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Tokuda, Masayoshi

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博士論文

Preparation of Functional Polymer Particles Utilizing Ionic Liquid Monomer

イオン液体モノマーを利用した機能性高分子微粒子の創製

平成 27 年 7 月

神戸大学大学院工学研究科

徳田　真芳

Masayoshi TOKUDA

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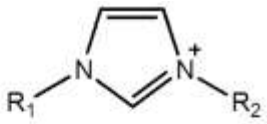
General introduction

Ionic liquids are the salts composed of cation and anion, but liquid state in a wide range of temperature (mainly below 100˚C).[1-3] Generally, inorganic salt is solid state at room temperature because of strong coulomb interaction between cation and anion: the melting point of sodium chloride (NaCl) is 801˚C. The inorganic salt at liquid state (molten salt), which is used in the electrochemical field, is obtained by mixture of multiple salts and heat treatment at high temperature over 1000˚C. On the other hands, the structure of ionic liquid is composed of organic cations and organic or inorganic anions. The melting pint of ionic liquids is depended on the combination the Lewis acidity of cation and Lewis basicity of anion, which could be decreased below room temperature because of week coulomb interaction between cation and anion.[4]

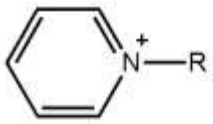
The first ionic liquid is ethylammonium nitrate ($C_2H_5NH_3^+$ NO_3^-, m.p. 12˚C) synthesized by Walden in 1914.[5] By the 1980s, the various ionic liquids having alkylpyridinium or alkylimidazolium cations with halide or tetrachloroaluminate anions were developed in the field of electrochemistry.[6-8] However, these ionic liquids were difficult to handle because of unstable for air and moisture. In 1992, the stable ionic liquid in the air and water, 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF_4]), was firstly reported by Wilkes and Zawarotko.[9] Following this report, many researchers were reported on the synthesis of various ionic liquids, which is stable in the air and water.[10] **Scheme 1** shows the typical structure of cations and anions as an element of ionic liquids.

Scheme 1. Chemical structure of cations and anions as an element of ionic liquids

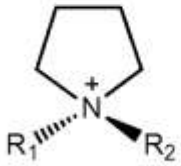
Cation



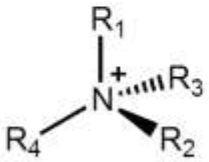
1, 3-dialkylimidazolium



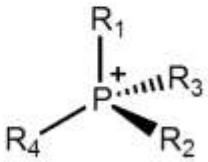
***N*-alkylpyridinium**



***N*, *N*-dialkylpyrrolidinium**

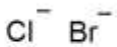


Tetraalkylammonium

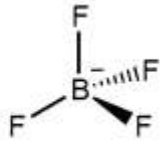


Tetraalkylphosphonium

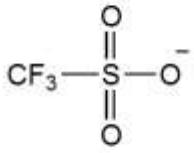
Anion



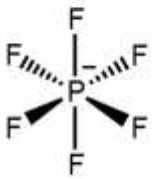
Halides



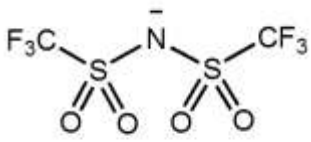
Tetrafluoroborate, [BF_4]



Trifluoromethanesulfonate, [CF_3SO_3]



Hexafluorophosphate, [PF_6]



Bis(trifluoromethanesulfonyl)amide, [TFSA]

At the present time, the synthesis of ionic liquid exceeded 1000 types was reported. Moreover, a number of synthesizable ionic liquid has no limits due to combination of organic ions.[11]

Application of ionic liquids

1. Reaction media

Ionic liquids have various unique properties such as low vapor pressure, thermal stability, nonflammability, wide range solubility and changing of solubility utilizing anion exchange reaction. Owing to these properties, ionic liquids have attracted attention to the reaction media as a substitute for volatile organic compounds in various fields.

In the following sections, the application of ionic liquids as reaction media is explained.

(i) Organic chemistry

In organic synthesis, ionic liquids have many advantages compared to volatile organic compounds. Ionic liquids have no risk of diffusion to air and explosive properties as well as are possible to recycle utilizing their low vapor pressure. Sedden and coworkers were reported that the ionic liquid (1-butyl-3-methylimidazolium tetraphosphate: [Bmim][PF_6]) was extremely useful reaction media in Mizoroki-Heck reaction because it was possible to separate and reuse [Bmim][PF_6] with palladium catalyst.[12] After this report, many literatures on the organic synthesis in ionic liquids, e.g. Friedel-Crafts reaction, Grignard reaction, Baeyer-Villiger reaction, Diels-Alder reaction, *etc.* were reported.[13-23] Utilizing ionic liquid as reaction media, the improvement of the selectivity and activity on synthesis reaction has been achieved.

(ii) Inorganic chemistry

Ionic liquids have good dissolution property for inorganic compounds by a combination of cation and anion. Utilizing this property, the synthesis of inorganic materials

in ionic liquids has been reported.[24-30] Antonietti group reported the synthesis of highly crystalline titania nanoparticles in ionic liquids at 80˚C without calcination at high temperature and the effect of imidazolium-based ionic liquid based on crystal growth.[31] Minami and coworkers reported the synthesis of crystalline alumina particles in ionic liquids.[32] Moreover, they have successfully carried out the preparation of polymer/inorganic composite particles in an ionic liquid.[33-35]

(iii) Biochemistry

Generally, in salt aqueous solution at high concentrations, the enzymic reaction is inactivated. On the other hands, the enzymic reaction in ionic liquid is proceeded and it is possible to recycle ionic liquid used as reaction media. Utilizing ionic liquids, the improvement of activity and selectivity in enzyme-catalyzed reaction was reported by many groups.[36-41]

Some ionic liquids readily dissolve cellulose, which is the most abundant natural polymer on Earth. In 2002, Rogers and coworkers firstly reported that ionic liquid (1-butyl-3-methylimidazolium chloride: [Bmim]Cl) dissolved the cellulose under mild heat treatment.[42] They also reported that this dissolution mechanism of cellulose in [Bmim]Cl was based on the breaking of extensive hydrogen bonding network in cellulose molecules and the formation of hydrogen bonding between the carbohydrate hydroxyl protons of cellulose and chloride ions of ionic liquid.[43] Thereafter, there has attracted attention to the treatment of cellulose using ionic liquids. Until now, the preparation of cellulose films, fibers, particles, cellulose/polymer composite materials and bioethanol production from cellulose were reported by utilizing specific dissolution property of ionic liquid for cellulose.[44-52]

(iv) Polymer chemistry

The conventional radical and ionic polymerizations proceed in volatile organic compounds as media, which have become a problem such as atmosphere pollution. Especially, free radical polymerization is important technique in industrial field. To solve this problem, ionic liquids have been used as polymerization media because of their low vapor pressure, thermal stability, nonflammability.[53-66] Radical polymerization in ionic liquids has important advantage of high polymerization rate and high molecular weight compared to that in organic solvents.[67-75] This reason was reported that the termination rate (k_t) was decreased and the propagation rate (k_p) was increased due to high viscosity of ionic liquid.[69]

The dissolution behavior of polymer in ionic liquids has been investigated. Watanabe group firstly reported that the poly(*N*-isopropyl acrylamide), which is typical polymer with the lower critical solution temperature (LCST) behavior in water, showed the upper critical solution temperature (UCST) behavior in ionic liquid (1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide: [Emim][TFSA]).[76] They also reported the LCST phase behavior of poly(benzyl methacrylate) and its derivatives in imidazolium-based ionic liquid, and their mechanisms of phase transition was based on thermodynamical and structural-chemical approach.[77-83] The thermosensitive gel particles incorporated ionic liquids have been anticipated many applications for functional materials such as drug delivery systems and switching devices.[84-86]

2. *Functional materials*

Ionic liquids have functional properties such as ionic conductivity and CO_2 absorbent. The composite materials, which are composed of polymer and ionic liquids, were

expected the functional materials such as polymer electrolyte and CO_2 separation membrane. Moreover, ionic liquids can be modified the additional properties such as liquid crystallinity[87], magnetism[88], and fluorescence[89] by changing cation and anion structures. In the following sections, the typical application of ionic liquids as functional materials is explained.

(i) Ionic conductive materials

Many researchers have investigated the ionic conductivity of ionic liquids and their application as electrolytes.[90-103] The ionic liquids having 1-ethyl-3-methylimidazolium ([Emim]) cation exhibit the highest ionic conductivity of the 10^{-2} mS cm^{-1} order in all ionic liquids. Moreover, the conductivity of ionic liquids has been influenced on cation and anion structures (viscosity), temperature and solvent. Watanabe group firstly reported the synthesis of polymer gels incorporated ionic liquids, which was called "ion gel", as development of solid electrolyte.[104,105] As these results, the obtained ion gels exhibited high ionic conductivity and stability for humidity. Mastumoto group also reported the ionic conductivity of ion gels composed of ionic liquid and cross-linked polymer based on the structure of ionic liquid.[106] Minami and coworkers reported the prepration of ionic liquid-encapsulated polymer particles and their ionic conductivity.[107] The polymer materials including ionic liquids have been expected to be application as solid-state electrolyte.

(ii) CO_2 separation materials

In 1999, Brennecke group discovered that large amounts of CO_2 dissolved in ionic liquid.[108] Thereafter, many researches have reported the solubility and selectivity of CO_2 in ionic liquids.[109-114] Utilizing this property, the gas-separated membrane has been developed

by combining polymer with ionic liquids and impregnating porous materials with ionic liquids.

Why CO_2 is dissolved in ionic liquids? This answer remains incompletely understood and is debated even now. The leading theory was considered as the Lewis acid-base interaction between CO_2 and anions of ionic liquids.[115] This is based on the experimental results that ionic liquids having [TFSA] anion exhibited high solubility of CO_2 as compared to those having PF_6 and BF_4 anions. In 2011, however, it was reported that the interaction between CO_2 and [TFSA] anion was weaker than between CO_2 and PF_6 anion[116], which was inconsistent with experimental result. Nowadays, many researchers support the theory of free volume effect of ionic liquids. This theory was reported by different research groups[116,117], in which the free volume of ionic liquids existed in the interionic space between cation and anion from molecular dynamic simulation and quantum chemical calculation, resulting that CO_2 solubility in ionic liquids was increased, as cation-anion interaction gets weaker.

Amino acid-based ionic liquids, which were firstly prepared by Ohno group in 2005[118], have also attracted attention to the CO_2 solubility because CO_2 was reacted with amino group[119] The development of CO_2 transport membrane containing amino acid-based ionic liquid have been reported.[120,121]

(iii) Solid-state materials

The solid-state materials having the property of ionic liquids is expected the improvement of stability when ionic liquids are used as materials. The polymerization of ionic liquids is one of the effective methods in terms of mechanical stability and

processability. The polymer materials prepared by polymerization of ionic liquid with vinyl and (meth)acrylate groups are called "poly(ionic liquids)" or "polymerized ionic liquids" (PILs).[122-126] In 1973, Salamone and coworkers were reported on the synthesis and polymerization of vinylimidazolium salt, which is the first report on the preparation of PIL.[127] In those days, the research object drew attention to not the property of PIL nature (e.g. ionic conductivity) but the solution behavior of PIL in water. Approximately 20 years later, Ohno group was reported the preparation of PIL as ionic conductive materials with the property of ionic liquids.[128] However, the low ionic conductivity of PIL was problem when the PILs were used as polymer electrolyte. Afterwards, the investigation and improvement on ionic conductivity of PILs and the application as solid electrochemical devices were reported by many researchers.[129-133] The lower glass transmission temperature of PILs had a significant effect on the ionic conductivity. Tsujii and coworkers were reported the preparation of the silica particles with concentrated PIL blushes by surface-initiated atom transfer radical polymerization, in which the colloid crystal consisted of hybrid particles exhibited the high ionic conductivity among solid polymer electrolyte.[134]

In 2005, Shen and coworkers reported the pioneering work on the CO_2 absorption of PIL.[135] The CO_2 sorption capacity of ammonium-based PIL was higher than that of imidazolium-based PIL, and the CO_2 sorption and desorption rate of PIL was fast compared with that of ionic liquid. Since this report, several research groups was investigated the usage as CO_2 capture of PIL.[136-140]

Imidazolium-based PILs also have been investigated to be application such as composite materials and dispersant of carbon nanotubes (CNTs) and graphenes via π-π interactions.[141-144] The dispersant of carbon materials in matrix and solvent is of great

significant to behave the excellent property. In addition to their applications above, the researches on the functional applications of PILs such as catalysts, porous materials, and microwave absorbents were reported, which is suggested that the PILs is anticipated to be functional materials in various fields.[125,126]

Recently, the polymer particles are desired the wide variety of functionality because they are expected to be the smart materials as particle state in the sophisticated industrial fields as well as the traditional applications such as coatings, adhesive and film. The polymer particles having the structure of ionic liquids (PILs particles) are the particle materials combined the properties of polymer particles and ionic liquids. Muldoon and Gordon firstly reported the preparation of imidazolium-based PIL beads by suspension polymerization in 2004, in which the application as catalyst was investigated with palladium-loaded PIL beads.[145] Mecerreyes and coworkers reported the synthesis of PIL microgel particles by water-in-oil concentrated emulsion polymerization and the entrapment of enzyme into PIL microgels toward a glucose sensor.[146] Texter group attempted to prepare poly(methyl methacrylate) (PMMA) latex using surfactant ionic liquid having polymerizable group by miniemulsion polymerization.[147] As the results, MMA and surfactant ionic liquid monomer were copolymerized and the stable nanoparticles (average diameter: 30 nm) was obtained under suitable condition. Although the application of ionic liquid as surfmer (surfactant + monomer) was revealed in this report, the obtained particles were not absolutely PIL particles because of copolymer. In 2009, Yan and coworkers have reported the preparation of polypyrrole nanoparticles bearing imidazolium-based ionic liquid moiety via chemical oxidative miniemulsion polymerization and the application for DNA detection and

CO_2 adsorption.[148] Moreover, they also reported the sysnthesis of imidazolium-based PIL particles via inverse miniemulsion polymerization and the catalytic activity of Pt-induced PIL particles.[149] In 2011, Yuan group reported the preparation of PIL particles by dispersion polymerization in water using the imidazolium-based ionic liquid monomer having long alkyl chain.[150] However, the nucleation mechanism was similar to microemulsion polymerization system because the oligomer propagated in the early stage of polymerization was self-assembled, resulting in micelles, and the polymerization proceeded therein[151], the nanometer-sized PIL particles were obtained. Since then, they also have reported some papers on the application using PILs nanoparticles.[151-153] The preparation of monodispersed PIL microgel particles by inversed suspension polymerization was reported by Khan and coworkers in 2013.[154] Utilizing anion exchange of PIL microgel particles, they investigated the volume transition, pH-responsive release, magnetism, and redox ability. The PIL micro/nano particles have a dozen possibilities as functional materials in various fields; however, there is hardly report on basic physical property and formation mechanism of PIL particles.

This dissertation aims at the acquirement of basic knowledge on the particle formation of PIL. **PART 1** covers the preparation of PIL particles. In ***Chapter 1***, the preparation of PIL particles by dispersion polymerization was carried out and the property of PIL particles was investigated. ***Chapter 2*** is aimed at the investigation of specific dissolution behavior of PIL particles by anion exchange. In ***Chapter 3***, the preparation of submicron-sized PIL particles by emulsion polymerization was carried out. Moreover, the surface property of emulsion film was investigated. **PART 2** covers the preparation of composite particles composed of PILs and conventional polymer. In ***Chapter 4***, the

polymer/PIL composite particles were prepared by seeded dispersion polymerization. The important factor to obtain the composite particles was investigated from the viewpoint of spreading coefficients. In ***Chapter 5***, the influence of polymer polarity of seed particles on the preparation of composite particles was investigated. Utilizing anion exchange, the functionality of composite particles was modified. In ***Chapter 6***, the synthesis of thermosensitive composite particles with imidazolium-based PIL and poly(phenylethyl methacrylate) was carried out. Moreover, the effects of ionic liquid monomer structure and molecular weight of poly(phenylethyl methacrylate) were also inventigated. In ***Chapter 7***, the preparation of cross-linked PIL composite particles with hollow structure was carried out by suspension polymerization utilizing the self-assembling of phase-separated polymer (SaPSeP) method. ***Chapter 8*** is aimed to prepare PIL particles containing reduced graphene oxide (rGO) by miniemulsion polymerization. We have also demonstrated the effect of imidazolium-based ionic liquid monomer/ethyl methacrylate ratio on dispersibility of rGO. In ***Chapter 9***, the preparation of conventional polymer/rGO composite particles was carried out by miniemulsion polymerization. Imidazolium-based PIL was used as dispersant of rGO and the rGO dispersibility in conventional monomer was also investigated.

