to observe the morphology of AMPS/TRIS copolymer micelles in aqueous solution using a HITACHI transmission electron microscope (model H-7650) operating at an acceleration voltage of 100 kV. Specimens were prepared without staining by placing a drop of the aqueous solution with a concentration of 1 wt% on the carbon-coated copper grid, dried at r.t. for 1 hour.

### 5.3 Results and Discussion

#### 5.3.1 Spectral Characterization

Figure 5.1 shows the FTIR spectrum of AMPS/TRIS copolymer. AMPS units had the largest broad-band, whose peak top is at 3,300-3,500 cm\(^{-1}\), attributed to the N-H stretching vibration
Figure 5.1. FTIR spectrum of AMPS/TRIS copolymer.
of amide groups. The stronger peak at 1,640 cm\(^{-1}\) is ascribed to the amide-I band due to the C=O stretching vibration of amide groups, whereas the weaker peak at 1,550 cm\(^{-1}\) is assigned to the amide-II band due to the N-H bending vibration strongly coupled with the C-N stretching vibration of amide groups. On the other hand, TRIS units gave the minor peak at 1,700 cm\(^{-1}\), which is the small shoulder of the strong peak at 1,640 cm\(^{-1}\) noted earlier, due to the C=O stretching vibration of ester groups. The units had the small peak at 1,390 cm\(^{-1}\) caused by the -CH\(_3\) asymmetric deformation of Si-CH\(_3\), and the large peak at 1,210 cm\(^{-1}\) attributed to the -CH\(_3\) symmetric deformation of Si-CH\(_3\). In the wavenumber area less than about 1,000 cm\(^{-1}\), three sharp peaks were detected at 1,040, 760, and 510 cm\(^{-1}\) ascribed to the Si-O-Si stretching vibration, the Si-C stretching and the CH\(_3\) rocking, and the Si-O-Si bending vibration, respectively. In addition, both AMPS and TRIS units had two small peaks at 2,980 and 2,930 cm\(^{-1}\) assigned to the -CH\(_3\) asymmetric stretching vibration and the -CH\(_2\)-asymmetric stretching vibration, which is supported by the presence of the -CH\(_2\)-bending vibration at 1,450 cm\(^{-1}\), respectively.

Figure 5.2 displays \(^1\)H NMR spectrum of AMPS/TRIS copolymer in D\(_2\)O. All the peaks corresponding to AMPS units were clearly observed, whereas no peaks due to TRIS units were observed. This result indicated that TRIS units do not have any affinity to water at all, unlike AMPS units having high affinity to water. In addition, this result implies that AMPS/TRIS copolymer in water has the form of the unique structure that water-insoluble TRIS units are confined inside the water-soluble AMPS units, meaning “micellization” in water. This unique structure in water would be a core-shell micelle consisting of TRIS core surrounded by AMPS shell. As described later, however, this micelle would be an imperfect core-shell micelle because AMPS/TRIS copolymer is not a diblock copolymer but a random copolymer.

### 5.3.2 Dilute Solution Property and Surface-Activity of AMPS/TRIS Copolymer

Figure 5.3 shows the decay rate distribution function in DLS for the aqueous solution of AMPS/TRIS copolymer at a concentration of 0.5 wt\%. The copolymer had a bimodal peak in the \(R_H\) range from 1 to 300 nm. It is considered that the larger peak is attributed to single polymer chains (unimers), whereas the smaller peak is due to polymer aggregates (micelles), whose presence was implied by NMR analysis. Note that the number of the micelles should
Figure 5.2. $^1$H NMR spectrum of AMPS/TRIS copolymer in D$_2$O.
Figure 5.3. Decay rate distribution function versus hydrodynamic radius for the aqueous solution of AMPS/TRIS copolymer with a concentration of 0.5 wt% at 23 °C and at θ = 60°.
be much less than that of the unimers as the light scattering is more sensitive to large particles. This result means that AMPS/TRIS copolymer exists not only as unimers but also as micelles in the concentration range studied. Figure 5.4 shows the Berry plots in SLS for the aqueous solution of AMPS/TRIS copolymer. The values of molecular weight $M_w$, apparent radius of gyration $\langle S^2 \rangle^{1/2}_{app}$ and second virial coefficient $A_2$ are given in Table 5.2. Note that $\langle S^2 \rangle^{1/2}$ obtained from SLS means $\langle S^2 \rangle^{1/2}_{app}$ because effect of electrostatic repulsion was ignored as described earlier. $M_w$ of the copolymer in the aqueous solution was calculated to be $1.42 \times 10^4$ g/mol from each intercept in the Berry plots. $\langle S^2 \rangle^{1/2}_{app}$ and $A_2$ of the copolymer in the aqueous solution were also determined to be 13.7 nm and $3.8 \times 10^{-3}$ cm$^3$/mol/g, respectively. Note that the scattered light detected in SLS should be due to both the unimers and the micelles in the dilute concentration region including $c = 0.5$ wt%. As explained later, micelles are formed in the low concentration range, that is, around 0.1 wt%. As supported by the GPC results with $M_w = 9,700$, thus, these values of $M_w$, $\langle S^2 \rangle^{1/2}_{app}$, and $A_2$ would be overestimated to some extent for the unimer. Figure 5.5 shows the concentration dependence of translational diffusion coefficient $D$ in DLS for the aqueous solution of AMPS/TRIS copolymer. The data points are seen to follow a straight line, and thus $k_D$ were accurately determined from its ordinate intercept and slope. As listed in Table 5.2, apparent hydrodynamic radius $R_{H_{app}}$ of AMPS/TRIS copolymer in the aqueous solution was determined to be 4.7 nm using the Stokes-Einstein equation. Note that $R_H$ obtained from DLS means $R_{H_{app}}$ because effect of electrostatic repulsion was ignored as described earlier. Because of the same reason as the SLS, this $R_{H_{app}}$ value would also be overestimated to some extent for the unimer.