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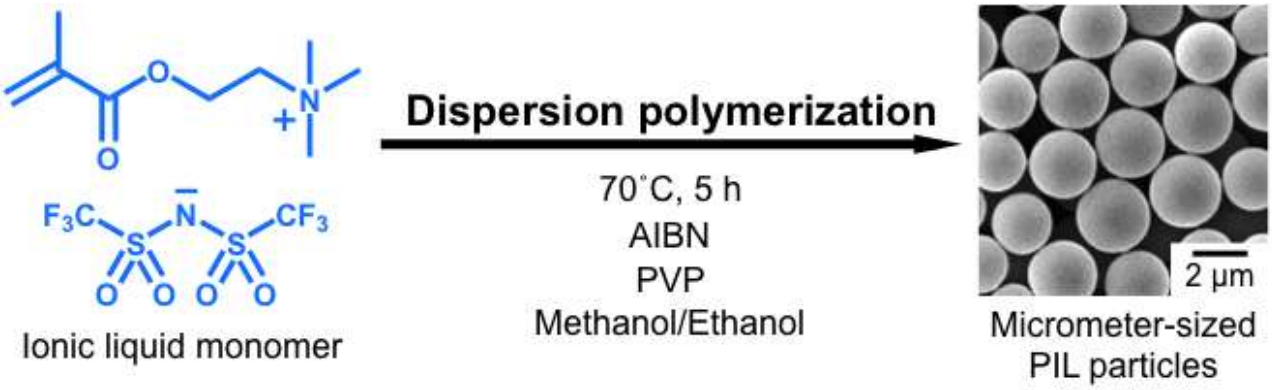
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Chapter 1

Preparation of Micron-sized Monodispersed Poly(ionic liquid) Particles by Dispersion Polymerization



Abstract: Micron-sized monodisperse poly(ionic liquid) (PIL) particles, poly([2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide), were prepared by dispersion polymerization at 70°C in methanol with poly(vinylpyrrolidone) (PVP) as a stabilizer. The obtained particle size could be controlled by addition of ethanol to the methanol medium while maintaining narrow monodispersity. This is thought to be the first report on the preparation of micron-sized monodisperse PIL particles by dispersion polymerization. The PIL particles exhibit unique properties; they can be observed by scanning electron microscopy (SEM) without platinum coating, which is generally used to avoid an electron charge. Moreover, the solubility of the PIL particles can be easily changed by changing the counter anion, similar to the process for ionic liquids. When LiBr was added to the PIL dispersion, it immediately became optically transparent, which indicates that the counter anion was replaced with Br anion and the PIL particles dissolved in methanol.

Introduction

Ionic liquids, which consist entirely of organic ions but are in a liquid state at ambient temperature, have attracted attention as environmental friendly media because of their low vapor pressures, thermal stability, and nonflammability.[1-6] Owing to these properties, ionic liquids have been used as media for chemical, biochemical, and polymer reactions as an alternative to volatile organic solvents.[7-16]

Recently, we succeeded in preparing polystyrene (PS) particles by dispersion polymerization in the ionic liquid *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)amide.[17] We also prepared nylon 6 and poly(acrylic acid) (PAA) particles in ionic liquids.[18,19] Furthermore, we succeeded in preparing PS/PAA and PS/η-Al_2O_3 composites having core-shell morphology in ionic liquids using PS particles as seeds.[20,21]

In addition to environmental friendly properties, ionic liquids have other functional properties such as ionic conductivity and high solubility of CO_2.[22-24] The attractive properties of ionic liquids, e.g., paramagnetism, liquid crystallinity, and fluorescence, can be easily modified by changing the combination of cations or anions.[25-27] Recently, the preparation of solid state materials having characteristic properties of ionic liquids have attracted much interest for developing functional materials. The immobilization of ionic liquids with a conventional polymer gel, the so-called "ion gel," has been reported.[28,29] Poly(ionic liquid)s (PILs) were prepared by direct polymerization of ionic liquid monomers, which have polymerizable groups on cationic or anionic parts.[30-37] They can have various applications such as sorbents of CO_2, polymer electrolytes, dispersants for nanomaterials, and microwave absorbing materials.[29,38,39] However, there are a few reports on the preparation of PILs as particle state. Gordon et al. reported the preparation of PIL beads by suspension

polymerization of a water-immiscible, imidazolium-based monomer.[40] Mecerreyes et al. carried out the water-in-oil concentrated emulsion polymerization of a water-soluble imidazolium-based monomer and obtained PIL microparticles.[41] Recently, Yuan et al., for the first time, reported the preparation of PIL nanoparticles by dispersion polymerization, in which self-stabilized nanoparticles were obtained in an aqueous solution when ionic liquid monomers having sufficiently long alkyl chains were used.[42] More recently, they reported that the PIL nanoparticles were formed spontaneously by precipitation polymerization from water, and the nucleation mechanism seemed to be similar to the models of microemulsion polymerization rather than dispersion polymerization.[43] However, the size of the obtained particles in the above studies was uncontrolled, and the particles had a broad size distribution.

In ***Chapter 1***, dispersion polymerization of a quaternary ammonium-based ionic liquid monomer was carried out to prepare micron-sized monodisperse PIL particles. This is believed to be the first report on the preparation of micron-sized monodisperse PIL particles by dispersion polymerization.

Experimental Section

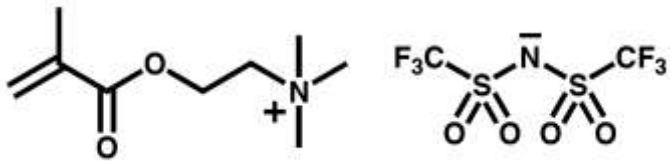
Materials

Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization in methanol. Poly(vinylpyrrolidone) (PVP, K-30, weight-average molecular weight: 3.6×10^5 g/mol), methanol and ethanol (Nakalai Tesque Inc., Kyoto, Japan), lithium bromide (LiBr) (99%, Aldrich), [2-(methacryloyloxy)ethyl]trimethylammonium chloride ([MTMA]Cl) solution (80 wt% in water, Aldrich), and lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) (99.7%, Kanto Chemical Co., Inc.) were used as received. Water used in all experiments was obtained from the Erix®UV (Millipore, Japan) purification system and had a resistivity of 18.2 MΩ cm.

Preparation of Ionic Liquid Monomer

The ionic liquid monomer was prepared with [MTMA]Cl and Li[TFSA]. After mixing aqueous solutions of 2.0 g [MTMA]Cl (7.7×10^{-3} mol) and 2.3 g Li[TFSA] (8.0×10^{-3} mol), the mixture was stirred for several minutes at room temperature. Then, phase separation gradually occurred, resulting in the formation of two layers. The lower oily layer was collected and washed five times with distilled water. After vacuum drying the oil, a colorless viscous liquid of [2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide ([MTMA][TFSA]) (3.1 g, 6.9×10^{-3} mol) was obtained in a high yield (89.4%). Original [MTMA]Cl showed clear melting point (T_m = 175˚C) , on the other hand, the obtained oil phase showed no clear melting point, but a glass trandition point in very low temperature (T_g = -52°C) from the DSC measurement, which is consistent with the T_g of [MTMA][TFSA] by catalog (Ionic Liquid, KOEI CHEMICAL CO., LTD.). In addition, chemical composition of the ionic liquid monomer was confirmed by FT-IR, in

which the new bands corresponding to the [TFSA] anion: $S(=O)_2$ (1353 cm^{-1}) and CF_3 (1190 cm^{-1}) were observed.



[MTMA][TFSA]

Preparation of PIL Particles

Dispersion polymerizations of [MTMA][TFSA] in methanol were carried out in sealed glass tubes (inner diameter; 9.6 mm, length; 70 mm), in which the boilling of methanol was inhibited, at 70°C for 5 h with shaking at 80 cycles min^{-1} (3 cm strokes) under the conditions listed in Table 1. AIBN and PVP were used as the initiator and the stabilizer, respectively. Furthermore, dispersion polymerizations in ethanol and methanol/ethanol mixtures were carried out under the same conditions, with the only difference being the medium.

Table 1. Recipes for preparation of Poly([MTMA][TFSA]) particles by dispersion polymerizations in methanol (Nos. 1-4) and methanol/ethanol mixture (Nos. 5-7) at 70˚C

Ingredients		**1**	**2**	**3**	**4**	**5**	**6**	**7**
[MTMA][TFSA]	(g)	0.25	0.25	0.25	0.25	0.25	0.25	0.25
AIBN	(mg)	2.5	2.5	2.5	2.5	2.5	2.5	2.5
PVP	(mg)	12.5	6	18	25	18	18	18
Methanol	(g)	2.5	2.5	2.5	2.5	1.7	1.25	0.8
Ethanol	(g)	-	-	-	-	0.8	1.25	1.7
D_n	(μm)	10.0	-	6.1	9.9	3.2	2.8	2.3
C_v	(%)	12.8	-	8.6	10.2	12.7	11.2	8.3

Characterization

Poly([MTMA][TFSA]) particles were observed by scanning electron microscopy (SEM, S-2460, Hitachi Science Systems, Ltd., Ibaraki, Japan) after centrifugal washing three times with ethanol, which is miscible in [MTMA][TFSA]. Number-average diameter (D_n) and coefficient of variation (C_v) were determined for 200 particles from SEM photographs by using an image analysis software (WinROOF®, Mitani Co., Ltd., Japan). Monomer conversions and molecular weight were measured by ^{1}H NMR. The ^{1}H NMR measurements were carried out with a Bruker Avance 500 MHz spectrometer at room temperature in CD_3COCD_3. The glass transition temperature (T_g) of polymer and thermal property of monomer were measured with a differential scanning calorimeter (DSC, 6200, Seiko Instruments Inc., Chiba, Japan) under N_2 flow at a scanning rate of 5°C min^{-1}. Chemical composition of monomer was confirmed with a Fourier transform infrared spectrometer (FT-IR, FT/IR-6200, JASCO Corporation, Tokyo, Japan) using a pressed KBr pellet technique. D_n of the particles in re-precipitated dispersion was measured using a dynamic light scattering (DLS, FPAR-1000 RK, Fiberoptics particle analyzer, PhotalOtsuka electronics, Osaka, Japan) at the light scattering angle of 90° at room temperature using the Contin analysis routine. 1–2 droplets of emulsion samples withdrawn from the reactor were diluted with approximately 8 ml of methanol before measurement in the dilution mode.

Results and Discussion

Preparation of PIL Particles by Dispersion Polymerization

In dispersion polymerization, the monomer, the initiator, and the stabilizer are miscible in the medium, but the obtained polymer is insoluble in the medium. Methanol and ethanol seemed to be suitable for the dispersion polymerization of [MTMA][TFSA] as shown in Table 2.

Table 2. Solubility test[a)] of [MTMA][TFSA] and poly([MTMA][TFSA]) prepared by bulk polymerization at 70°C

	[MTMA][TFSA]	Poly([MTMA][TFSA])
Water	×	×
Methanol	○	×
Ethanol	○	×
Acetone	○	○
THF	○	×
Ethyl acetate	○	×
Hexane	×	×

[a)] ○: soluble, ×: insoluble

The system before polymerization in which [MTMA][TFSA], AIBN, and PVP were soluble in methanol was homogeneous. After polymerization, the system became turbid, suggesting the preparation of poly([MTMA][TFSA]) particles. Figure 1(b) shows the SEM photographs of particles prepared by dispersion polymerization under the conditions of No.1 listed in Table 1. The obtained particles were spherical and micron-sized with a somewhat broad size distribution, which indicated that the poly([MTMA][TFSA]) particles were successfully prepared by dispersion polymerization.

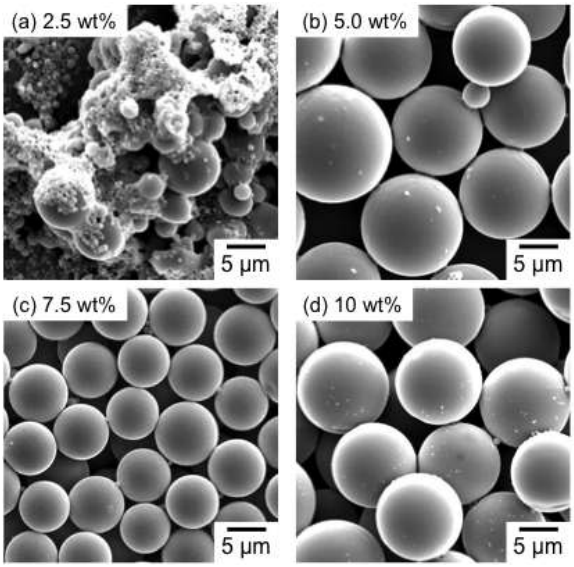


Figure 1. SEM photographs of poly([MTMA][TFSA]) particles prepared by dispersion polymerizations in methanol at various PVP concentrations. PVP concentration (wt% based on [MTMA][TFSA]): (a) 2.5; (b) 5.0; (c) 7.5; (d) 10.

To investigate the influence of PVP concentrations, dispersion polymerization of [MTMA][TFSA] was carried out at various PVP concentrations. For the PVP system with a low concentration (2.5 wt%), the obtained particles were colloidally unstable and coagulum was obtained (Fig. 1a). In the case of other concentration systems, the obtained particles were colloidally stable as shown in Figures 1b-d, although regularity between D_n and the PVP concentration could not be observed (Nos. 1-4 in Table 1). At 7.5 wt% PVP concentration (Fig. 1c), micronsized (D_n = 6.1 μm) PIL particles having high monodispersity (C_v = 8.6%) were successfully prepared by dispersion polymerization. On the other hands, PIL particles synthesized in Schlenck flask had a broad size distribution, which is indicated that the reactor have an effect on size distribution of obtained particles.

In case of a conventional monomer, the particle size can be controlled by changing the nature of the medium, which affects the critical chain length, that is, the number of nuclei. It has been reported that the affinity between an ionic liquid and alcohol decreases with the

increase in the alkyl chain length of alcohol.[44,45] To control particle size, dispersion polymerizations of [MTMA][TFSA] were carried out for various methanol/ethanol mixture compositions (ethanol concentration, wt% based on medium: 0, 33, 50, and 66) at a PVP concentration of 7.5 wt% at 70°C for 5 h (Figure 2).

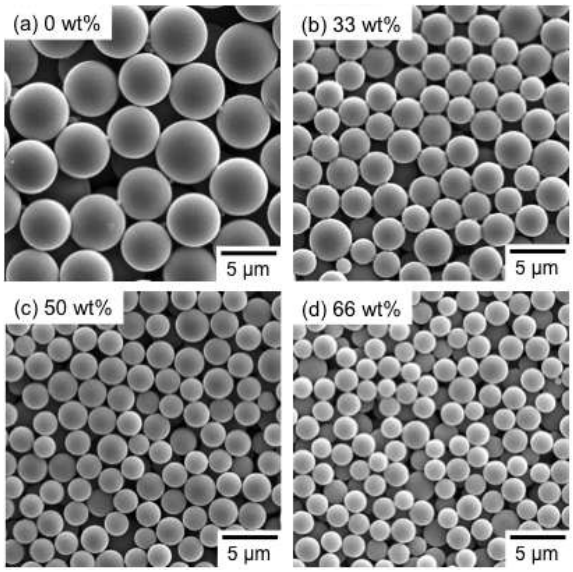


Figure 2. SEM photographs of poly([MTMA][TFSA]) particles prepared by dispersion polymerizations in various methanol/ethanol media. Ethanol concentration (w/w): (a) 0; (b) 33; (c) 50; (d) 66.

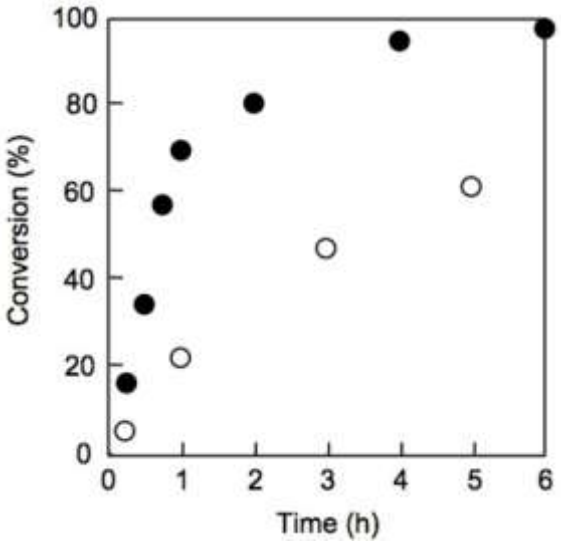


Figure 3. Conversion–time plots for dispersion polymerizations of [MTMA][TFSA] in methanol (open circles) and ethanol (closed circles)

At all compositions of methanol/ethanol, micron-sized PIL particles were obtained and the size distribution had relatively low C_v of approximately 10% (Nos. 5-7 in Table 1). D_n decreased with increase in the ethanol concentration as shown in Figure 2, indicating that it is possible to control particle size by changing the medium in the same manner as in conventional monomer systems.

Figure 3 shows conversion–time plots measured with ^{1}H NMR for the dispersion polymerization of [MTMA][TFSA] at 7.5 wt% PVP concentration in ethanol and methanol. It is difficult to measure the conversion of the ionic liquid monomer by gas chromatography and gravimetry because of the nonvolatility of the ionic liquid. Thus, conversions were determined with ^{1}H NMR using vinyl signals of the monomer at 6 ppm in acetone-d_6. The peak of vinyl protons decreased with polymerization time (Fig. 4). In both systems, polymerization proceeded smoothly without an induction period, with the conversion reaching 100% after 6 h and 62% after 5 h in ethanol and methanol systems, respectively. However, the polymerization rate was low in methanol.

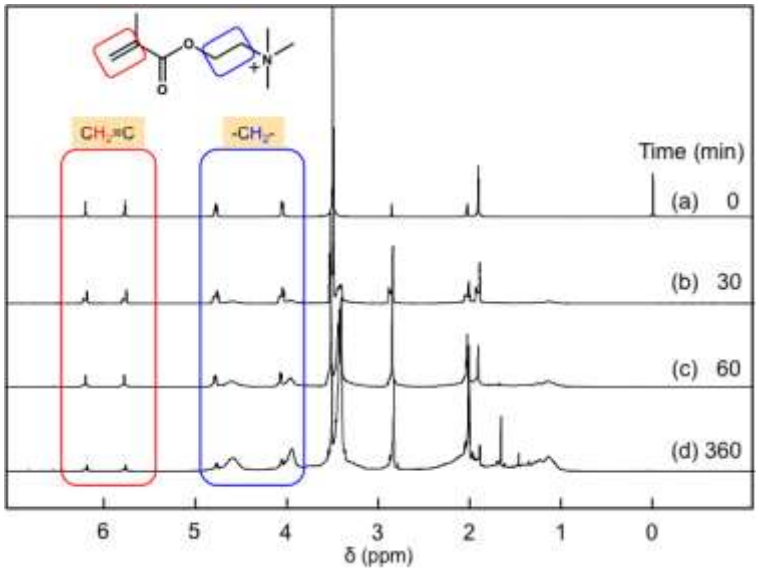


Figure 4. ^{1}H NMR spectra of [MTMA][TFSA] in CD_3COCD_3. Polymerization time (min): (a) 0; (b) 15; (c) 60; (d) 180; (e) 300.