Figure 5.6 shows the concentration dependence of surface tension $\gamma$ for the aqueous solutions of AMPS/TRIS copolymer and sodium dodecyl sulfate (SDS). The surface tension data of SDS was shown to compare the surface-activity of AMPS/TRIS copolymer with that of this reference surfactant. The typical low-molecular weight surfactant SDS exhibits a classical surface-activity behavior, that is, a continuous decrease of $\gamma$ with increase in concentration, till a concentration above what $\gamma$ remains constant. This concentration is attributed to the critical micelle concentration (CMC) of SDS. Commercial surfactants usually have this classical surface-activity behavior. In contrast, AMPS/TRIS copolymer exhibited the different surface-activity behavior with SDS. In particular, $\gamma$ continuously decreased from 71 to 50 mN/m with increasing concentration from $10^{-2}$ to 10 g/L. Interestingly, no plateau of $\gamma$ versus concentration and no CMC were detected in the whole concentration range studied. Given the presence of micelles confirmed by DLS for the polymer solution with $c = 0.5$ wt%,
Figure 5.4. Berry plots in SLS for the aqueous solution of AMPS/TRIS copolymer.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$</th>
<th>$\langle S^2 \rangle^{1/2}_{app}$</th>
<th>$10^3 A_2$</th>
<th>$R_{Happ}$</th>
<th>$k_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMPS/TRIS copolymer</td>
<td>14,200</td>
<td>13.7</td>
<td>3.8</td>
<td>4.7</td>
<td>47.6</td>
</tr>
</tbody>
</table>
Figure 5.5. Concentration dependence of translational diffusion coefficient in DLS for the aqueous solution of AMPS/TRIS copolymer.
Figure 5.6. Concentration dependence of surface tension for the aqueous solutions of AMPS/TRIS copolymer (present data) and SDS (Praktikum\textsuperscript{26}).
at which \( \gamma \) is continuously decreasing, it is conceivable to assume that AMPS/TRIS copolymer has its CMC out of the concentration range studied, that is, below 10\(^{-2}\) g/L. Alternatively, its CMC may not be able to be detected by the measurement of surface tension, as amphiphilic diblock copolymers having non-surface-activity and weak surface-activity with micellization reported by Matsuoka and coworkers.\(^{27}\) This weak surface activity of AMPS/TRIS copolymer, accompanied by the formation of micelles, is a curious and novel phenomenon in surface and interface science. They reported an interesting phenomenon with micellization of amphiphilic diblock copolymers having strong acid groups in water. The copolymers with shorter hydrophobic chains have non-surface-activity than the hydrophilic ones, whereas the copolymers with longer hydrophobic chains have weak surface-activity than the hydrophilic ones. In the latter case, their surface tension slightly reduces at the high polymer concentration range. Regarding this curious surface-activity behavior, they considered that those polymers are practically adsorbed at the air/water interface, unlike a typical low-molecular weight surfactant, such as SDS with classical surface-activity due to complete adsorption. Even though AMPS/TRIS copolymer is not a diblock copolymer but a random copolymer, the copolymer could also exhibit the similar weak surface-activity, due to the bulk hydrophobic TRIS units, as their samples. With respect to the surface-activity behavior including CMC of AMPS/TRIS copolymer, we would like to limit ourselves to the above-mentioned rough consideration because this study focuses on the aggregation behavior.

### 5.3.3 Aggregation Behavior of AMPS/TRIS Copolymer

Figure 5.7(a) and (b) displays TEM micrographs of AMPS/TRIS copolymer micelles. The single micelle depicted in Figure 5.7(a) is smaller than the micellar aggregates shown in Figure 5.7(b), meaning that the micellar size varies widely. Actually, micelles having wide-range of sizes were observed by TEM. As described earlier, the TEM sample was prepared by drying the aqueous polymer solution with a concentration of 1 wt%. This concentration of 1 wt% is in dilute \( c^* = 5.6 \) wt %, calculated using the following equation:

\[
c^* = \frac{3M_w}{4\pi N_A R_H^3}
\]  

In other words, AMPS/TRIS copolymer forms not only single micelles but also large micellar
Figure 5.7. TEM micrographs of a single micelle (a) and a large micellar aggregate (b) of AMPS/TRIS copolymer.
aggregates below $c^\ast$. In terms of micellar size, it may be regarded as strange that the dried micellar aggregates with a diameter of around 300 nm observed by TEM (Fig. 5.7(b)) is larger than the swelled micelles with a diameter of below 200 nm detected by DLS. As for this discrepancy of micellar size, we consider that some micellar aggregates grow larger while the concentration of polymer solution increases during the preparation process of the TEM sample described earlier. The micellar aggregates displayed in Figure 5.7(b) would probably be one of the largest micelles observed by TEM. In both the TEM micrographs, slight contrast was observed between the central parts and the outer ones for each micelle. This suggests that AMPS/TRIS copolymer micelle has a different structure from ordinal micelles, which is probably caused by the sequence type of monomer units, that is, random type. Generally, diblock copolymers form perfect core-shell micelles consisting of hydrophobic core surrounded by hydrophilic shell in water.\(^{28}\) However, as AMPS/TRIS copolymer is a random copolymer, it would not form perfect core-shell micelles described earlier but form imperfect core-shell micelles, whose core and shell are formed with TRIS and AMPS, respectively. In addition, it can be considered that AMPS shell is harder and TRIS core is less dense than respective parts of ordinary polymer core-shell micelles on the basis of the following separate discussions for AMPS and TRIS.

According to the report by Hagino et al.\(^{29}\) chain stiffness of sodium poly(2-acrylamido-2-methylpropanesulfonate) (Na PAMPS) increases with lowering ionic strength by the electrostatic stiffening effect. This indicates that Na PAMPS has a value of persistence length $q$ with much more than 10 nm in water. $q$ has a relationship with the stiffness parameter $\lambda^{-1}$ defined in terms of the flexible elastic constant $\varepsilon$, $k_B$, and $T$.

\[
\lambda^{-1} = \frac{2 \varepsilon}{k_BT}
\]  

(5.2)

$\lambda^{-1}$ is related to $q$ with $\lambda^{-1} \geq 2q$ for helical worm-like chain and $\lambda^{-1} = 2q$ for worm-like chain.\(^{30}\) Generally, $\lambda^{-1}$ may be considered to be smaller and larger than 10 nm for flexible and semiflexible (or stiff) polymers, respectively, proving to be a measure of polymer chain stiffness.\(^{30}\) Because Na PAMPS mostly equals to AMPS homopolymer with respect to polymer chain stiffness in aqueous NaCl solutions at the same salt concentrations,\(^{31,32}\) the homopolymer should have a $\lambda^{-1}$ value with much more than 20 nm given the $q$ value in water. Thus, AMPS homopolymer is not a flexible polymer but a stiff polymer in water, resulting in
that AMPS shell of the micelle is considered as a hard shell.

On the other hand, it is known that TRIS plays a role to improve oxygen permeability of contact lens.\textsuperscript{33,34} This suggests that incorporation of TRIS provides matrix polymers with partial low-density domains, in which small molecules, such as oxygen molecule can smoothly pass through. TRIS chain could not densely aggregate in water because of the large steric hindrance between bulky trimethylsiloxy groups despite its hydrophobic nature. Thus, TRIS core of the micelle is considered to be less dense than the core parts of ordinary polymer core-shell micelles.

Our understanding for the aggregation into the micelle having less-dense core and hard shell in water is as follows. As evidenced by the difference of molecular structure between both polymer parts, AMPS units have much higher affinity to water than TRIS units. As noted earlier, AMPS chain is stiff, and TRIS chain is bulky and less dense. These differences between both the polymer parts induce the aggregation in water. In particular, the balance between the spreading force of stiff AMPS chain and the cohesion force of bulky TRIS chain provides the driving force for forming the unique micelle. The micellar core would not be packed with TRIS chain completely due to the stiffness of AMPS chain and the bulkiness of TRIS chain, thereby providing the less-dense structure. As shown in Scheme 5.2, therefore, it is concluded that the imperfect core-shell micelle of AMPS/TRIS copolymer has a form of less-dense TRIS core and hard AMPS shell, in which TRIS chain is folded back into the core surrounded by AMPS shell. Note that the micellar structure is illustrated as a matter of convenience by unsphering each unit with different colors to help to imagine the particular micellar structure. We would emphasize that the micellar core and shell are not formed with TRIS “sphere” and AMPS “sphere,” respectively. Furthermore, the micellar surface would not be completely covered with AMPS shell as AMPS/TRIS copolymer is a random copolymer, meaning the above-mentioned imperfect core-shell micelle.

As concluded earlier, AMPS/TRIS copolymer proved to self-associate into the particular micelle in water. This micelle with unique structure is expected to be retained even in the solid state after solvent evaporation, and might perhaps form the specific domains in PEM, leading to much more excellent binder performances.

5.4 Conclusion
**Scheme 5.2.** Micellar structure having less-dense TRIS core and hard AMPS shell formed by AMPS/TRIS copolymer in water.
Amphiphilic random AMPS/TRIS copolymer exhibited weaker surface-activity than a typical low-molecular weight surfactant SDS in water, that is, there were no plateau of $c$ versus concentration and no CMC in the whole concentration studied. This weak surface-activity is caused by the presence of imperfect core-shell micelles having hydrophobic TRIS core surrounded by hydrophilic AMPS shell in water. AMPS shell is considered as a hard shell because of the stiffness of AMPS chain in water. TRIS chain could not densely aggregate in water due to the large steric hindrance between bulky trimethylsiloxy groups despite its hydrophobic nature, thereby providing TRIS core with less-dense structure. As AMPS/TRIS copolymer is not a diblock copolymer but a random copolymer, the balance between the spreading force of stiff AMPS chain and the cohesion force of bulky TRIS chain provides the driving force for forming the unique micelle having less-dense TRIS core and hard AMPS shell.

References


6 Aggregation Behavior of Organic-soluble Semi-aromatic Polyimides in N-Methylpyrrolidone Systems

6.1 Introduction

Aromatic polyimides having stiff backbone have been widely used as a high-performance material because of their excellent thermal, mechanical, and electrical properties.\textsuperscript{1-3} Unfortunately, however, the aromatic polyimides are limited in practical use due to their insolubility in ordinary organic solvents.\textsuperscript{4,5} Actually, there have been some troubles in preservation stability by the occurrence of aggregates while the product solutions of the organic-soluble polyimides are stored for a long term. Polyimides soluble and stable without aggregation in organic solvents have been desired, in particular, for processing of films. In order to provide aromatic polyimides with high solubility while maintaining the above-stated excellent properties, the monomers having substituent groups, i.e. aliphatic,\textsuperscript{6-8} benzophenone\textsuperscript{9,10} and benzhydrol tetracarboxylic dianhydrides,\textsuperscript{11} and aromatic diamines having trifluoromethyl groups,\textsuperscript{12-14} phenyl groups attached to side chains\textsuperscript{15-17} and hydroxyl groups,\textsuperscript{18} have been used.

We have then been developing semi-aromatic polyimides composed of 4,4’-diamino-3,3’-dihydroxybiphenyl (DDB), 4,4’-oxydianiline (ODA), and bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA), for the application to the surface protection, interlayer dielectric, and high-density mounting broad dielectric films.\textsuperscript{19} For establishment of the semi-aromatic polyimides as film materials, it is necessary to examine their solubility and stability in organic solvents.

In this chapter, we carry out static and dynamic light scattering (SLS and DLS) measurements for the semi-aromatic polyimides with lower and higher degree of imidization in N-methylpyrroridone (NMP), the mixed solvent of NMP and cyclohexane (CHX), and that of NMP and \(\gamma\)-butyrolactone (GBL), these solvents being usually used for the synthesis of polyimides, and examine their solubility and/or aggregation behavior.
6.2 Experimental

6.2.1 Sample Preparation

We tested six partially imidized poly(amic acid)s, i.e. three polyimides with lower degree of imidization and three polyimides with higher degree of imidization, in three solution systems of NMP, NMP/CHN and NMP/GBL. NMP, CHN and GBL were used as received without further purification. NMP was used as a single solvent, whereas both CHN and GBL were used as mixed solvents with NMP, i.e. NMP/CHN=50/50 and NMP/GBL=50/50 (wt%). Note that the three solvents have a tiny amount of water below 10 ppm because they are canister-bottle grade, and thus the presence of water in each solvent would have less impact on the reactions and aggregation behavior mentioned below.