Characterization of PIL Particles

The molecular weight of PIL was measured with ^{1}H NMR by comparing the peak integral of chain end group derived from AIBN at 1.7 ppm to that of the methylene groups contained in PIL at 4.2 ppm and 4.7 ppm in acetone-d_6 using the sample prepared by dispersion polymerization for 6 h in ethanol. The molecular weight considering both coupling and disproportionation terminations was 3.0×10^5–6.0×10^5 g mol^{-1}. The obtained PIL particle had a relatively high glass transition temperature (T_g = 90°C) and thermal stability, similar to the properties of an ionic liquid monomer.

It is well known that ionic liquids can be observed by SEM without coating because of their low vapor pressure and conductivity.[46] To confirm whether PIL particles exhibit a similar property, they were observed by SEM without coating. In general, conventional polymer particles such as PS and polycation cannot be observed by SEM without coating because of electron charges. As shown in Figure 5a, The boundary of the PS particles was unclear. In contrast, PIL particles could be clearly observed even without coating (Fig. 5b). This result strongly suggests that PIL particles maintain the properties of an ionic liquid.

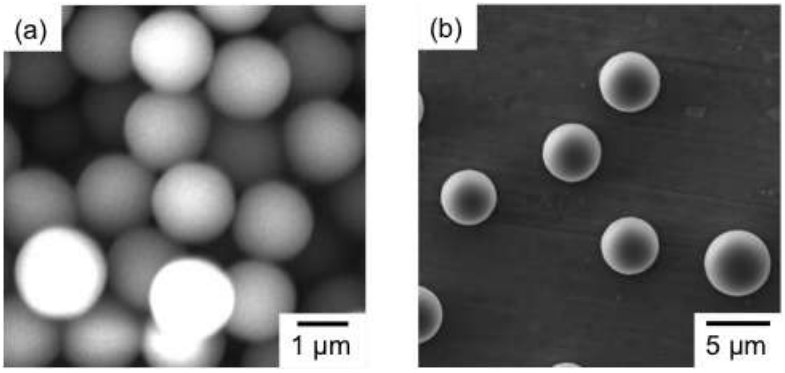


Figure 5. SEM photographs of (a) PS particles and (b) poly([MTMA][TFSA]) particles prepared by dispersion polymerization without coating.

Figure 6 shows the anion change process of PIL. Solubility of ionic liquids can be easily exchanged by changing the anion. When 50 wt% (3 mol%) LiBr relative to PIL was

added to the dispersion, it was observed that the dispersion instantaneously became transparent (Figures. 6(a)-(b)). This phenomenon suggests that the anion, [TFSA], of PIL should be replaced with bromide, which results in a change in solubility and PIL particles were completely dissolved in methanol. Furthermore, the same amount of Li[TFSA] was subsequently added to the clear solution. Interestingly, the system became turbid, suggesting that the particles should form by aggregation of the precipitated polymer due to the replacing the anion from bromide to [TFSA]. As shown in Figure 6c, the dispersion was obtained again, where the submicron sized polymer particles were obtained (measured by DLS). We clearly demonstrated that PIL exhibits salt sensitivity similar to ionic liquid.

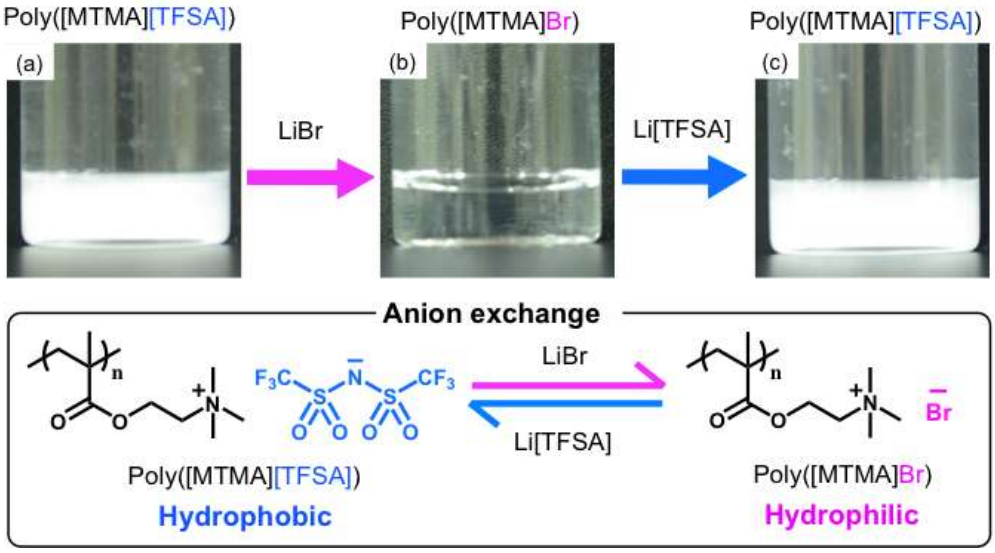


Figure 6. Visual appearance of anion exchange process: (a) poly[MTMA][TFSA] dispersion prepared by dispersion polymerization in methanol; (b) after adding LiBr to poly([MTMA][TFSA]) dispersion; (c) after adding Li[TFSA] to poly([MTMA]Br) solution

Conclusion

PIL particles were successfully prepared by dispersion polymerization at 70°C in methanol and methanol/ethanol mixtures. The particle size and distribution could be controlled by changing the PVP concentration and adding ethanol to the medium. These results were similar to those of conventional monomer systems. Furthermore, PIL particles exhibited unique properties that could be observed by SEM without coating. Solubility of PIL was easily changed by addition of LiBr and Li[TFSA]. These results suggest that PIL maintains the properties of ionic liquids.

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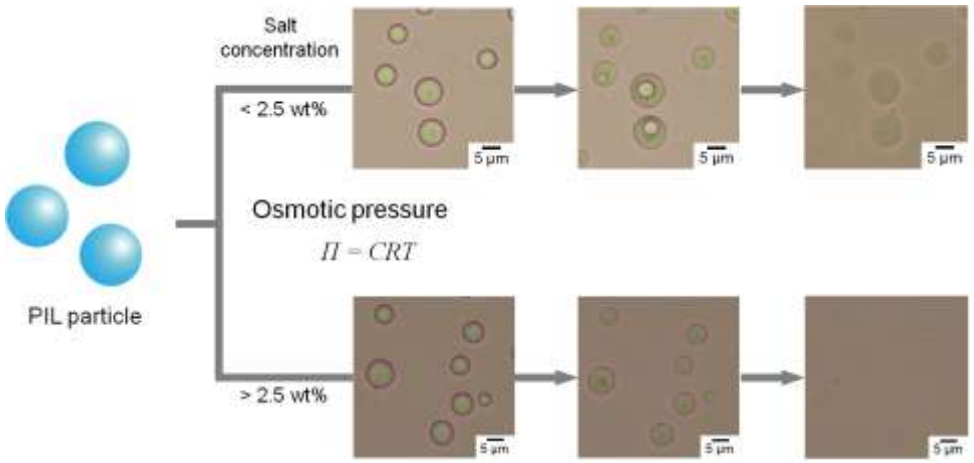
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Chapter 2

Specific Dissolution Behavior of Poly(ionic liquid) Particles by Changing the Counter Anion



Abstract: The dissolution behavior of poly(ionic liquid) (PIL) particles, which were prepared by dispersion polymerization of ([2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide), [MTMA][TFSA], was observed in detail. The dissolution of a PIL was variable by changing the counter anion. A PIL with [TFSA] anion does not dissolve in polar solvents such as ethanol; however, a PIL with Br anion does dissolve in ethanol. Upon the addition of LiBr ethanol solution at high concentrations (>2.5 wt%), the PIL particles dissolved from their outer surface and the counter anion [TFSA] was replaced with Br anion from the particle surface. On the other hand, in the case of the ethanol solution at low LiBr concentrations (<2.5 wt%), a specific dissolution behavior was observed: domains inside the PIL particles were generated before their dissolution, most likely due to osmotic pressure. Moreover, the PIL particles having hollow structure were prepared using this specific dissolution behavior.

Introduction

Ionic liquids exist in the liquid state at room temperature despite containing organic cations and organic or inorganic anions. Many researchers have focused on ionic liquids as an alternative media to volatile organic solvents in chemical, biochemical, and polymer synthesis because of their unique properties such as negligible vapor pressure, thermal stability, and nonflammability.[1-16]

We have reported the preparation of a polystyrene (PS), Nylon 6, at high polymerization temperature, utilizing the advantages of nonvolatility and thermal stability of the ionic liquid, along with poly(acrylic acid) (PAA) particles by dispersion polymerization in an ionic liquid.[17-19] Moreover, the preparation of polymer composite particles such as PS/PAA, PS/ η-Al_2O_3, and PS/$Mg(OH)_2$ using PS particles as seed were demonstrated.[20-22]

Ionic liquids also possess functional properties such as ionic conductivity and high CO_2 absorption[23-25] and can easily add properties such as paramagnetism, liquid crystallinity, and fluorescence by changing the structure of cation and anion.[26-28] To utilize these properties for functional materials, the preparation of solid-state materials having the properties of ionic liquids has been widely investigated. Watanabe and coworkers[29] reported the preparation of poly(methyl methacrylate) (PMMA) gel containing an ionic liquid, (1-ethyl-3-methyl)imidazolium bis(trifluoromethanesulfonyl)amide ([Emim][TFSA]), called "ion gels." This gel showed a highly ionic conductivity comparable with that of pure [Emim][TFSA]. Mastumoto et al. reported that the ion gels, which were composed of an ionic liquid and cross-linked polymethacrylate having an ionic liquid structure, possessed higher ionic conductivity than that of conventional networked polymer.[30,31] In recent times, poly(ionic liquid)s (PILs) have also attracted much interest as a functional material.[32-43] PILs have been prepared by the radical polymerization of an ionic liquid monomer, which has a

polymerizable functional group. The major advantage of PILs is their mechanical stability and processability and they are expected to be applied in various fields such as energy, environment, and biochemistry.[44,45] Moreover, the preparation of PIL particles has been reported by suspension polymerization[46], water-in-oil concentrated emulsion polymerization[47], and dispersion polymerization in water without stabilizer using ionic liquid monomers having long alkyl chains.[48,49]

We have also reported the PIL particles poly([2-(methacryloyloxy)ethyl] trimethylammonium bis(trifluoromethanesulfonyl)amide) ([MTMA][TFSA]) prepared by dispersion polymerization in methanol with poly(vinylpyrrolidone) (PVP) as a stabilizer in ***Chapter 1***. In addition, we succeeded in controlling the particle size and size distribution by the addition of ethanol to the methanol medium. Moreover, an interesting phenomenon was observed that the obtained PIL particles instantaneously dissolved in the medium by the addition of LiBr because of the anion exchange.[50] In this chapter, we investigate in more detail the dissolution behavior of PIL particles by anion exchange.

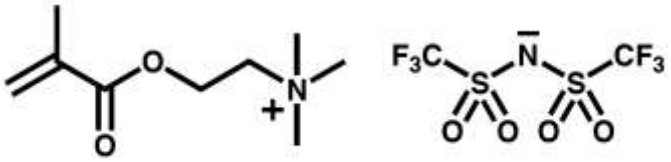
Experimental Section

Materials

Reagent grade 2,2'-azobis(isobutyronitrile) (AIBN) was purified by recrystallization in methanol. Poly(vinylpyrrolidone) (PVP, K-30, weight-average molecular weight: 3.6×10^5 g mol^{-1}), ethanol (Nakalai Tesque Inc., Kyoto, Japan), lithium bromide (LiBr, 99%; Aldrich), [2-(methacryloyloxy)ethyl]trimethylammonium chloride solution ([MTMA]Cl, 80 wt% in water; Aldrich), and lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA], 99.7%; Kanto Chemical Co., Inc.) were used as received. Water used in all experiments was obtained from the Erix®UV (Millipore, Japan) purification system and had a resistivity of 18.2 MΩ cm.

Preparation of Ionic Liquid Monomer

The ionic liquid monomer [MTMA][TFSA] was synthesized by mixing [MTMA]Cl and Li[TFSA] aqueous solutions as previously published.[50] A typical polymerization procedure is described as follows. Monomer (0.25 g), PVP (18 mg), and AIBN (2.5 mg) were dissolved in ethanol (2.5 g). The solution was added into a glass tube, degassed using several vacuum/N_2 cycles, and then sealed off. The sealed glass tube was placed in a water bath at 70°C for 6 h with shaking at 80 cycles min^{-1} (3-cm strokes).



[MTMA][TFSA]

Characterization

The PIL particles precipitated by anion exchange were observed by a transmission electron microscope (TEM; JEM-1230, JEOL Ltd., Japan). The dissolution behavior of poly([MTMA][TFSA]) particles after the addition of an ethanol solution of salt was observed

with an optical microscope (ECLIPSE 80i, Nikon, Japan). The ethanol solutions of LiBr and LiCl at various concentrations were added at room temperature to the PIL dispersion (solid content: 1.0 wt%) on a glass slide. The chemical composition of the polymer before and after the addition of salt was measured with a Fourier transform infrared spectrometer (FT-IR; FT/IR-6200, JASCO Corporation, Tokyo, Japan) using a pressed KBr pellet technique.

Preparation of PIL Particles having hollow structure

The PIL dispersion was dropped on an SEM plate and spin coated. A 0.005 wt% LiBr ethanol solution was added to the PIL particles dried on the SEM plate, and then dried at room temperature. The morphology of the PIL particles was observed by scanning electron microscopy (SEM, S-2460, Hitachi Science Systems, Ltd., Ibaraki, Japan). In the case of the preparation of hollow particles of the PIL dispersion, a 0.5 wt% LiBr/ethanol solution (80 mg) was added to the 0.5 wt% PIL dispersion (1.0 g), in which LiBr concentration in the PIL dispersion was 0.04 wt%. After standing for 30 min, the dispersion was dried at room temperature. To observe the interior morphology of the PIL particles, the dried particles were embedded in an epoxy matrix, cured at 40°C overnight, and then subsequently microtomed. Ultrathin cross-sections of approximately 100 nm thickness were observed with TEM at a voltage of 100 kV.

Results and Discussion

Specific dissolution behavior of PIL particles

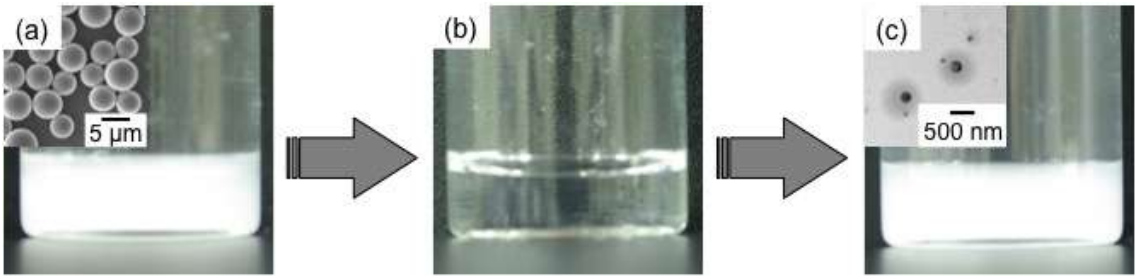


Figure 1. Visual appearance of the anion exchange process: (a) poly([MTMA][TFSA]) dispersion prepared by dispersion polymerization in ethanol, (b) after the addition of LiBr to the poly([MTMA][TFSA]) dispersion, and (c) after the addition of Li[TFSA] to the poly([MTMA]Br) solution. Insets: (a) SEM photograph of the poly([MTMA][TFSA]) dispersion prepared by dispersion polymerization in ethanol and (c) TEM photograph of the poly([MTMA][TFSA]) particles reprecipitated by anion exchange.

The dissolution behavior of 5 μm-sized PIL particles, which were prepared by dispersion polymerization in ethanol at 70°C for 6 h with PVP as the stabilizer, was observed by the exchange of counter anion. Figure 1 shows the visual appearance of the PIL particle dispersions. After the addition of LiBr to the dispersion, the dispersion instantaneously (within several seconds) became transparent (Figures 1a and b), indicating that the PIL particles had dissolved in ethanol. This instantaneous responsiveness of the dispersion was due to the rapid anion exchange, which was caused by a high degree of dissociation of the PIL.[51,52] Furthermore, when Li[TFSA] was added to the clear solution, the solution became turbid (Figures 1b and c). The dispersion had submicron-sized polymer particles (600–800 nm) with broad size distribution, according to the measurements with dynamic light scattering. This suggests that the micron-sized PIL particles were completely dissolved in ethanol by the

addition of LiBr and submicron-sized PIL particles were generated by reprecipitation due to anion exchange.

Figure 2 shows the consecutive optical micrographs of the PIL particles in ethanol after the addition of 1 wt% LiBr/ethanol solution. In general, when polymer particles such as polystyrene are mixed in an effective solvent, the particles swell and subsequently dissolve in the medium (Figure 3).