In a 500 mL round-bottom flask purged with dry nitrogen fitted with a stirrer were placed 3.92 g ODA (0.019 mol), 9.88 g DDB (0.046 mol) (Table 6.1) and 120 g of each polymerization solvent described above. After the monomer solution was stirred at room temperature (r.t.) for 1 hour to dissolve both monomers into each solvent, the polymerization was initiated by the addition of 16.2 g BCDA (0.065 mol) (Table 6.1) into the monomer solution. Polyimides with lower degree of imidization in NMP, NMP/CHN and NMP/GBL, i.e. PIL-N, -C and -G, were obtained by stirring at 120 °C for 5 hours (First reaction step), and then additionally dehydration-condensed to give polyimides with higher degree of imidization in the three solvents, i.e. PIH-N, -C and -G, by heating for another 5 hours (Second reaction step). Note that the dehydration-condensation reaction for the NMP/CHN solution was carried out at 145 °C because CHN has a boiling point of 155 °C, although the reaction for both the NMP and the NMP/GBL solution were made at 180 °C.

Because these polyimides did not dissolve into respective reaction solvents once they were precipitated, polymer solutions for light scattering measurements were prepared by diluting the un-precipitated and concentrated polymer solutions (20 wt%) directly with each solvent at six concentrations of 0.1, 0.2, 0.3, 0.4, 1.0 and 5.0 wt%. Solvents and polymer solutions were filtered through 0.2 and 0.5 μm PTFE filters, respectively, and measured directly into the scattering cell.

6.2.2 Characterization
### Table 6.1. The monomers used for the preparation of polyimides

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Molecular structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>4,4’-Oxydianiline (ODA)</td>
<td><img src="image1" alt="Molecular structure of 4,4’-Oxydianiline" /></td>
</tr>
<tr>
<td>4,4’-Diamino-3,3’dihydroxybiphenyl (DDB)</td>
<td><img src="image2" alt="Molecular structure of 4,4’-Diamino-3,3’dihydroxybiphenyl" /></td>
</tr>
<tr>
<td>Bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BCDA)</td>
<td><img src="image3" alt="Molecular structure of Bicyclo[2.2.2]-oct-7-ene-2,3,5,6-tetracarboxylic dianhydride" /></td>
</tr>
</tbody>
</table>
Gel permeation chromatography (GPC) was performed in NMP as an eluent using a TOSOH HLC-8220 GPC apparent equipped with a TSKgel column (TSKgel α-M) using RI detector and polystyrene calibration at 40 °C. GPC results were listed in Table 6.2.

Fourier transform infrared (FTIR) spectroscopy was made with a Thermo Electron NICOLET 6,700 fourier transform infrared spectrometer to determine degrees of imidization for the polyimides. The polyimide samples were prepared by precipitating the earlier-obtained polymer solutions with methanol and then drying the precipitated polymers at 35 °C for overnight. The solid polymer was milled with potassium bromide (KBr) to form a very fine powder, and then compressed into a thin pellet that can be analyzed. Meanwhile, a fully imidized polymer sample as a reference to calculate degrees of imidization was made by spin-coating a concentrated solution (10 wt%) of PIH-N on silicon wafer and then thermally curing in nitrogen atmosphere at 350 °C for 1 hour. As shown in Figure 6.1, the peak around 1,500 cm\(^{-1}\) (aromatic C-C stretching) was used as a reference because it is independent of bond orientation change during imidization. The peak intensity at 1,720 cm\(^{-1}\) (symmetric C=O stretching) was compared with that at 1,500 cm\(^{-1}\) to calculate the degrees of imidization, which were also summarized in Table 6.2.

### 6.2.3 Static Light Scattering (SLS)

SLS measurements were carried out to determine mean-square radius of gyration \(<S^2>\), second virial coefficient \(A_2\) and weight average molecular weight \(M_w\) for four dilute solutions of the polyimides (\(c = 0.1, 0.2, 0.3, 0.4\) wt\%) in the scattering angle range 30-150° at 15° intervals at 23 °C. The measurements were made with an ALV/DLS/SLS-5000 light-scattering system, with a 22 mW He-Ne laser emitting vertically polarized light of 632.8 nm wavelength as the light source. The detail of measurement principle and analysis method using a Berry plot\(^{20}\) of SLS is described in Chapter 2. The refractive indexes of NMP, NMP/CHN and NMP/GBL at \(\lambda_0 = 589\) nm and 23 °C were determined with a Kyoto Electronics refractometer (model RA-500N) to be 1.4693, 1.4585 and 1.4530, respectively. The densities of NMP, NMP/CHN and NMP/GBL at 23 °C were determined with a Kyoto Electronics density/specific gravity meter (model DA-505) to be 1.0280, 0.9875 and 1.0740 g\(\text{cm}^{-3}\), respectively. The values of \(\partial n/\partial c\) for the NMP, the NMP/CHN and the NMP/GBL solutions of PIL at 23 °C were 0.127, 0.153 and 0.149 cm\(^3\)g\(^{-1}\), respectively. Those of \(\partial n/\partial c\) for the three solutions of PIH at 23 °C were 0.125, 0.142 and 0.134 cm\(^3\)g\(^{-1}\), respectively.
Mixing ratio 50/50 wt%.

Determined by FTIR using the formula:

\[ \frac{A_{@\text{1,720 cm}^{-1}} / A_{@\text{1,500 cm}^{-1}}}{A_{@\text{1,720 cm}^{-1}} / A_{@\text{1,500 cm}^{-1}}} \times 100 \% \]  

The error is below 2.5 %.

The error is below 9.3 %.

Table 6.2. Characterization results of FTIR and GPC for PILs and PIHs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Polymerization solvent</th>
<th>Imidization rate(^b) / %</th>
<th>Molecular weight</th>
<th>(M_w/M_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIL-N</td>
<td>NMP</td>
<td>75.3</td>
<td>43,500</td>
<td>20,800</td>
</tr>
<tr>
<td>PIL-C</td>
<td>NMP/CHN(^a)</td>
<td>74.4</td>
<td>57,300</td>
<td>26,200</td>
</tr>
<tr>
<td>PIL-G</td>
<td>NMP/GBL(^a)</td>
<td>69.4</td>
<td>61,100</td>
<td>28,000</td>
</tr>
<tr>
<td>PIH-N</td>
<td>NMP</td>
<td>83.6</td>
<td>98,400</td>
<td>41,000</td>
</tr>
<tr>
<td>PIH-C</td>
<td>NMP/CHN(^a)</td>
<td>95.8</td>
<td>91,300</td>
<td>38,200</td>
</tr>
<tr>
<td>PIH-G</td>
<td>NMP/GBL(^a)</td>
<td>84.9</td>
<td>124,000</td>
<td>51,700</td>
</tr>
</tbody>
</table>

\(^a\) Mixing ratio 50/50 wt%.

\(^b\) Determined by FTIR using the formula:  

\[ \frac{A_{@\text{1,720 cm}^{-1}} / A_{@\text{1,500 cm}^{-1}}} {A_{@\text{1,720 cm}^{-1}} / A_{@\text{1,500 cm}^{-1}}} \times 100 \% \]

The error is below 2.5 %.

\(^c\) Measured by GPC using NMP as an eluent. The error is below 9.3 %.
Figure 6.1. FTIR spectra of PILs, PIHs and the fully imidized polymer.
6.2.4 Dynamic Light Scattering (DLS)

DLS measurements were carried out to determine translational diffusion coefficient $D$ for three dilute solutions of PILs and PIHs ($c = 0.2, 0.3, 0.4$ wt%) at five scattering angles of $30^\circ$, $60^\circ$, $90^\circ$, $120^\circ$ and $150^\circ$ at $23$ °C. Additionally, diffusion second virial coefficient $k_D$ and hydrodynamic radius $R_H$ were calculated, respectively. We also investigated the aggregation behavior of PILs and PIHs at two concentrations of $1$ and $5$ wt% at $23$ °C and at $\theta = 60^\circ$. No aggregation peak was observed at $0.5$ wt% for all BCDA-based polyimide solutions, and thus both SLS and DLS were performed to investigate dilute solution property of them in the concentration region below $0.5$ wt%. The measurements were made with the same apparatus as SLS measurements. The detail of measurement principle using Siegert's relation$^{21}$ and analysis method using CONTIN analysis$^{22}$ of DLS is described in Chapter 2. Note that $k_D$ could be a solubility index of polymers because $k_D$ is related to $A_2$. The viscosities of NMP, NMP/CHN and NMP/GBL at $23$ °C were determined with a Toki Sangyo rotational viscometer (model RE-80L) to be $1.757, 1.873$ and $1.773$ cP, respectively.

6.3 Results and Discussion

6.3.1 The Correlation between Imidization Rate and Dilute Solution Property of BCDA-based Polyimides

As shown in Table 6.2, FTIR revealed that PILs had the degrees of imidization of $69$-$75$ %, whereas PIHs had those of $83$-$95$ %. This indicates that the polymerization was followed by the dehydration-condensation to give PILs during the first reaction step, and then the second reaction step further advanced the dehydration-condensation to give PIHs. The difference in degree of imidization among PIHs is larger than that among PILs, suggesting that the dehydration-condensation reactivity depends more highly on each reaction condition with the three different solution systems at the second reaction step than that at the first reaction step. In particular, it is interesting that the degree of imidization of PIH-C (95.8 %) is higher than those of both PIH-N (83.6 %) and -G (84.9 %). This difference in degree of imidization among them would be ascribed to the kind of the reaction solvents on the basis of the following findings. It is well known that poly(amic acids)s form stable complex with aprotic
polar solvents via strong hydrogen bond, which can prevent the dehydration-condensation to give the final polyimides. Given the presence of the hydrogen-bonded complex, it is conceivable that both PIL-N and PIL-G also form the stable complex with aprotic polar solvents, i.e. NMP and NMP/GBL, respectively. On the other hand, PIL-C would be hard to have the stable complex compared to both PIL-N and -G because the former was synthesized in the mixed solvent of both the aprotic polar, i.e. NMP, and the less polar solvent, i.e. CHN, resulting in the highest degree of imidization of all BCDA-based polyimides.

Table 6.3 summarizes the characterization results of SLS and DLS for PILs and PIHs. SLS results were analyzed using the Berry plot, which is typically displayed in Figure 6.2 for PIL-N with the lowest molecular weight ($M_w = 36,600$) and PIL-H with the highest molecular weight ($M_w = 59,200$). $M_w$ values of PILs and PIHs were calculated from each intercept in their Berry plots, and then their $A_2$ values were also determined, respectively, from the Berry plots. Note that their $<S^2>^{1/2}$ values were not obtained as mentioned later.

Figure 6.3 depicts the concentration dependence of $D$ in DLS for PILs and PIHs. The data points are seen to follow a straight line, and thus $k_D$ were accurately determined from its ordinate intercept and slope. As listed in Table 6.3, $R_H$ of PILs and PIHs were also calculated using the Stokes-Einstein equation. Molecular weights of PIHs ($M_w = 55,000-60,000$) proved to be larger than those of PILs ($M_w = 36,000-40,000$), indicating that not only dehydration-condensation but also polymerization further advanced during the second reaction step. From the above-mentioned considerations, it is concluded that the dehydration-condensation reaction for the amic-acid segments in PILs proceeds simultaneously with the polymerization reaction using the remaining monomers at the both the first and the second reaction step. As for the size of polymer chain, no accurate $<S^2>^{1/2}$ values of both PILs and PIHs were obtained, meaning that they have certain values of $<S^2>^{1/2}$ below 10-15 nm given the minimum limit of detection in SLS. Note that it is impossible to discuss polymer conformation using the dimensionless parameter $\rho$ defined as the ratio of $<S^2>^{1/2}/R_H$, which means that polymer conformation changes from a rigid rod ($\rho = \infty$) to a hard sphere ($\rho = 0.775$) through a random coil ($\rho = 1.2-1.5$). On the other hand, their $R_H$ values were accurately calculated; PILs had $R_H = 6-7$ nm and PIHs had $R_H = 7-8$ nm.