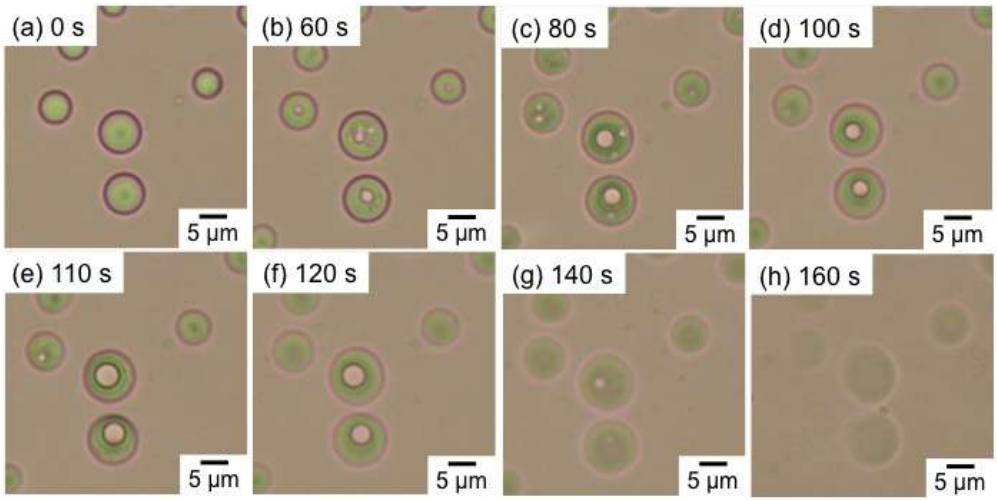


Figure 2. Consecutive optical micrographs of the dissolution process of the poly([MTMA][TFSA]) particles: (a) the poly([MTMA][TFSA]) particles prepared by dispersion polymerization in ethanol and (b–h) after the addition of the LiBr/ethanol solution (1.0 wt%) to the poly([MTMA][TFSA]) dispersion.

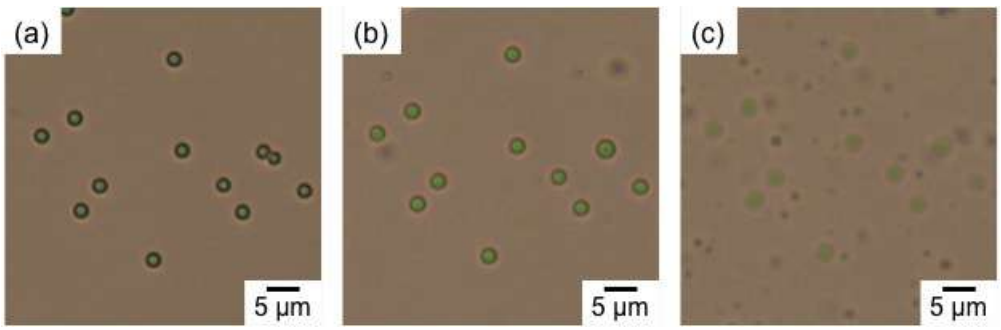


Figure 3. Consecutive optical micrographs of the dissolution process of the poly([MTMA][TFSA]) particles: (a) the poly([MTMA][TFSA]) particles prepared by dispersion polymerization in ethanol and (b–h) after the addition of the LiBr/ethanol solution (1.0 wt%) to the poly([MTMA][TFSA]) dispersion.

On the other hand, in the case of the PIL particles, as soon as the LiBr/ethanol solution was added to the PIL particle dispersion, low-contrast domains were generated inside the PIL particles. The size of these domains increased with time, and then, the domains disappeared and the boundaries of the PIL particles became flat and dull. After sometime, the PIL particles completely dissolved in the medium. The domains generated in the PIL particles were likely the penetrated medium because the diameter of the PIL particles increased. This was confirmed by the observations of confocal laser scanning microscope, in which rhodamine-colored medium was observed in the domains (Figure 4).

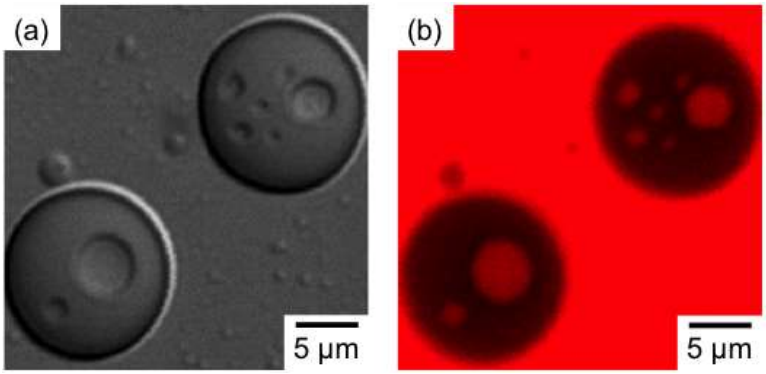


Figure 4. Transmission (a) and confocal laser scanning (b) micrographs of poly([MTMA][TFSA]) particles after addition of 1 wt% LiBr ethanol solution containing Rhodamine B

To confirm the influence of the type of counter anion, the same procedure used to observe the dissolution behavior of the PIL particles dispersed in ethanol was performed by the addition of 1 wt% LiCl/ethanol solution, in which the [TFSA] anion should replace the chloride anion. As shown in Figure 5, the dissolution behavior of the PIL particles after the addition of the LiCl/ethanol solution was similar to that of the LiBr system. This indicated that the dissolution behavior of the PIL particles was not related to the type of anion.

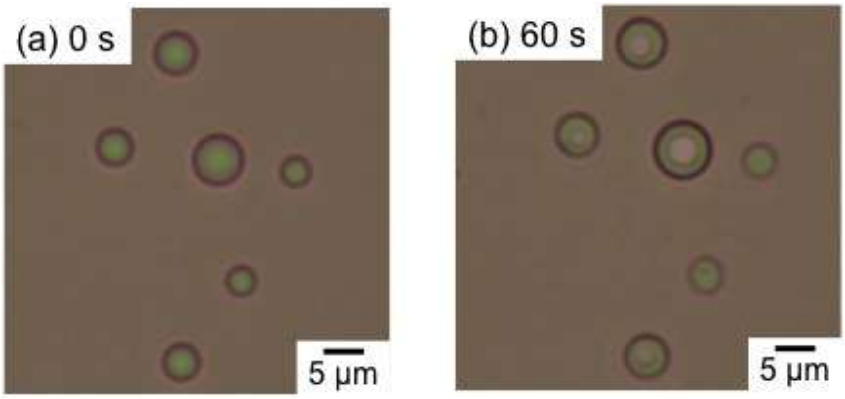


Figure 5. Optical micrographs of the dissolution process of the poly([MTMA][TFSA]) particles: (a) the poly([MTMA][TFSA]) particles prepared by dispersion polymerization in ethanol and (b) after the addition of the LiCl/ethanol solution (1.0 wt%) to the poly([MTMA][TFSA]) dispersion.

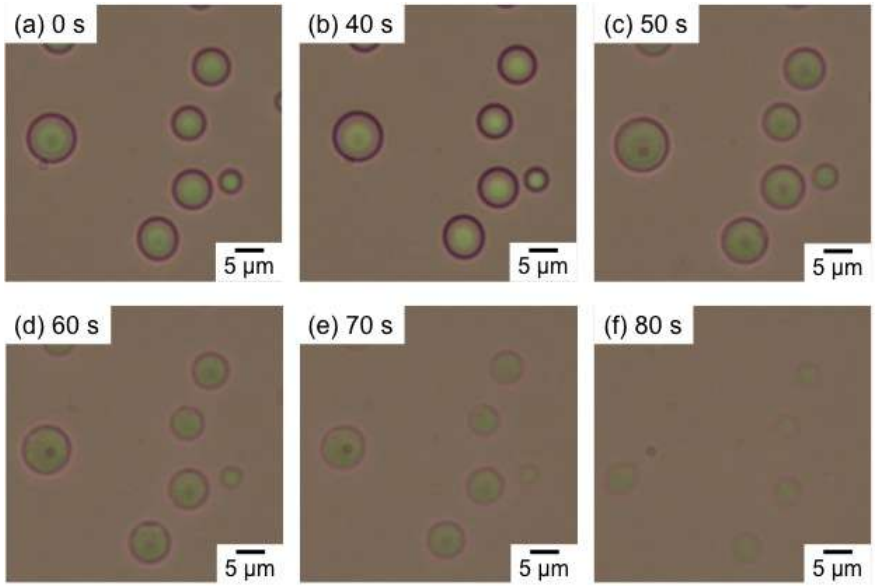


Figure 6. Consecutive optical photomicrographs of the poly([MTMA][TFSA]) particles prepared by dispersion polymerization in ethanol after the addition of the 15 wt% LiBr/ethanol solution.

To investigate the influence of salt concentration, the dissolution behavior of the PIL particles in ethanol was observed by the addition of various concentrations of the LiBr/ethanol solution. As shown in Figure 2, the domains were observed in the PIL particles

after the addition of the 1 wt% LiBr concentration in ethanol. On the other hand, in the case of the 15 wt% LiBr concentration system (Figure 6), the PIL particles dissolved without forming domains inside the particles. As a result of the investigation at various concentrations, there appeared to be a critical LiBr concentration at approximately 2.5 wt% in ethanol, above which the domains were not observed.

When the LiBr/ethanol solution was added, an anion exchange in the PIL occurred. At the beginning of the LiBr addition, only part of the PIL exchanged for the Br anion and dissolved only a small amount of the ethanol medium in the particles. In this situation, the inside of the PIL particles was likely a salt solution. When the salt concentration of the bulk solution became different from that on the inside of the PIL, osmotic pressure was generated between the interior of the PIL particles and LiBr solution. It is well known that osmosis occurs between two solutions of different salt concentrations, in which the medium flows from the less-concentrated to more-concentrated solution. Below the LiBr concentration of the 2.5 wt% system, the salt concentration of the PIL particles was higher than that of the solvent; hence, the ethanol medium penetrated into the PIL particles as shown in Figure 2. On the other hand, above the LiBr concentration of the 2.5 wt% system, the salt concentration of the bulk solution was higher than that on the inside of the PIL; hence, the PIL particles gradually dissolved from the surface without being penetrated by the medium as shown in Figure 6.

The difference in the dissolution behavior around the 2.5 wt% LiBr/ethanol solution was due to the change in osmotic pressure, at which the salt concentration was equal inside the PIL particles and in the bulk solution. The molar concentration of the 2.5 wt % LiBr/ethanol solution was 0.58 mol L^{-1}. If all ionic liquid units had dissociated and been replaced with Br anions in the PIL particles, the molar concentration of Br inside the PIL

particles would be 3.25 mol L^{-1}, which was calculated from the density of PIL (1.47 g cm^{-3}). At a Br anion molar concentration of 0.58 mol L^{-1}, which was equal to the concentration of the bulk solution, the degree of replacement of the anion was calculated to be 18%. To confirm this assumption, the degree of anion replacement in the PIL particles before and after the addition of the 2.5 wt% LiBr/ethanol solution was estimated with FT-IR (Figure 7).

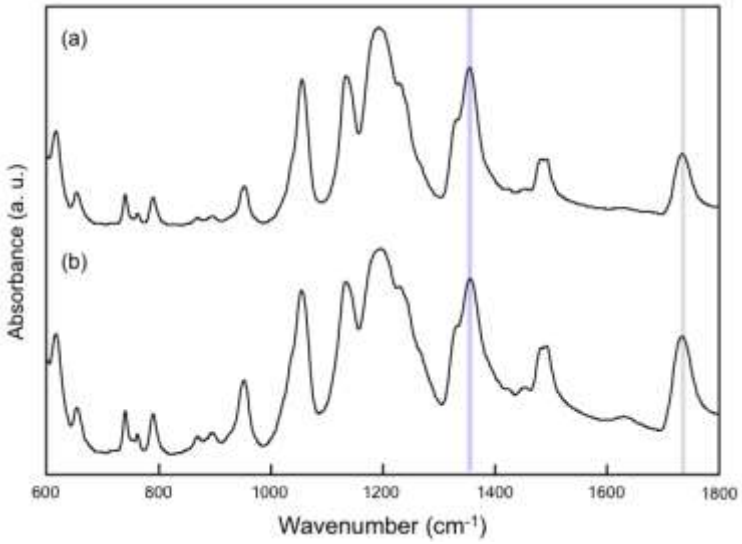


Figure 7. FT-IR spectra of the PIL particles (a) before and (b) after the addition of the 2.5 wt % LiBr/ethanol solution.

The bands at 1355 cm^{-1} and 1735 cm^{-1} were assigned to the $S(=O)_2$ of [TFSA] anion and C=O of the cation of PIL, respectively. As [TFSA] was replaced by Br anion, the anion intensity at 1355 cm^{-1} should have decreased. Thus, the degree of replacement of anion (P_L) was semiquantitatively calculated by the following equation:

$$P_L = 100\left(1 - \frac{I'_{anion}/I'_{cation}}{I_{anion}/I_{cation}}\right)$$

where I and I' are the intensity of the bands before and after the addition of the LiBr/ethanol solution, respectively. The calculated P_L value was about 21%. This value is consistent with

the above assumption, indicating strongly that the dissolution behavior of the PIL particles is affected by osmotic pressure.

Preparation of PIL particles having hollow structure

In the case of the addition of a small amount (7 mg or 21 mg) of LiBr solution at 5.0×10^{-3} wt% to the dry PIL particles dispersed on the SEM plate, the PIL particles assumed an interesting structure as shown in Figure 8. The size of the obtained particles (Fig. 8b and c) was larger than that of the original PIL particles (Fig. 8a). Thus, the obtained particles should have a hollow structure. Especially, in Figure 8c, the size of the obtained particles increased approximately twofold, indicating a porosity greater than 90%. This drastically changed morphology of the particles appeared to be similar to the anomalous oligostyrene particles reported by Tauer.[53] However, the formation mechanism of the anomalous oligostyrene particles was different from our mechanism.

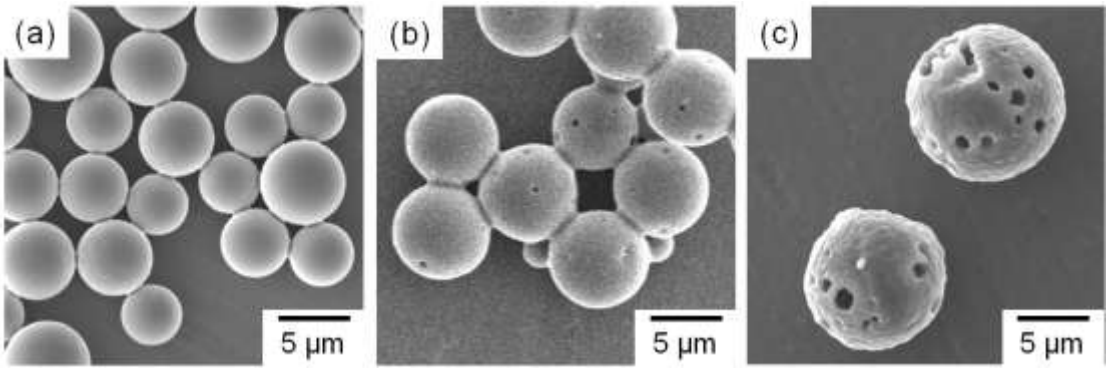


Figure 8. SEM photographs of the poly([MTMA][TFSA]) particles (a) before and (b, c) after the addition of the 5.0×10^{-3} wt% LiBr ethanol solution. Amount of LiBr/ethanol solution at 5.0×10^{-3} wt%: (b) 7 mg and (c) 21 mg.

To obtain large amount of PIL particles having hollow structure, the LiBr solution was added to a dispersion. According to the result of dissolution behavior of the PIL particles

described above, a 0.5 wt% of LiBr/ethanol solution was added to prepare the PIL particles with the domain inside the particles. Figure 8 shows the optical micrograph and SEM photograph of the obtained PIL particles after drying at room temperature in 0.04 wt% of the LiBr/ethanol solution and TEM photograph of the ultrathin cross-sections of the obtained PIL particles. By observing the optical micrograph (Fig. 8a), a heterogeneous structure was observed inside the particles, whereas the hollow structure were observed on the surface of the PIL particles in Fig. 8b. The TEM observation of the ultrathin cross-sections of the obtained PIL particles clearly indicates that they had porous morphology (Fig. 8c). This result indicated that PIL particles having hollow structure were successfully prepared as a dispersion.

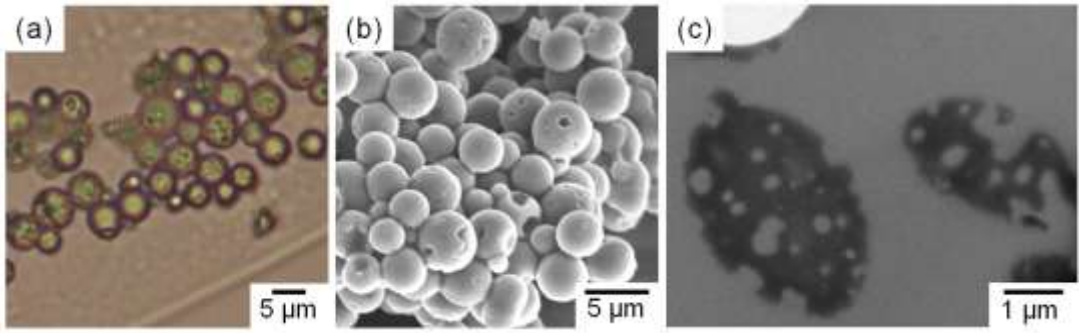


Figure 9. SEM photographs of the poly([MTMA][TFSA]) particles (a) before and (b, c) after the addition of the 5.0×10^{-3} wt% LiBr ethanol solution. Amount of LiBr/ethanol solution at 5.0×10^{-3} wt%: (b) 7 mg and (c) 21 mg.

Conclusion

The interesting phenomenon has been reported that the PIL particles were instantaneously dissolved in ethanol by addition of LiBr.[50] This dissolution phenomenon was occurred by changing counter anion of PIL. Because this dissolution process was different from addition of effective solvent, the different dissolution process may be observed. When the PIL particles dissolved in ethanol by an anion exchange mechanism, a specific dissolution behavior was observed in which the domains of the medium were generated inside the PIL particles below a salt concentration of 2.5 wt%. This dissolution behavior was dependent on the salt concentration and the driving force was determined to be related to the osmotic pressure inside the PIL particles and outside (the medium).

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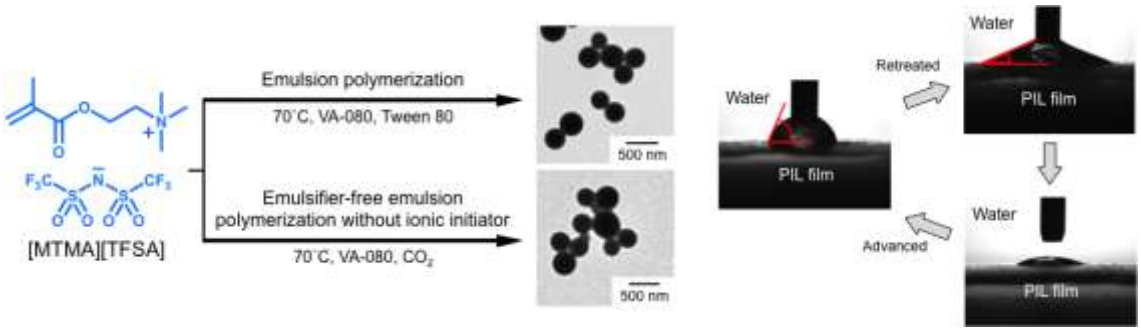
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Chapter 3

Preparation of Submicron-sized Poly(ionic liquid) Particles by Emulsion Polymerization and Switchable Responsiveness of Emulsion Film



Abstract: In emulsion polymerization of ionic liquid monomer, when potassium persulfate and sodium dodecyl sulfate were used, the system was colloidally unstable and coagulated, owing to anion exchange between the ionic liquid monomer, the ionic initiator and emulsifier. Poly(ionic liquid) (PIL) particles were successfully prepared using nonionic initiator and emulsifier. Moreover, the surface of the PIL emulsion film was relatively hydrophobic as determined by measurement of the water contact angle in the dried state. On the other hand, according to the retreating water contact angle, the same PIL film exhibited water wettability. Interestingly, when water was dropped on the PIL film after water on the surface had retreated completely, the PIL film was instantaneously hydrophobic again.

Introduction

Ionic liquids (ILs),[1-5] which are molten salts at room temperature, have attracted much interest due to their unique properties such as non-flammability, low vapor pressure, ionic conductivity,[6-8] and CO_2 absorbence.[9-11] Moreover, specific combinations of cations and anions can provide additional functional properties, e.g., paramagnetism,[12] liquid crystallinity,[13] and fluorescence.[14] However, leakage of ILs is a problem when they are used in various applications. To solve this problem, it is important to prepare solid-state materials having properties of ILs.

Poly(ionic liquids) (PILs) have attracted attention as functional materials with combined properties of ionic liquids and polymers.[15-24] PILs are prepared by radical polymerization of ionic liquids with vinyl and (meth)acrylate groups. In the 1970s, Salamone and co-workers reported the synthesis and polymerization of vinylimidazolium salt which was the first report of the preparation of PIL.[15] Approximately 20 years later, Ohno and co-workers[16] reported the preparation of PILs as energy materials with the property of ILs. Although the ionic conductivity of the polymer state was lower than that of the monomer state for their initially prepared PILs, improvement of the ionic conductivity was achieved using ionic liquids with a flexible spacer between the vinyl group and ionic liquid structure.[25-28] Currently, many researchers have focused on PILs as functional materials for use in electrochemistry, environmental chemistry, and biochemistry.[24] In addition, the preparation of PILs as particles via suspension polymerization,[29] water-in-oil concentrated emulsion polymerization,[30] and precipitation polymerization in water without stabilizers using ionic liquid monomers with long alkyl chains has been reported.[31,32] We have investigated the dispersion polymerization of the ionic liquid monomer [2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide

([MTMA][TFSA]) in methanol and ethanol, using poly(vinylpyrrolidone) (PVP) as a stabilizer[33] and obtained micrometer-sized monodisperse PIL particles. In this case, the particle size and size distribution were controlled via addition of ethanol to a methanol solution. Furthermore, we investigated the specific dissolution behavior of PIL particles utilizing anion exchange on addition of an ethanolic LiBr solution and observed that domains were generated inside PIL particles prior to their dissolution at low salt concentrations (<2.5 wt.%), most likely due to the difference in the osmotic pressure of the PIL particles and salt solution[34].

In ***Chapter 3***, we report our investigation of emulsion polymerization of [MTMA][TFSA] with the goal of expanding the applicable polymerization methods for the preparation of PIL particles. To the best of our knowledge, emulsion polymerization of ionic liquid monomer has not been reported, because the system would become complicated because of the addition of ionic substances. Emulsion polymerization is widely used in the industrial process and has attracted attention as environmental-friendly process, in which water is used as a medium.[35] The contact angles of an emulsion film prepared from PILs particles were also examined.

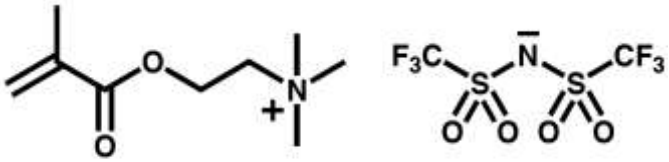
Experimental Section

Materials

Analytical grade potassium persulfate (KPS, Nacalai Tesque Inc., Kyoto, Japan) was purified via recrystallization. Commercial grade tetradecyltrimetylammonium bromide (TTAB; Tokyo Chemical Industry Co., Ltd.), sodium dodecyl sulfate (SDS; Wako Pure Chemicals, Japan), polyoxyethylenesorbitan monooleate (Tween 80; HLB 15.0; Wako Pure Chemicals, Japan), 2,2'-azobis 2-methyl-*N*-[1,1-bis(hydroxymethyl)-2-hydroxyethyl propionamide] (VA-080; Wako Pure Chemicals, Japan), ethanol (Nakalai Tesque Inc., Kyoto, Japan), [2-(methacryloyloxy)ethyl]trimethylammonium chloride ([MTMA]Cl) solution (80 wt% in water, Aldrich) and lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]; 99.7%, Kanto Chemical Co., Inc.) were used as received. The monomer 2-hydroxyethyl methacrylate (HEMA) (Nakalai Tesque Inc., Kyoto, Japan) was purified via distillation under reduced pressure in a nitrogen atmosphere. Water used in all experiments was obtained using the Erix®UV (Millipore, Japan) purification system and had a resistivity of 18.2 MΩ cm.

Preparation of ionic liquid monomer and its solubility in water

The ionic liquid monomer [MTMA][TFSA] (see Figure 1) was synthesized by mixing aqueous solutions of [MTMA]Cl and Li[TFSA] as mentioned in ***Chapter 1***.[33] To determine the solubility of [MTMA][TFSA] in water, [MTMA][TFSA] (0.1 g) was added to water (5.0 g) in a flask, and the mixture was left to stand for 6 h at temperatures, at which [MTMA][TFSA] remained as droplets in the water. A portion of the aqueous solution was then removed from the flask, and the water solubility of the [MTMA][TFSA] was determined via gravimetry (the ionic liquid monomer is nonvolatile).



[MTMA][TFSA]

Preparation of PIL particles by emulsion polymerization

A typical emulsion polymerization procedure was conducted as follows. A solution of emulsifier (SDS: 25 mg, TTAB: 25 mg, or Tween 80: 100 mg (> critical micelle concentration)) in water (9.0 g) and [MTMA][TFSA] (1.0 g) were added to a round-bottom Schlenk flask, which was then sealed with a silicon rubber septum and degassed using several N_2/vacuum cycles. The flask was placed in a water bath at 70°C for 30 min with stirring at 400 rpm. Emulsion polymerization was begun on addition of a solution of an initiator (KPS: 22 mg or VA-080: 70 mg) in water (1.0 g).

Characterization

The PIL particles were observed via transmission electron microscopy (TEM, JEM-1230, JEOL Ltd., Japan). Each emulsion was diluted to approximately 50 ppm, and a drop of each was placed on a carbon-coated copper grid and dried at room temperature in a desiccator. Monomer conversion was measured via 1H NMR spectroscopy. The 1H NMR analyses were performed on a Varian Gemini 300 at room temperature in CD3COCD3. The number- and weight-average diameters (Dn and Dw, respectively) were determined via dynamic light scattering (DLS, FPAR-1000 RK, Fiberoptics particle analyzer, Photal Otsuka electronics, Osaka, Japan) at a light scattering angle of 90° at room temperature using the Contin analysis routine. One to two droplets of each emulsion sample was withdrawn from the reactor and diluted with water (~8 ml) prior to measurement in the dilution mode. The zeta

potential of the PIL particles dispersed in water was determined using a zeta potential and particle size analyzer (ELSZ-1M, Otsuka Electronics Co., Ltd., Osaka, Japan). Qualitative analyses of the products were conducted on a Fourier transform infrared spectrometer (FT-IR, FT/IR-6200, JASCO, Tokyo, Japan) using the pressed KBr pellet technique.

Measurement of the contact angle of PIL emulsion and PolyHEMA (PHEMA) films

The contact angle of water on the films was measured using a DropMaster 300 (Kyowa Interface Science, Saitama, Japan) instrument at room temperature. The PIL emulsion film was prepared by casting the PIL emulsion solution on a glass substrate followed by drying at 80 °C for 1 h and then 120 °C for 3 h. To flatten the obtained PIL film, it was melt-pressed at 120 °C for 10 s under a pressure of 1 MPa. The PolyHEMA (PHEMA) film was prepared by casting a PHEMA solution, which was prepared via solution polymerization in ethanol at 60 °C for 12 h, on a glass substrate, drying at 80 °C for 5 h and then melt-pressing at 120 °C for 30 s under a pressure of 1 MPa.

Results and Discussion

Preparation of submicron-sized PIL particles

Prior to performing emulsion polymerization of [MTMA][TFSA], the solubility of [MTMA][TFSA] in water was investigated. Figure 1 shows the solubility dependence of [MTMA][TFSA] on temperature. This value was comparable with the solubility of methyl methacrylate (MMA) in water (the solubility of MMA in water is 1.5 wt% at room temperature). This solubility property suggested that [MTMA][TFSA] has the potential for use as a monomer in emulsion polymerizations. In emulsion polymerization, the monomer must diffuse from the monomer droplets through the water to micelles, because polymerization proceeds in these micelles. In other words, some monomer must be dissolved in water.

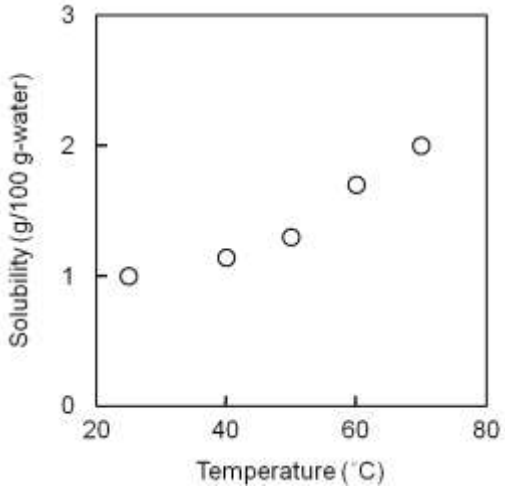


Figure 1. Solubility curve for [MTMA][TFSA] in water as a function of temperature

Emulsion polymerization of [MTMA][TFSA] (10 wt% to water) was performed at 70 °C using KPS and SDS as the initiator and emulsifier, respectively. Before polymerization, the system was separated, with the monomer as the lower layer and aqueous solution as the upper layer without stirring (high density of the monomer (1.47 g cm^{-3})), and monomer

droplets were generated by stirring in the same manner as that of the emulsion polymerization with a conventional monomer. As polymerization proceeded, aggregates were formed and prevented stirring after 30 min. After 3 h, a bulk polymer was obtained. Aggregates were also obtained when emulsion polymerization was performed at a low solid content (3 wt% to water).

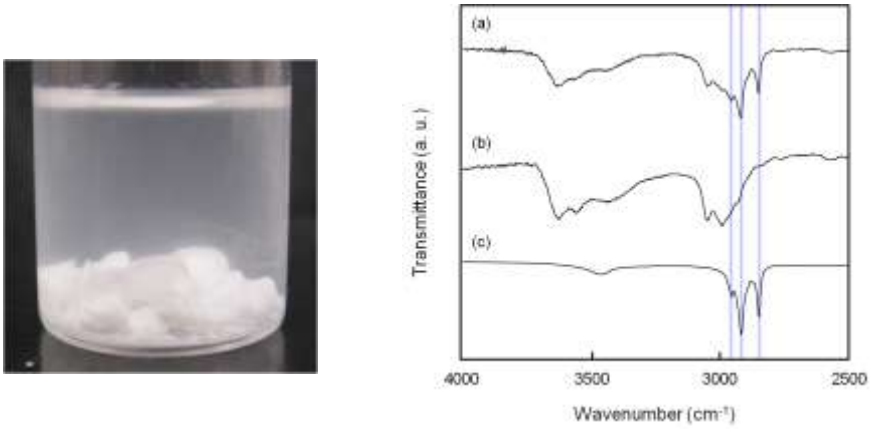


Figure 2. Visual appearance (left) of the product obtained via emulsion polymerization of [MTMA][TFSA] using KPS and SDS. FT-IR spectra (right) of the product prepared via (a) emulsion polymerization of [MTMA][TFSA], (b) PIL prepared via dispersion polymerization of [MTMA][TFSA], and (c) SDS.

To investigate the chemical composition of the coagulum, FT-IR analysis of the sample after washing in ethanol was performed. As can be seen in Figure 2, the characteristic band for PIL was observed at 3300–3700 cm^{-1}, along with bands at 2852 cm^{-1}, 2920 cm^{-1}, and 2954 cm^{-1} in the spectrum of the coagulum obtained after emulsion polymerization. The latter bands do not appear in the spectrum of the PIL prepared via dispersion polymerization, and thus were attributed to the R-SO_4-group in SDS. This result suggests that the [TFSA] anion was replaced with dodecyl sulfate anion, because the ionic liquid can readily exchange counter anions. A similar anion exchange was reported by Ohno and co-workers, in which *N*, *N*'-dimethylimidazolium dodecylsulfonates were prepared via the ion-exchange reaction of *N*,

N'-dimethylimidazolium iodides and silver dodecylsulfonate in dichloromethane at room temperature.[36]

When the cationic emulsifier (TTAB) was used with nonionic initiator, a similar result was obtained, i.e., a coagulum was formed, indicating that anion exchange occurred between [MTMA][TFSA] and TTAB. Moreover, in the case of the nonionic emulsifier (Tween 80) and anionic initiator (KPS), the coagulum was also formed. These results suggest that the ionic materials were unsuitable for this system.

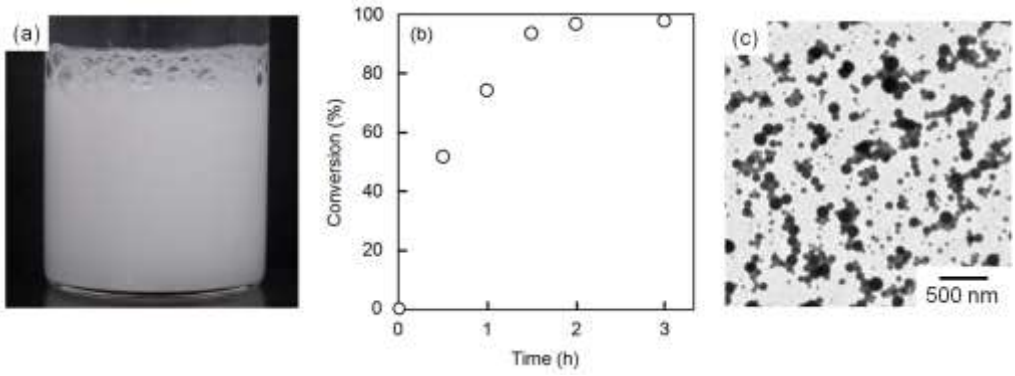


Figure 3. (a) Visual appearance and (b) time-conversion plot for emulsion polymerization of [MTMA][TFSA]. (c) TEM photograph of poly([MTMA][TFSA]) particles prepared via emulsion polymerization of [MTMA][TFSA] using VA-080 (70 mg) and Tween 80 (0.1 g) at 70 °C

On the other hand, when emulsion polymerization was performed using a nonionic emulsifier (Tween 80) and initiator (VA-080), a stable emulsion was obtained without coagulation (Fig. 3a). Figure 3b shows the time-conversion plot for emulsion polymerization of [MTMA][TFSA] at 70 °C. The conversion was determined via 1H NMR analysis as published previously.33 The polymerization proceeded smoothly without an induction period and was complete in 3 h. As can be seen in Figures 3c, submicrometer sized PIL particles with a broad size distribution were formed via emulsion polymerization using the nonionic

initiator and emulsifier. These results suggest that ionic compounds are unsuitable for the preparation of PIL particles via emulsion polymerization of ionic liquid monomers.

Next, to investigate the effect of the emulsifier concentration on the particle size, emulsion polymerization of [MTMA][TFSA] was performed at various emulsifier concentrations in a manner similar to that used for conventional monomers. As shown in Figure 4, the obtained particle size decreased with an increase in the emulsifier concentration.