As shown in Figure 6.4, it is distinctive trend for PILs and PIHs that their $A_2$ values decrease over independent of the variety of the reaction solvents as their degrees of imidization increase. Although there should exist the effect of molecular weight on $A_2$, this trend suggests that the degree of imidization has a large impact on solubility of BCDA-based polyimides.
### Table 6.3. Characterization results of SLS and DLS for PILs and PIHs

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$</th>
<th>$10^4A_2$</th>
<th>$R_H$</th>
<th>$k_D$</th>
<th>$c^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PIL-N</td>
<td>36,600</td>
<td>9.28</td>
<td>6.2</td>
<td>7.19</td>
<td>6.0</td>
</tr>
<tr>
<td>PIL-C</td>
<td>41,900</td>
<td>7.75</td>
<td>6.6</td>
<td>-17.1</td>
<td>5.7</td>
</tr>
<tr>
<td>PIL-G</td>
<td>36,500</td>
<td>11.5</td>
<td>6.6</td>
<td>3.25</td>
<td>5.0</td>
</tr>
<tr>
<td>PIH-N</td>
<td>59,200</td>
<td>7.31</td>
<td>7.8</td>
<td>-4.68</td>
<td>4.9</td>
</tr>
<tr>
<td>PIH-C</td>
<td>55,800</td>
<td>4.42</td>
<td>7.8</td>
<td>-19.3</td>
<td>4.6</td>
</tr>
<tr>
<td>PIH-G</td>
<td>58,700</td>
<td>8.03</td>
<td>8.1</td>
<td>-2.68</td>
<td>4.3</td>
</tr>
</tbody>
</table>

* $M_w$: gram moles^{-1}, $A_2$: cm$^3$mol$^{-2}$, $R_H$: nm, $k_D$: cm$^3$g$^{-1}$, $c^*$: wt%.

The error is below 1.7 %.

The error is below 4.9 %.
Figure 6.2. Berry plots in SLS for PIL-N and PIH-N.
Figure 6.3. Concentration dependence of translational diffusion coefficient in DLS for PILs and PIHs.
Figure 6.4. Correlation between degree of imidization and $A_2$ for PILs and PIHs.
From Figure 6.5, on the other hand, \( k_D \) proved to show a different trend that \( k_D \) values of both PIL-C and PIH-C were much smaller than those of both PIL-N, -G and PIH-N, -G, respectively. In other words, the impact of the reaction solvents on solubility of BCDA-based polyimides can be more easily found in the difference of \( k_D \) than that of \( A_2 \) as displayed in Figure 6.4 and 6.5. As for the lower solubility of both PIL-C and PIH-C than those of PIL-N, -G, and PIH-N, -G, respectively, the above-noted consideration for the difference in degree of imidization among them would be better to explain this difference of solubility among them. Given that both poly(amic acid)s and polyimides have higher solubility in aprotic polar solvents than non and less polar solvents, we would have no doubt that both PIL-C and PIH-C synthesized in the mixed solvent with less polar solvent, i.e. CHN, have lower solubility than PIL-N, -G and PIH-N, -G obtained in the aprotic polar solvents, i.e. NMP and NMP/GBL. On the basis of the above-stated findings, it is concluded that BCDA-based polyimides have the characteristics that the higher degree of imidization gives the lower solubility.

### 6.3.2 Aggregation Behavior of BCDA-based Polyimides

In a dilute solution, the dynamic behavior of polymer chain is highly sensitive to the solvent quality. As the solution concentration increases up to the overlapping concentration \( c^\ast \), where polymer coils start to touch each other, the effect of chain entanglements becomes more important. Once the overlapping concentration has been reached, polymer motion will be dominated by the presence of direct polymer-polymer interaction. Accordingly, chain aggregation in polymer solution should take place beyond the overlapping concentration. For the polymer solutions prepared in the present study, as listed in Table 6.3, the concentration of 1 and 5 wt% proved to be in dilute and semi-dilute region, respectively, according to the overlapping concentration, \( c^\ast = 5-6 \) (PILs) and 4-5 (PIHs) wt% calculated using the following equation:

\[
c^\ast = \frac{3M_w}{4\pi N_A R_H^3}
\]

The present study primarily discusses the aggregation behavior of BCDA-based polyimides in the dilute and the semi-dilute region.

Figure 6.6 depicts the decay rate distribution functions in DLS for PILs at 1 wt% (a) and 5
Figure 6.5. Correlation between solution system and $k_D$ for PILs and PIHs.
Figure 6.6. Decay rate distribution function versus hydrodynamic radius of PILs with a concentration of (a) 1 and (b) 5 wt% and PIHs with a concentration of (c) 1 and (d) 5 wt% at 23 °C and at $\theta = 60^\circ$. 
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\[ G(\Gamma) \]

log \( \frac{R_H}{\text{nm}} \)