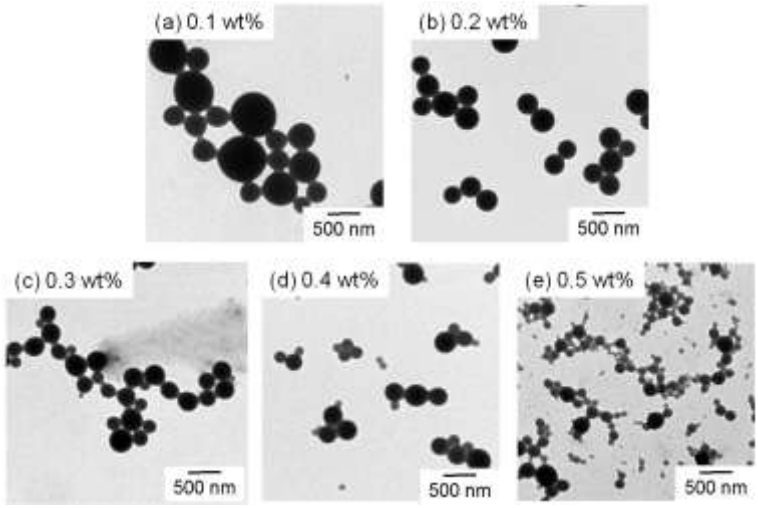
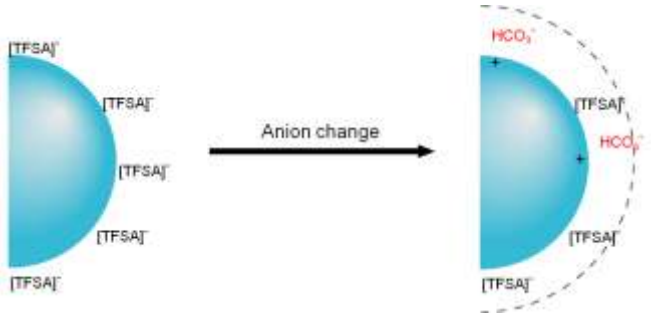


Figure 4. TEM photographs of poly([MTMA][TFSA]) particles prepared via emulsion polymerization at various Tween 80 concentrations (wt% based on water): (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4, and (e) 0.5

At a Tween 80 concentration of 0.2 wt%, the particle size distribution was relatively monodisperse (coefficient of variation: 14%), and the zeta potential of the obtained PIL particles was +40.4 mV despite the use of a nonionic emulsifier and initiator. In general, the hydrophobic polymer particles prepared via emulsion polymerization, using nonionic emulsifiers and initiators exhibit nearly zero or slightly negative zeta potentials. For example, polystyrene particles and poly(methyl methacrylate) particles prepared using the same procedure exhibited zeta potentials of −14.0 mV and −11.8 mV, respectively. The positive zeta potential of the poly([MTMA][TFSA]) particles is attributed to the charge of PIL. While

the surface charge of the PIL particles should be zero owing to the formation of ion pairs between the cations and hydrophobic anions on the surface, it is thought that hydrogen carbonate (HCO_3) ions derived from the carbon dioxide in the water exchange with the [TFSA] anions on the surface of the PIL particles. Thus, a diffuse electric double layer was formed due to the dissociation of the hydrogen carbonate ions from the PIL surface, leading to a positive zeta potential. (Scheme 1)



Scheme 1. Formation of diffuse electric double layer on the surface of PIL particles

With this high positive charge on the surface of the PIL particles, stabilization of the PIL particles without ionic materials was expected to be possible. Thus, emulsifier-free emulsion polymerization of [MTMA][TFSA] using VA-080 (nonionic initiator) was performed. However, a stable emulsion was not obtained after the polymerization was complete, and a large amount of polymer (over 80%) aggregated. This result indicated that the electrostatic potential was insufficient for stabilization of the PIL particles.

Next, carbon dioxide was bubbled for 5 min through a PIL emulsion prepared via emulsion polymerization to determine if the anion exchange between [TFSA] and HCO_3 anions could proceed further. In fact, a moderate increase of the value of the zeta potential from +40.4 mV to +45.5 mV was observed. It was thus concluded that the emulsion should remain more stable under a CO_2 atmosphere compared with an N_2 atmosphere. Therefore, the emulsifier-free emulsion polymerization of [MTMA][TFSA] was performed under a CO_2

atmosphere, and a stable emulsion was obtained with a minimal amount of coagulation. Figure 6 (left) shows the TEM photograph of the obtained spherical PIL particles, which were determined to have a zeta potential = +54.0 mV. Thus, PIL particles were successfully prepared via emulsifier-free emulsion polymerization under the CO_2 atmosphere.

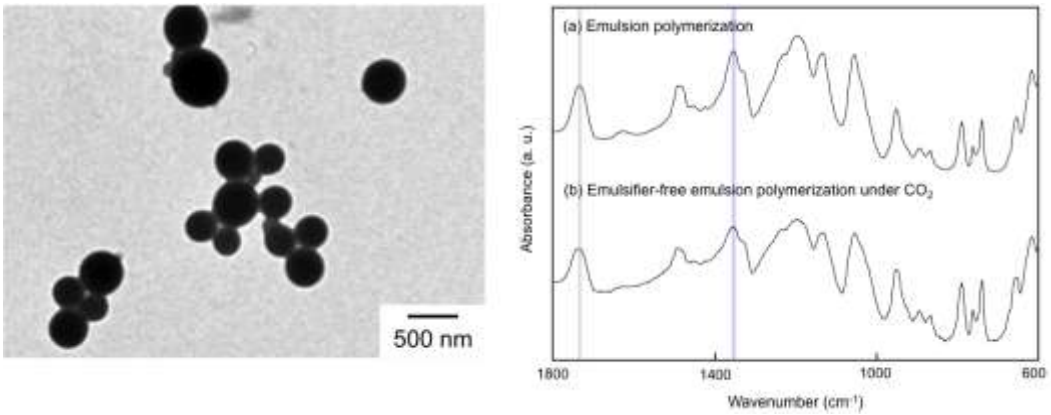


Figure 5. TEM photograph (left) of poly([MTMA][TFSA]) particles prepared via emulsifier-free emulsion polymerization at 70°C under CO_2 atmosphere. FT-IR spectra of poly([MTMA][TFSA]) (right) prepared via emulsion polymerization (a) and emulsifier-free emulsion polymerization under CO_2 atmospheres (b).

Figure 5 (right) shows the FT-IR spectra of the PILs prepared via emulsion polymerization and emulsifier-free emulsion polymerization under CO_2 atmospheres. As reported previously[34], the degree of anion exchange was estimated by FT-IR when the anion exchange occurred. In this system, the ratio of intensity between the cation (1735 cm^{-1}) and anion (1355 cm^{-1}) has different approximately 8%. This result suggests that some of the [TFSA] anions in the PIL were exchanged for HCO_3 anions, which enabled stabilization of the PIL particles.

Surface properties of the PIL emulsion film

To investigate the surface properties of a film prepared from the PIL emulsion obtained via emulsifier-free emulsion polymerization, the contact angle was measured. The obtained film was transparent, and the water contact angle on the PIL emulsion film was less than 30°. On the other hand, the PIL film prepared by casting a PIL solution obtained via solution polymerization had a water contact angle of ~80°[37], hence its surface was hydrophobic. The low water contact angle (30°) for the PIL emulsion film prepared via emulsion polymerization is due to the residual initiator (hydrophilic) in emulsion and because some of the anions were exchanged to hydrophilic HCO_3 groups. When the PIL emulsion film was soaked in water overnight to remove the residual initiator, the water contact angle increased to ca. 67° and water whitening of the film was not observed. The wettability of films bearing PIL units on the surface can be switched between hydrophobic and hydrophilic because of the anion exchange.[38-40] Therefore, to confirm the hydrophilic-hydrophobic reversibility of the PIL film prepared via emulsion polymerization, the water contact angle of the PIL film was measured after treatment in the presence of moisture under a CO_2 atmosphere at 60 °C (to exchange [TFSA] anions for HCO_3 anions on the surface). However, the water contact angle of the PIL film after treatment remained ca. 70°.

Figure 6 shows consecutive visual images of the water contact angle for the PIL emulsion and PHEMA films. As mentioned above, the static water contact angle on the PIL emulsion film was 69°, while the advanced contact angle was ca. 70° (no image). On the other hand, the contact area between the PIL film and water remained constant as the water retreated (retreating angle: 28.6°). This result indicates that the relatively hydrophobic PIL emulsion film became hydrophilic. However, immediately after the water retreated completely, the contact angle of the newly water drop on the PIL emulsion film returned to

approximately 70°, as was measured for the initial state. This phenomenon is not observed for conventional hydrophilic (water-insoluble) polymer film systems.

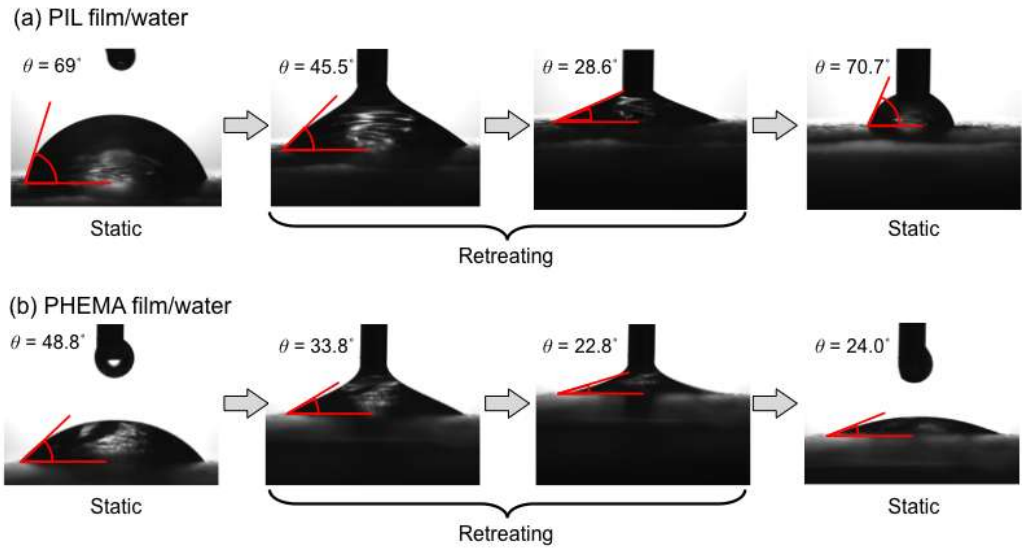


Figure 6. Consecutive visual images of the water contact angle on the (a) PIL emulsion film and (b) PHEMA film.

As shown in Figure 6b, the PHEMA film exhibited the same behavior as the PIL film, exhibiting water wettability based on the value of the retreating contact angle. When the water contact angle was measured just after the water completely retreated on the PHEMA film, the film surface remained hydrophilic (water contact angle ~24°), because hydrophilic portions on the surface were oriented due to contact with water. On the surface of the PIL emulsion film, hydrophilic portions of the IL are oriented in the water contact area in the same manner as the hydrophilic groups on the surface of the PHEMA film, resulting in water wettability. However, when the water retreated from the PIL film, the surface of the emulsion film returned to its hydrophobic state (~70°) instantaneously, thus exhibiting rapid switchability. As mentioned above, after treatment with water under CO_2, the PIL emulsion film should

remain hydrophobic at drying state owing to the rapid switchability. Moreover, to confirm the rapid switchability of the PIL film's property, the movement of water and CH_2I_2 droplets on the film was investigated. Water and CH_2I_2 drops (8~10 μl) were placed on the PIL film, then the PIL film was tilted. In the case of the water drop, pinning of contact line on the film surface was observed. On the other hand, the CH_2I_2 drop slid smoothly on the slightly tilted PIL film. The contact angle hysteresis value ($\Delta\theta$) and minimum tilt angle of the PIL film on the CH_2I_2 drop were 15° and 10°, respectively. This result indicates that the molecular chain on the surface of the PIL film has a high mobility, as reported by Hozumi and co-workers.[41,42] The CH_2I_2 drop smoothly slid on the PIL film retreated the water drop completely, which indicates rapid switchable responsiveness. In the PHEMA film system, the CH_2I_2 drop slid on the tilted film (minimum tilt angle is 22°); however, it did not slide on the PHEMA film retreated water drop completely because the molecular chain on the film surface remained hydrophilic. These results suggest that PIL films have unique surface properties owing to their structures. A similar phenomenon was reported by Yuan and co-workers,[43] in which PIL dispersions changed their properties from hydrophilic to hydrophobic on drying.

Conclusion

When emulsion polymerization of an ionic liquid monomer was conducted using ionic initiators and emulsifiers such as KPS and SDS, respectively, a stable emulsion was not obtained, and nearly all the polymer was aggregated. This result was due to anion exchange of the ionic liquid monomer with the ionic emulsifier, leading to reduced effectiveness of the surfactant. When a nonionic initiator and emulsifier were used, submicron-sized PIL particles were successfully prepared without coagulation for the first time, and the zeta potential of the obtained particles had a high positive charge. Utilizing this surface charge, PIL particles were successfully prepared via emulsifier-free emulsion polymerization under a CO_2 atmosphere without using an ionic material. Moreover, the surface of the PIL emulsion film was relatively hydrophobic as determined by measurement of the water contact angle in the dried state. On the other hand, according to the measured retreating water contact angle, the same PIL film exhibited water wettability. Interestingly, when water was dropped on the PIL film after water on the surface had retreated completely, the PIL film was once again hydrophobic. This result suggests that surface properties of the PIL emulsion film readily switched between hydrophobic (in air) and hydrophilic (in water).

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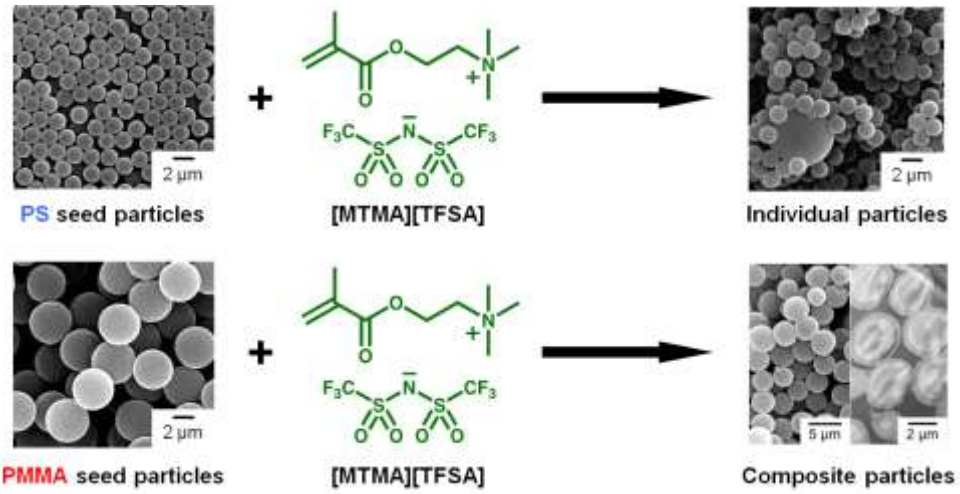
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Chapter 4

Preparation of Polymer/Poly(ionic liquid) Composite Particles by Seeded Dispersion Polymerization



Abstract: Seeded dispersion polymerization of the ionic-liquid monomer ([2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide) ([MTMA][TFSA]) was performed in ethanol by using either polystyrene (PS) or poly(methyl methacrylate) (PMMA) particles as seeds. In the presence of PS seed particles, secondary nucleated poly(ionic liquid) (PIL) particles were formed, but no PS/PIL composite particles were observed. In case of PMMA seeds particles, the PMMA/PIL composite particles were successfully prepared. TEM studies of ultrathin cross-sections of the PMMA/PIL particles revealed that the obtained particles had a sea-island structure consisting of PIL domains. These results are consistent with the theoretical considerations based on the spreading coefficients calculated from the interfacial tensions.

Introduction

Polymer/polymer composite particles prepared by multistep seeded polymerization (e.g., seeded emulsion polymerization[1-4] and seeded dispersion polymerization[5-8]) have been used in various applications such as coatings and impact-modifiers. The functionality strongly depends on the particle morphology, controlled by the combination of kinetic and thermodynamic factors. Various morphologies such as core-shell[9-11] and polymeric oil-in-oil[12,13] of the preparation of composite polymer particles by seeded polymerization were reported.[14-17]

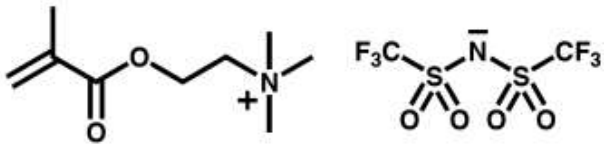
Ionic liquids, which are room-temperature molten salts consisting entirely of organic ions, have attracted attention as environmental friendly media because of their low vapor pressures, thermal stability, and nonflammability. In addition to environmental friendly properties, ionic liquids have other functional properties such as ionic conductivity and high solubility of CO_2. Due to these properties, ionic liquids have attracted much interest for developing functional materials. Poly(ionic liquid)s (PILs) combine mechanical stability, processability as polymeric material and the unique properties of ionic liquids.[18-20] They have been attracting attention as functional materials such as sorbents of CO_2, polymer electrolytes and microwave absorbing materials.[21-23] PILs were prepared by direct polymerization of ionic liquid monomers having vinyl groups on cationic or anionic parts.[24-31] Recently, the PIL as particle state prepared by suspension polymerization and precipitation polymerization were reported.[32-35] We also reported on preparing micron-sized monodisperse PIL particles by dispersion polymerization and confirmed that they maintained the properties of ionic liquid.[36,37] However, to the best of our knowledge, there has been no report of PIL/polymer composite polymer particles.

In ***Chapter 4***, the preparation of PIL composite polymer particles was carried out by seeded dispersion polymerization of a quaternary ammonium-based ionic liquid monomer with seed particles of commodity polymer. The morphology of the obtained particle was discussed from the viewpoint of the spreading coefficients.

Experimental Section

Materials

Styrene (S) and methyl methacrylate (MMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) and was purified by recrystallization in methanol. 2,2′-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries, Ltd., Osaka, Japan), poly(vinylpyrrolidone) (PVP, K-30, weight-average molecular weight: 3.6×10^5 g/mol), methanol and ethanol (Nakalai Tesque Inc., Kyoto, Japan), lithium bromide (LiBr) (99%, Aldrich), [2-(methacryloyloxy)ethyl]trimethylammonium chloride ([MTMA]Cl) solution (80 wt% in water, Aldrich), and lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) (99.7%, Kanto Chemical Co., Inc.) were used as received. Water used in all experiments was obtained from the Erix®UV (Millipore, Japan) purification system and had a resistivity of 18.2 MΩ cm. The ionic liquid monomer (Figure 1) was prepared by mixing [MTMA]Cl and Li[TFSA] aqueous solutions.[36]



[MTMA][TFSA]

Figure 1. Chemical structure of [MTMA][TFSA]

Preparation of PS and PMMA Seed Particles

Monodispersed PS and PMMA seed particles were prepared by dispersion polymerizations as follows. The homogeneous solutions, PS: S (1.0 g), PVP (0.2 g), and AIBN (0.01 g) were dissolved in ethanol (6.0 g); PMMA: MMA (1.2 g), PVP (0.12 g) and AIBN (0.012 g) were dissolved in methanol/water (7/3 w/w, 10.8 g), were added into glass tubes, degassed using several vacuum/N_2 cycles, and then sealed glass tubes was placed in a

water bath at 60°C for 24 h and 5 h, respectively, with shaking at 80 cycles min^{-1} (3 cm strokes).

Seeded dispersion polymerization of ionic liquid monomer

Seeded dispersion polymerization of [MTMA][TFSA] with PS and PMMA seed particles were carried out under the conditions listed in Table 1. Seeded dispersion polymerization with PS and PMMA seed particles were carried out at 60°C and 30°C, respectively because PMMA is soluble in hot ethanol.

Table 1. Recipes for preparation of PIL composite particles by seeded dispersion polymerizations[a)] of [MTMA][TFSA] in ethanol with PS seed particles (Nos. 1-3) and PMMA seed particles (No. 4)

Ingredients		**1**	**2**	**3**	**4**
PS seed particles	(g)	0.25	0.25	0.25	-
PMMA seed particles	(g)	-	-	-	0.25
[MTMA][TFSA]	(g)	0.25	0.25	0.25	0.25
AIBN	(mg)	2.5	2.5	1.25	-
V-70	(mg)	-	-	-	2.5
Ethanol	(g)	2.5	2.5	2.5	2.5
Temp.	(°C)	60	50	60	30

[a)] In a sealed glass tube; N_2; 10 h; 80 cycles min^{-1}

In semi-batch seeded dispersion polymerization system, [MTMA][TFSA] (0.05 g) and V-70 (0.5 mg) were dissolved in ethanol (0.5 g) and then this solution was post-added to the dispersion (PMMA seed particles (0.2 g) and ethanol (2.0 g)) every two hours (0.05 g × 4 times).

Contact-Angle Measurements of Polymers film

To calculate the interfacial tensions, the contact angles of water and CH_2I_2 were measured with a DropMaster 300 (Kyowa Interface Science, Saitama, Japan) at room temparature. To prepare the PS and PMMA films, a homogeneous toluene solution of PS or PMMA were cast onto a glass substrate and then dried at room temparaturte for 24 h. PIL film was prepared by the same way with acetone solution.

Characterization

Scanning electron microscopy (SEM, JSM-6510, JEOL, Tokyo, Japan) observation of the particles coated with osmium was performed at 20 kV. Number-average diameter (D_n) and coefficient of variation (C_v) were determined for 200 particles from SEM photographs by using an image analysis software (WinROOF®, Mitani Co., Ltd., Japan). Transmission electron microscopy (TEM, JEM-1230, JEOL, Tokyo, Japan) observation of the particles was performed at 100 kV. To observe the interior morphology of the particles, the dried particles were embedded in an epoxy matrix, cured at room temperature overnight, and subsequently microtomed. The ultrathin cross-sections of approximately 100 nm thickness were stained with 3 wt% phosphotungstic acid aqueous solution at room temperature for 30 min and then observed with TEM. Formation of by-produced particles was confirmed using a dynamic light scattering (DLS; FPAR-1000 RK, Fiber-optics particle analyzer, Photal Otsuka electronics, Osaka, Japan) at the light scattering angle 90° at room temperature using the Contin analysis routine. 1-2 droplets of emulsion samples withdrawn from the reactor were diluted with approximately 8 mL of distilled water before measurement in the dilution mode.

Results and Discussion

Seeded Dispersion Polymerization of [MTMA][TFSA] with PS seed particles

Figure 2a and b show SEM photographs of polymer particles before and after seeded dispersion polymerization of [MTMA][TFSA] with PS seed particles (No. 1 in Table 1). PS seed particles had high monodispersity (Dn, 1.7 μm; Cv, 2.3%). On the other hand, the particles obtained by seeded dispersion polymerization of [MTMA][TFSA] had broad size distribution, in which there were many monodispersed particles having the same size as PS seed particles. After washing the obtained particles with toluene, which dissolves PS but poly([MTMA][TFSA]) (Figure 2c), the same size particles as PS seed particles were disappeared and the particles with broad size distribution were remained. These results indicated that the composite particles were not obtained and secondary nucleation of PIL was occurred, which would be because the polymerization rate of [MTMA][TFSA] was faster than the formation of composite particles.

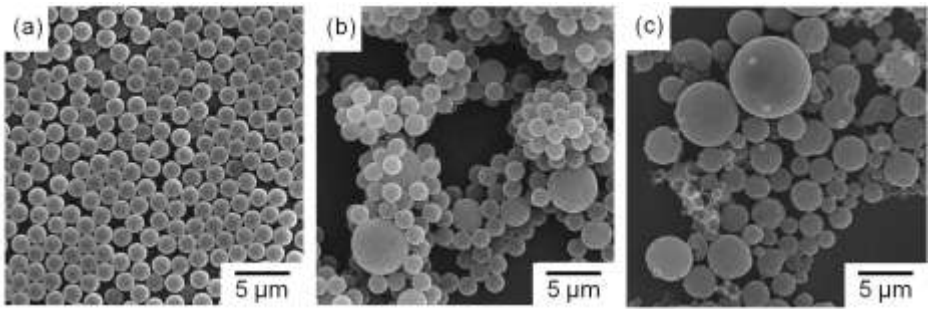


Figure 2. SEM photographs of PS seed particles (a) and obtained particles (b, c) prepared by seeded dispersion polymerization of [MTMA][TFSA] before (b) and after (c) the extraction of PS with toluene

To decrease the polymerization rate of [MTMA][TFSA], the polymerization temperature and concentration of initiator were decreased (Table 1, No2 and 3). However, in both cases, the similar results were observed, in which the mixture of PS seed particles and the particles with broad size distributions was obtained (Fig. 3).

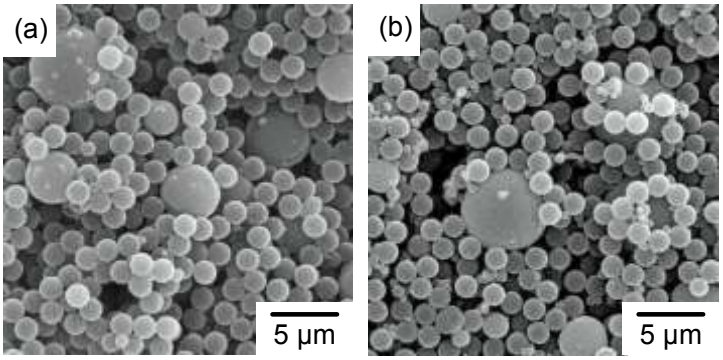


Figure 3. SEM photographs of obtained particles prepared by seeded dispersion polymerization of [MTMA][TFSA] with PS seed particles. Polymerization conditions: (a) 50˚C, AIBN (2.5 mg); (b) 60˚C, AIBN (1.3 mg).

Conversely, seeded dispersion polymerization of styrene with PIL seed particles (2.0 μm) was carried out. Figure 4a and b show SEM photographs of the PIL seed particles and obtained particles prepared by seeded dispersion polymerization. After the seeded dispersion polymerization, raspberry-like particles were observed in SEM photograph (Figure 4b) indicating that the formation of composite particles was likely to be obtained. However, the obtained dispersion contained a large amount of 200 nm-sized particles according to the measurement with dynamic light scattering. This was indicated that the secondary nucleation of PS was occurred and the raspberry-like particles should be obtained during the drying process.

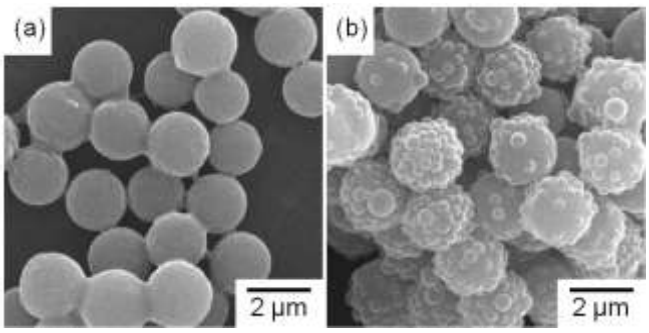


Figure 4. SEM photographs of PIL seed particles (a) and obtained particles prepared by seeded dispersion polymerization of styrene (b)

These results were suggested that the composite particles consisting of PS and PIL could not be obtained, and the formation of composite particles was not influenced by kinetic factor but thermodynamic factor.

To discuss the influence of thermodynamic factor, the spreading coefficient (S, mN/m), which is useful to predict the particle morphology,[38] given by eq 1 was estimated.

$$S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik}) \quad (1)$$

where γ is the interfacial tensions (mN/m) among three components (ij, jk, ik) and suffixes (i, j, k) refer to PS, PIL, and the medium (ethanol), respectively. In case of seeded dispersion polymerization, there are three possible sets of values of S_i because seed particles can not spread on the other components.

$$S_{PS} < 0,\ S_{PIL} > 0,\ S_{ethanol} < 0 \quad (2)$$

$$S_{PS} < 0,\ S_{PIL} < 0,\ S_{ethanol} < 0 \quad (3)$$

$$S_{PS} < 0,\ S_{PIL} < 0,\ S_{ethanol} > 0 \quad (4)$$

These three sets of relations correspond to the three different thermodynamically stable morphologies illustrated in Figure 5.

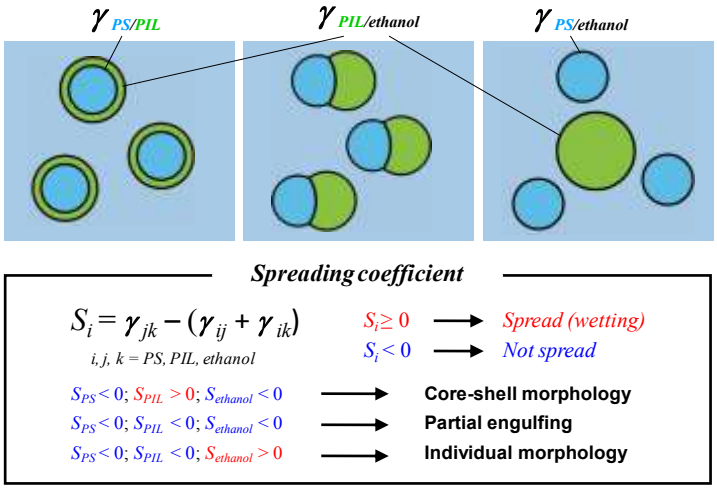


Figure 5. Possible thermodynamically stable morphologies predicted using spreading coefficients.

The γ values of each polymer were determined by contact angle measurements and using the Young–Owens equation (eq 5).

$$(1+\cos\theta)\gamma_L = 2(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}) \quad (5)$$

where θ is contact angle of liquid droplet on the solid (polymer) surface. γ^d and γ^p are the dispersive and polar components of surface tensions, respectively. The γ^d and γ^p of each polymer were determined by the contact angle measurements using water (γ^d = 21.8 mN/m, γ^p = 51 mN/m)[39] and CH_2I_2 (γ^d = 49.5 mN/m, γ^p = 1.3 mN/m)[39]. The contact angles with water-PIL and CH_2I_2-PIL interfaces were 60.2° and 47.6°, respectively. The calculated γ^d_{PS} and γ^p_{PS} values were 28.9 mN/m and 17.0 mN/m, respectively. The γ^d_{PS} and γ^p_{PS} were calculated in the same method. The surface tension values of each component were summarized in Table 2.

Table 2. Dispersive (γ^d), polar (γ^p), and total (γ) components of the surface tensions (mN/m) at 298 K

	γ^d	γ^p	γ
Poly([MTMA][TFSA])	28.9	17.0	45.9
PS	43.4	2.5	45.9
Ethanol[a)]	18.8	2.6	21.4

[a)] ref. 40

Interfacial tensions between polymer and ethanol were calculated by the Fowkes equation (eq 6) and interfacial tension between PS and poly([MTMA][TFSA]) was calculated by the Wu equation (eq 7).

$$\gamma_{ij} = \gamma_i + \gamma_j - 2(\sqrt{\gamma_i^d \gamma_j^d} + \sqrt{\gamma_i^p \gamma_j^p}) \quad (6)$$

$$\gamma_{ij} = \gamma_i + \gamma_j - (\frac{4\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} + \frac{4\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p}) \quad (7)$$

The Wu equation has been used to precisely predict the interfacial tension between solid/solid. In this system, the spreading coefficients were calculated S_{PS} = -11.4 < 0, S_{PIL} = -16.0 < 0 and $S_{ethanol}$ = 1.2 > 0. These relations indicated that the thermodynamically stable morphology should be the formation of individual particles in seeded dispersion polymerization system with PS seed particles in ethanol, which was consistent with the experimental results (Fig. 2-4). This should be based on the higher polarity of PIL, resulting the high interfacial tension between PS and PIL (13.5 mN/m) as compared to interfacial tension between commodity polymers, ex. PS and PMMA (3.4 mN/m).[9]

Seeded Dispersion Polymerization of [MTMA][TFSA] with PMMA seed particles

The seeded dispersion polymerization of [MTMA][TFSA] was carried out in the presence of PMMA seed particles in a similar way except for polymerization temperature (30˚C). PMMA (γ^d = 40.4 mN/m, γ^p = 8.5 mN/m) has higher polarity than PS. In the case of PMMA seed, the spreading coefficients were calculated S_{PMMA} = -3.1 < 0, S_{PIL} = -6.3 < 0 and $S_{ethanol}$ = -8.4 < 0. This is suggested that composite polymer particle can be prepared without secondary nucleation of PIL. Figure 6a and b show the SEM photographs of PMMA seed particles and obtained particles prepared by seeded dispersion polymerization (No. 4 in Table 1). After polymerization, the diameter of the obtained particles (3.4 μm) was larger than that of PMMA seed particles (2.8 μm) with maintaining monodispersity. This was indicated that the seeded dispersion polymerization was proceeded smoothly. Figure 6c shows the TEM photograph of the ultrathin cross sections of the obtained particles stained with phosphotungstic acid. The contrast of PIL phase stained by phosphotungstic acid is darker than that of PMMA. The obtained particles had a sea-island structure, in which many small PIL domains were dispersed in the PMMA matrix, and these results indicate that

PMMA/PIL composite particles were successfully prepared. In the case of PMMA seed particles, they were swollen by some amount of [MTMA][TFSA]. PIL domains should be trapped, because the viscosity of swollen particles became high during polymerization, resulting the thermodynamically unstable sea-island structure should be formed.

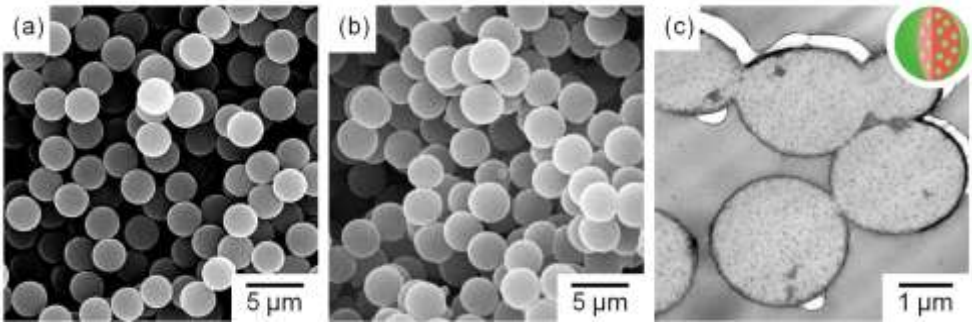


Figure 6. SEM photographs of PMMA seed particles (a) and obtained particles prepared by seeded dispersion polymerization of [MTMA][TFSA] (b) and TEM photograph of ultrathin cross-sections of obtained particles stained with 3 wt% phosphotungstic acid aqueous solution for 30 min (c)

To control the morphology of the PMMA/PIL composite particles, semi-batch seeded dispersion polymerization was carried out, in which [MTMA][TFSA] was fed dropwise (0.05 g ×4 times) to the polymerization reactor in the presence of PMMA seed particles. Figure 7a and b show the SEM photographs of PMMA seed particles and obtained particles prepared by seeded dispersion polymerization in semi-batch system. The diameter of the obtained particles (3.3 μm) after seeded dispersion polymerization in semi-batch system was larger than that of PMMA seed particles (2.8 μm) with maintaining monodispersity, indicating that PMMA/PIL composite particles were obtained.

Figure 7c shows the TEM photograph of phosphotungstic acid-stained ultrathin cross section of PMMA/PIL particles after seeded dispersion polymerization in semi-batch system. It was observed that PMMA cores with weak contrast surrounded by PIL shells

with high contrast. In the case of semi-batch system, the viscosity of interior of the PMMA seed particle is very high at 30˚C, thus the PIL was unable to diffuse to the inside particles. As a result, the composite particles having a core-shell structure consisting of a PMMA-core and a PIL-shell can be prepared.