PIL-N
PIL-C
PIL-G

\[ 0 \quad 1 \quad 2 \quad 3 \quad 4 \]

\[ b \]

\[ 0.0 \quad 0.2 \quad 0.4 \quad 0.6 \quad 0.8 \quad 1.0 \quad 1.2 \]

\[ \log (R_H / \text{nm}) \]

\[ b \]
wt% (b) and for PIHs at 1 wt% (c) 1 and 5 wt% (d) at 23 °C and at $\theta = 60^\circ$. Note that $R_H$ is used instead of $\tau$ for the horizontal axes in all of the figures displaying decay rate distribution function in order to compare the size of single polymer chain directly with that of aggregated polymer. Because all of the solutions investigated for aggregation behavior in DLS to give decay rate distribution functions have the equal concentrations of 1 and 5 wt%, we considered the comparison of both sizes using $R_H$ to be preferable to make both interpretation and consideration easy for all of the data. Both PILs and PIHs had two peaks, i.e. fast and slow mode, at 1 wt% and three peaks, i.e. fast, middle and slow mode, at 5 wt%. In particular, both PILs and PIHs had larger peaks (fast mode) with a peak top at around $R_H = 5$-$10$ nm and smaller peaks (slow mode) with a peak top at around $R_H = 100$-$300$ nm at 1 wt% as shown in Figure 6.6 (a) and (c). Meanwhile, they had larger peaks (fast mode) with a peak top at around $R_H = 3$-$7$ nm, tiny peaks (middle mode) with a peak top at around $R_H = 30$-$80$ nm and smaller peaks (slow mode) with a peak top at around $R_H = 1,000$-$4,000$ nm at 5 wt% as displayed in Figure 6.6 (b) and (d).

These results let us discuss the aggregation behavior of BCDA-based polyimides on the basis of Figure 6.7, which shows the $q^2$-dependence of $\Gamma$ for PIL-G with the lowest degree of imidization (69.4 %) and PIH-C with the highest degree of imidization (95.8 %) of all the six samples at 1 wt% (a) and 5 wt% (b) at 23 °C for convenience. Note that the other BCDA-based polyimides, i.e. PIL-N, -C and PIH-N, -G, have the same trends as both PIL-G and PIH-C. $\Gamma$ of all relaxation modes at 1 wt% and at 5 wt% for each polymer solution are proportional to $q^2$, indicating that they are diffusive. It can be concluded, therefore, that the fast mode is ascribed to the diffusive motion of single polymer chains, whereas the middle and the slow mode are caused by the diffusive motion of small and large aggregated polymers, respectively. With respect to the correlation of these multi-mode peaks between 1 and 5 wt%, the slow-mode peaks at 1 wt% would corresponds to the middle-mode peaks at 5 wt% given the $R_H$ range for each peak. On the other hand, although both PILs and PIHs have the aggregation peaks corresponding to both the middle and the slow mode, the aggregation peaks of PIHs are larger than those of PILs over independent of the variety of the reaction solvents. This means that PIHs aggregates more highly than PILs in all of the three solution systems. Given the general trend that polyimides have much stiffer chains than most of all flexible polymers, it is suggested that BCDA-based polyimides also have stiff chains, which could be described as rigid-rods. Furthermore, PIHs would have stiffer chains than PILs because the former has higher degree of imidization than the latter. Thus, the primary factor for the
Figure 6.7. Scattering vector dependence of the decay rates for PIL-G and PIL-C with a concentration of 1 wt% (a) and 5 wt% (b) at 23 °C.
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\[ \Gamma (\text{Fast mode}) / \text{s}^{-1} \]

\[ \Gamma (\text{Middle mode}) / \text{s}^{-1} \]

\[ \Gamma (\text{Slow mode}) / \text{s}^{-1} \]

- PIL-G/Fast mode
- PIH-C/Fast mode
- PIL-G/Middle mode
- PIH-C/Middle mode
- PIL-G/Slow mode
- PIH-C/Slow mode

\[ 10^{15}q^2 / \text{m}^{-2} \]
aggregation of BCDA-based polyimides is considered to be the stiffness of the polymer chain. Because the higher degree of imidization gives the lower solubility of BCDA-based polyimides as noted earlier, it is conceivable to assume that the increase in the degree of stiffness of the polymer chains leads to the decrease in the solubility, resulting in the aggregation.

As displayed in Figure 6.8, all of the data points D (fast mode) are seen to start to deviate from each straight line at around \( c/c^* \sim 0.1-0.2 \). On the basis of Figure 6.6-6.8, it is suggested that BCDA-based polyimides associate into small clusters at \( c/c^* \sim 0.1-0.2 \) and form large aggregates at \( c/c^* \sim 1 \). It is concluded, therefore, that the single BCDA-based polyimide chains first associate with each other to form small clusters in the dilute region \( (c < c^*) \), and then expand to large aggregates by the entanglements between the small clusters with an increasing concentration into the semi-dilute region \( (c \sim c^*) \). This peculiar aggregation behavior of BCDA-based polyimides cannot be explained by only the difference of both their solubility and degree of imidization. This is because the respective aggregation peaks at 1 and 5 wt% have almost equal intensity over independent of the type of the reaction solvents although the solubility of BCDA-based polyimides depends highly on the solution systems as found in the difference of the \( k_D \) values in Table 6.3 and Figure 6.5. It is interesting that the intensity of the aggregation peaks in both NMP and NMP/GBL is almost equal to that in NMP/CHN. It may be related to the inherent characteristics of BCDA-based polyimides other than both their solubility and degree of imidization that they start to aggregate in the dilute region given that most of all flexible polymers tend to form clusters in the semi-dilute or concentrated region, i.e. \( c > c^* \).

We consider that the specific aggregation behavior of BCDA-based polyimides would be attributed to their original molecular structure, which can provide both “organic-solubility” and “organic-insolubility”. The aggregation caused by the difference of solubility would depend highly on the bulkiness of the main chain in addition to the following three interactions: 1) charge transfer (CT), 2) hydrogen-bonded and 3) \( \pi-\pi \) interaction. First, alicyclic structure is bulkier than aromatic structure as shown in the fact that BCDA has larger bulkiness than PMDA.\(^{26}\) To be more precise, BCDA-based polyimides have the bulky BCDA moieties, which include the bridging linkage, i.e. -C=C-, over the cyclohexane rings, and cause a breakdown of the main-chain planarity, resulting in the increase of their solubility. Thus, the increase in bulkiness would depress the aggregation of BCDA-based polyimides, leading to “organic-solubility”.

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Figure 6.8. Double logarithmic plots of the diffusion coefficient for fast mode versus $c/c^*$. 

\[ \log D \text{ (Fast mode)} / \text{cm}^2\text{s}^{-1} \]

\[ \log \left( \frac{c}{c^*} \right) \]
Secondly, it is noteworthy that polyimides form CT complex, which causes the coloration of polyimide solution and film. In the case of BCDA-based polyimides, CT interaction would occur 1) between the diamine (electron-donor) and the dianhydride (electron-acceptor) moieties, 2) between the phenol (electron-rich) and the imide-ring (electron-poor) units and 3) between the residual amic-acid (electron-rich) and the imide-ring (electron-poor) moieties. The first mention of CT in aromatic polyimides was made by Dine-Hart et al. in 1971. Kotov et al. confirmed the occurrence of CT in aromatic polyimides in a study of the UV-VIS spectra of several poly(pyromellitimide)s and their model compounds using pyromellitic dianhydride, i.e. PMDA-based polyimides. The formation of CT complex depends on the combination of diamines and dianhydrides, which classify polyimides into three types: type A of “aromatic” polyimides (aromatic diamine and aromatic dianhydride), type B of “semi-aromatic” polyimides (aromatic (or alicyclic) diamine and alicyclic (or aromatic) dianhydride) and type C of “alicyclic” polyimides (alicyclic diamine and alicyclic dianhydride). According to Matsumoto et al., the transmission UV-VIS spectra of polyimide films increases in the order of type A, B and C. The three types of polyimide films exhibit a cut-off wavelength, which is defined as the point where the transmittance becomes less than 1 % in the spectrum, around (A) 400, (B) 280-320 and (C) 230 nm, respectively. This means that the incorporation of alicyclic units into the polyimide backbone weakens the formation of CT complex because the coloration of the polyimide films is derived from the presence of CT complex. It is conceivable to assume that the trend for the formation of CT complex in solution would be the same as that in film. In other words, polyimides in solution would also be likely to form CT complex in the order of type A, B and C. In solution, CT complex is considered to become an origin resulting in polymer aggregates because CT interaction occurs between intra- and/or intermolecular of the polymer chain. The correlation between the solubility and the CT interaction leading to polymer aggregates would be demonstrated by the fact that type A such as PMDA-based polyimides is insoluble in organic solvents, whereas both type B including BCDA-based polyimides and type C are soluble in them. BCDA-based polyimides have alicyclic moieties, which reduce the CT interaction between the diamines (ODA and DDB) and the dianhydride (BCDA) unit. Thus, the decrease in the CT interaction would weaken the aggregation of BCDA-based polyimides, giving “organic-solubility”.

Thirdly, given the recent finding that the functional groups along the poly(amic acid)s chain determine the aggregations, it is conceivable that hydrogen bond promotes aggregation. Under this consideration, BCDA-based polyimides having both phenolic hydroxyl groups of
DDB units and carboxylic hydroxyl groups of residual amic-acid units in the main chain would have some possible driving force originating from hydrogen-bonded interaction for the aggregation. Due to the presence of these hydroxyl groups, three types of hydrogen-bonded interaction would arise in the following order in strength: 1) between the phenol groups on separate chains, 2) between the phenol groups and the residual amic acids, and 3) between the end phenols and the end aniline of ODA units. In particular, the interaction between the phenol groups on separate chains would be much stronger, and thus would enhance the aggregation of BCDA-based polyimides, resulting in “orgnic-insolubility”.

Fourthly, it is well known that an increase of the planarity of the polymer chain due to the introduction of phenyl groups result in stronger \( \pi-\pi \) stacking, leading to aggregation.\(^\text{32}\) Similar to PMDA-based polyimides, BCDA-based polyimides also have the aromatic diamine (ODA and DDB) units, which would stack via the \( \pi-\pi \) interaction of their phenyl rings. Given that \( \pi-\pi \) interaction causes aggregation as stated above, the \( \pi-\pi \) stacking between the phenyl rings of the both diamines would make BCDA-based polyimide chains aggregate even in dilute region, causing “orgnic-insolubility”. With respect to the interest how the degree of the main-chain bulkiness and these interaction of BCDA-based polyimides, i.e. the CT, hydrogen-bonded, and the \( \pi-\pi \) interaction, have an impact on their solubility, we would like to limit ourselves to the above-mentioned rough consideration because this study focuses on the aggregation behavior. In addition to all of the above-noted conceivable interactions, as reported in the previous study,\(^\text{31}\) complicated factors such as effects of polyelectrolytes and the difference in chain rigidity between the residual amic-acid and the fully imidized units may perhaps come into play.

It is concluded, therefore, that the unique aggregation behavior of BCDA-based polyimides is dominated by the balance between the driving force for the “organic-solubility” given by the introduction of alicyclic BCDA units into the polyimide backbone leading to both the increase in bulkiness and the decrease in the CT interaction, and that for the “organic-insolubility” resulting from the incorporation of the phenolic diamine units into the polyimide backbone causing the hydrogen-bonded interaction of the phenolic hydroxyl groups and the \( \pi-\pi \) interaction of the phenyl rings.

### 6.4 Conclusion
Six organic-soluble semi-aromatic polyimides, i.e. BCDA-based polyimides, with different degree of imidization, which range from 69 to 75 % (PIL-N, -C and -G) and from 83 to 96 % (PIH-N, -C and -G), were synthesized using ODA, DDB and BCDA in NMP, NMP/CHN and NMP/GBL. BCDA-based polyimides have the characteristics that the higher degree of imidization gives the lower solubility. The single BCDA-based polyimide chains first associate with each other to form small clusters in the dilute region ($c < c^*$), and then expand to large aggregates by the entanglements between the small clusters with an increasing concentration into the semi-dilute region ($c \sim c^*$). The unique aggregation behavior of BCDA-based polyimides is dominated by the balance between the driving force for the “organic-solubility” obtained by the introduction of alicyclic BCDA units into the polyimide backbone leading to both the increase of bulkiness and the decrease of the CT interaction, and that for the “organic-insolubility” resulting from the incorporation of the phenolic diamine units into the polyimide backbone inducing both the hydrogen-bonded interaction of the phenolic hydroxyl groups and the $\pi-\pi$ interaction of the phenyl rings.

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List of Publications

CHAPTER 2

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Other Publications

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