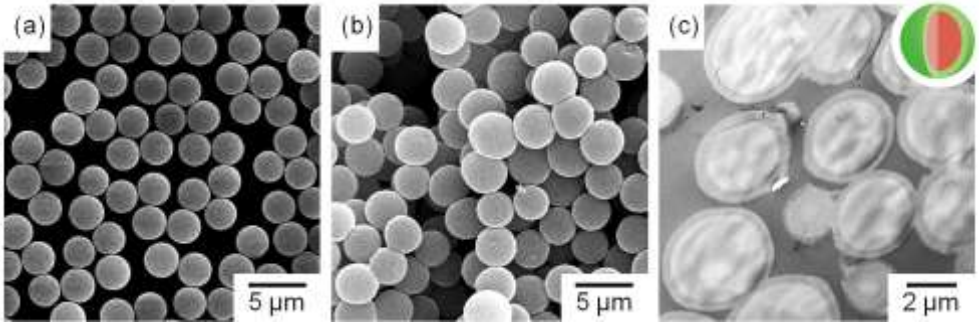


Figure 7. SEM photographs of PMMA seed particles (a) and obtained particles prepared by seeded dispersion polymerization of [MTMA][TFSA] in semi-batch system (b) and TEM photograph of ultrathin cross-sections of obtained particles stained with 3 wt% phosphotungstic acid aqueous solution for 30 min (c)

Conclusion

When the seeded dispersion polymerization of ionic liquid monomer, [MTMA][TFSA], in ethanol was carried out with PS seed particles, the secondary nucleated PIL particles were observed and composite particles were not obtained. By using spreading coefficients calculated from the interfacial tensions, it was found that a thermodynamically stable morphology of the obtained particles was formation of individual particles. This result was caused by low polarity of PS. On the other hand, in the case of PMMA seed particles, having higher polarity than PS particles, composite particles having the sea-island structure were successfully prepared. Moreover, we successfully prepared PMMA/PIL composite particles having a core-shell morphology with a PMMA core and PIL shell by seeded dispersion polymerization in semi-batch system.

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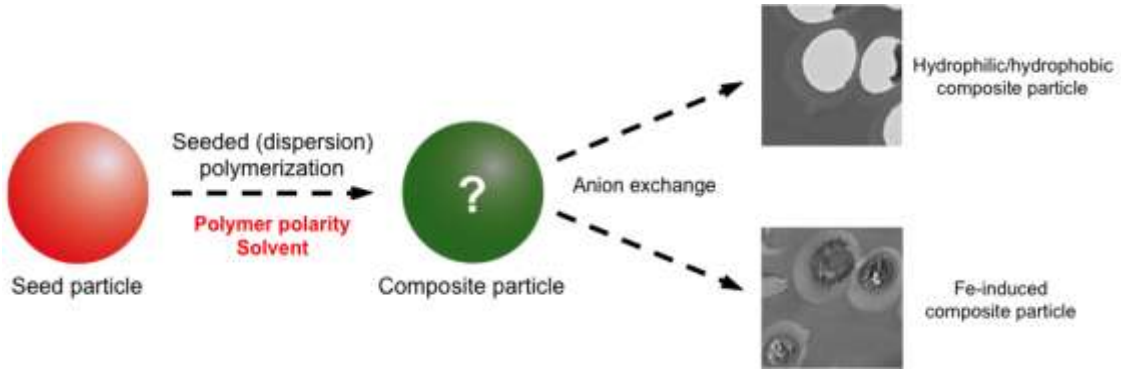
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Chapter 5

Effect of Polarity of Seed polymer and Solvent on the Preparation of Poly(ionic liquid) Composite Particles and Property Modification Utilizing Anion Exchange



Abstract: Seeded dispersion polymerization of the ionic liquid monomer ([2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide) ([MTMA][TFSA]) was carried out in methanol/water mixture with three kinds of methacrylate seed particles. In the presence of PMMA and PEMA seed particles, polymer/poly(ionic liquid) (PIL) composite particles were successfully obtained. However, secondary nucleated PIL particles were formed and no P*t*BMA/PIL composite particles were obtained in the presence of P*t*BMA seed particles. When seeded polymerization was carried out in water, PMMA/PIL core-shell composite particles were obtained, which is consistent with the theoretical consideration based on the spreading coefficients calculated from the interfacial tensions. Utilizing anion exchange of PIL-core from TFSA to Br and $FeCl_4$ anions with PIL/P(MMA-EGDM) core-shell composite particles, the properties of composite particles could be modified.

Introduction

Ionic liquids, which are mostly composed of organic ions, are molten salts at room temperature.[1-4] They have been researched in various fields due to their low vapor pressures, high thermal stability, and nonflammability. Ionic liquids also have the functional characteristics such as ionic conductivity and CO_2 solubility, which is expected for the development of functional materials.[5-8] Moreover, the signature property of ionic liquids is possible to design their properties such as solubility (hydrophilic/hydrophobic) and magnetic responsiveness by changing the structure of cations and anions.[9-14] Utilizing these properties, many researchers have been reported on the preparation of solid-state materials with property of ionic liquids.[15-19] PILs are polymer materials combined the mechanical stability and processability of polymeric materials with the unique properties of ionic liquids. PILs are prepared by the polymerization of ionic liquid containing vinyl and (meth)acrylate groups on the cationic or anionic parts.[20-26] Ohno and coworkers reported the investigation on the ionic conductivity of PIL, which is firstly indicated that PILs have potential as functional materials.[27] Tsujii groups prepared the concentrated PIL blushes by atom transfer radical polymerization on the surface of silica particles, and reported that the colloid crystal consisted of hybrid particles exhibited the high ionic conductivity.[28] The research on PIL was also reported the property modification using anion exchange.[29-31] Recently, many researchers reported the investigation on functional properties of PIL at bulk state as well as particle state.[32-36]

We have reported the preparation of PIL particles by dispersion polymerization of [2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide ([MTMA][TFSA]) in methanol and ethanol with poly(vinylpyrrolidone) (PVP) as stabilizer, in which the obtained PIL particles dissolved in medium by addition of LiBr due to anion

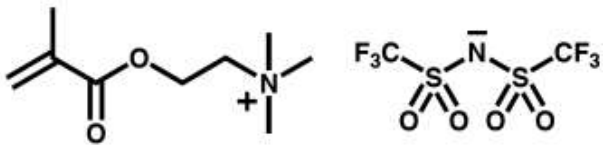
exchange and exhibits the property of ionic liquid.[37] Moreover, we also carried out the preparation of polymer/PIL composite particles by seeded dispersion polymerization.[38] The composite particle was not obtained in the presence of PS seed particles, however, the PMMA/PIL composite particles was successfully prepared. The morphologies of the composite particles were consistent with the theoretical considerations based on the spreading coefficients calculated from the interfacial tensions.

In ***Chapter 5***, in order to investigation the effect of polarity of seed polymer and media, we carried out the preparation of PIL composite particles by seeded dispersion polymerization of quaternary ammonium-based ionic liquid monomer ([MTMA][TFSA]) with three kinds of seed particles and by seeded polymerization in water media. Moreover, the modified property of polymer/PIL composite particles was carried out utilizing anion exchange.

Experimental Section

Materials

Methyl methacrylate (MMA), ethyl methacrylate (EMA) and *t*-butyl methacrylate (*t*BMA) were purified by distillation under reduced pressure in a nitrogen atmosphere. Ethylene glycol dimethacrylate (EGDM; Nakalai Tesque Inc., Kyoto, Japan) was washed with 1 mol L^{-1} sodium hydroxide and purified water to remove polymerization inhibitors before use. Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization in methanol. 2,2′-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, Wako Pure Chemical Industries, Ltd., Osaka, Japan), poly(vinylpyrrolidone) (PVP, K-30, weight-average molecular weight: 3.6×10^5 g/mol), methanol and ethanol (Nakalai Tesque Inc., Kyoto, Japan), lithium bromide (LiBr) (99%, Aldrich), [2-(methacryloyloxy)ethyl]trimethylammonium chloride ([MTMA]Cl) solution (80 wt% in water, Aldrich), lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) (99.7%, Kanto Chemical Co., Inc.) and the emulsifier, polyoxyethylene sorbitan monooleate (Tween 80) (Nacalai tesque, Kyoto, Japan) were used as received. The water used in all the experiments was obtained from an Erix®UV (Millipore, Japan) purification system, and had a resistivity of 18.2 MΩ cm. The ionic liquid monomer (Fig. 1) was prepared by mixing the aqueous solutions of [MTMA]Cl and Li[TFSA] as previously reported.[37] 1-Butyl-3-methylimidazolium tetrachloroferrate ([Bmim][$FeCl_4$]) was prepared by mixing 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) and anhydrous $FeCl_3$.[14]



[MTMA][TFSA]

Figure 1. Structure of ionic liquid monomers

Preparation of poly(methyl methacrylate) (PMMA), poly(ethyl methacrylate) (PEMA) and poly(t-butyl methacrylate) (PtBMA) seed particles

Monodispersed PMMA, PEMA and P*t*BMA seed particles were prepared by dispersion polymerization as follows. Preparation of PMMA and PEMA seed particles: monomer (1.2 g), PVP (0.12 g) and AIBN (0.012 g) were dissolved in methanol/water (7/3 w/w, 10.8 g). The mixtures were then poured into glass tubes and degassed using several vacuum/N_2 cycles, and then sealed glass tubes were placed in a water bath at 60°C for 5 h with 80 cycles min^{-1} (3 cm strokes). Preparation of P*t*BMA seed particles: *t*BMA (1.2 g), PVP (0.24 g) and V-70 (0.024 g) were dissolved in methanol/water (7/3 w/w, 10.8 g). The mixtures were then poured into round-bottom Schlenk flask, sealed off with silicon rubber septum, and then degassed using several N_2/vacuum cycles. The sealed flask placed in a water bath at 30°C for 24 h with magnetic stirring at 200 rpm.

Table 1. Recipes for the preparation of PIL composite particles by seeded dispersion polymerizations[a)] of [MTMA][TFSA] in ethanol.

Ingredients		**1**	**2**	**3**
PMMA seed particles	(g)	0.25	-	-
PEMA seed particles	(g)	-	0.25	-
P*t*BMA seed particles	(g)	-	-	0.25
[MTMA][TFSA]	(g)	0.25	0.25	0.25
V-70	(mg)	2.5	2.5	2.5
Methanol	(g)	2.1	2.1	2.1
Water	(g)	0.9	0.9	0.9

[a)] In a sealed glass tube; N_2; 10 h; 80 cycles/min

Seeded dispersion polymerization of the ionic liquid monomer

Seeded dispersion polymerizations of [MTMA][TFSA] in the presence of PMMA, PEMA and P*t*BMA seed particles were performed under the conditions listed in Table 1 using V-70 as initiator at 30°C in methanol/water (7/3, w/w) which is insoluble for each polymer.

Seeded polymerization of the ionic liquid monomer with PMMA seed particles

The homogeneous oil phase consisted of [MTMA][TFSA] (0.1 g) and AIBN (1.0 mg) was ultrasonicated using ultrasonic homogenizer (NISSEI CORPORATION, US-600T, 12-mm diameter tip, set at "Power 10") for 5 min in Tween 80 aqueous solution (0.35 wt%, 1.0 g). The suspension was added to the dispersion [PMMA seed particles (0.1 g) and water (4.0 g)] in round-bottom Schlenk flask, sealed off with silicon rubber septum, and then degassed using several N_2/vacuum cycles. After absorption of [MTMA][TFSA] and AIBN for 3 h at room temperature, seeded polymerization was performed at 60˚C for 10 h.

Preparation of poly([MTMA][TFSA]) seed particles

Monodispersed poly([MTMA][TFSA]) (PIL) seed particles were prepared by dispersion polymerization as follows: Starting solution of [MTMA][TFSA] (1.0 g), PVP (0.1 g), and AIBN (0.01 g) was dissolved in methanol/water (7/3 w/w, 10 g). The mixture was then poured into glass tubes and degassed using several vacuum/N_2 cycles, and then sealed glass tubes were placed in a water bath at 70°C for 5 h with agitation at 80 cycles min^{-1} (3 cm strokes).

Seeded dispersion copolymerization of MMA and EGDM with PIL seed particles

PIL/P(MMA-EGDM) composite particles were prepared by seeded dispersion copolymerization as follows: After MMA (0.05 g), EGDM (0.05 g), PVP (0.01 g), and V-70 (0.002 g) was dissolved in ethanol (1.0 g), the mixture was added to the dispersion [PIL seed particles (0.1 g) and ethanol (3.0 g)]. The dispersion was poured into glass tubes, degassed using several vacuum/N_2 cycles, and then sealed glass tubes. The glass tube was placed in a water bath at 30°C for 24 h with agitation at 80 cycles min^{-1} (3 cm strokes). The cross-linker (EGDM) was copolymerized with MMA to prevent PMMA from dissolving in anion exchange reaction.

Anion exchanges of PIL/P(MMA-EGDM) composite particles using LiBr and [Bmim][$FeCl_4$]

The ethanol dispersion of PIL/P(MMA-EGDM) composite particles [composite particles (0.05 g) and ethanol (2.0 g)] was added to the ethanol (2.0 g) which dissolved LiBr (0.2 g) or [Bmim][$FeCl_4$] (0.2 g). The mixture was moderately stirred at room temperature for 24 h to exchange the counter anion from TFSA to Br or $FeCl_4$ anions. To remove residual salts, the as-prepared dispersion was washed by centrifugation with ethanol.

Characterization

Scanning electron microscopy (SEM, JSM-6510, JEOL, Tokyo, Japan) studies of the particles coated with platinum were performed at 20 kV. Transmission electron microscopy (TEM, JEM-1230, JEOL, Tokyo, Japan) characterization was performed at 100 kV. To observe the interior morphology of the particles, dry samples were embedded in an epoxy matrix, cured at room temperature overnight, and subsequently microtomed. The

ultrathin cross sections (approximately 100 nm thick) were stained by floating on a 3 wt% aqueous phosphotungstic acid solution for 30 min at room temperature, and then observed with TEM. Qualitative analyses of the products after anion exchange were conducted with a Fourier transform infrared spectrometer (FT-IR, FT/IR-6200, JASCO, Tokyo, Japan) using a pressed KBr pellet technique. To calculate the interfacial tensions, the contact angle measurement was carried out with a DropMaster 300 (Kyowa Interface Science, Saitama, Japan) instrument at room temperature.

Results and Discussion

Effect of seed particles and solvent on seeded dispersion polymerization of [MTMA][TFSA]

We previously reported that the polarity of seed particles had effect on the formation of PIL composite particles.[38] In order to investigate in detail the effect of polarity of seed particles, seeded dispersion polymerizations of [MTMA][TFSA] were carried out using three kinds of methacrylate seed particles. The polar components of surface tension (γ^p, mN/m) of PMMA, PEMA and P*t*BMA as seed particles are 8.5, 3.0, and 2.6 mN/m, respectively. Before polymerization, the value of spreading coefficient, which is defined as $S_i = \gamma_{jk} - (\gamma_{ij} + \gamma_{ik})$ (where γ_{jk}, γ_{ij}, and γ_{ik} are interfacial tensions between each components), was calculated according to previous report. However, the surface tension of PIL needed to recalculate because the surface of PIL film for water have unique property[39].

Table 2. Dispersive (γ^d), Polar (γ^p), and Total (γ) Components of the Surface Tension (mN/m) at 298 K

	γ^d	γ^p	γ
PMMA	40.4	8.5	48.9
PEMA	35.2	3.0	38.2
P*t*BMA	33.9	2.6	36.5
Poly([MTMA][TFSA])	25.6	10.6	36.2
Methanol[40]	18.2	4.3	22.5

When the surface tension of PIL was recalculated by contact angle measurement with hexadecane and CH_2I_2 and using Young-Owens equation, the γ^d (dispersive component

of surface tension) and γ^p values were 25.6 and 10.6 mN/m, respectively. The surface tensions for each component are summarized in Table 2.

Table 3 shows the calculated *S* values for each system. The relationship between morphology and each *S* value shows as follows[41]:

When $S_{seed} < 0$, $S_{PIL} \geq 0$, and $S_{solvent} < 0$ are satisfied, the morphology of particles after polymerization is "core-shell".

When $S_{seed} < 0$, $S_{PIL} < 0$, and $S_{solvent} < 0$ are satisfied, the morphology of particles after polymerization is "partial engulfing".

When $S_{seed} < 0$, $S_{PIL} < 0$, and $S_{solvent} \geq 0$ are satisfied, the morphology of particles after polymerization is "individual".

In the case of PMMA seed particles, it is suggested the potential for the formation of composite particles by seeded dispersion polymerization. On the other hands, in the case of PEMA and P*t*BMA seed particles, it is suggested that the synthesis of composite particles is difficult because $S_{solvent}$ value is positive.

Table 3. The value of spreading coefficient for each system

Seed Polymer	Spreading coefficient[a]		
	S_{seed}	S_{PIL}	$S_{solvent}$
PMMA	-6.6	-0.5	-3.6
PEMA	-6.6	-4.9	0.8
P*t*BMA	-6.6	-5.4	1.3

[a] $S_i \geq 0$: Spread (wetting); $S_i < 0$: Not spread

To confirm whether the morphological prediction of composite particles using spreading coefficient is correct, seeded dispersion polymerizations of [MTMA][TFSA] using

PMMA, PEMA, and P*t*BMA seed particles were carried out. In seeded dispersion polymerization system with PMMA seed particles, the diameter of obtained particles after polymerization was larger than that of PMMA seed particles with maintaining monodispersity (Fig. 2a-a''). In the case of P*t*BMA seed particles, the particles obtained after polymerization had broad size distribution and the formation of individual particles was observed (Fig. 2c-c''). These results are consistent with the prediction using spreading coefficient. Although the morphology of particles obtained after seeded dispersion polymerization with PEMA seed particles was predicted "individual", the obtained particles were observed the formation of composite particles (Fig. 2b-b''). This result indicated that PEMA seed particles were swollen with [MTMA][TFSA] in initial stage of polymerization because $S_{solvent}$ value is close to zero.

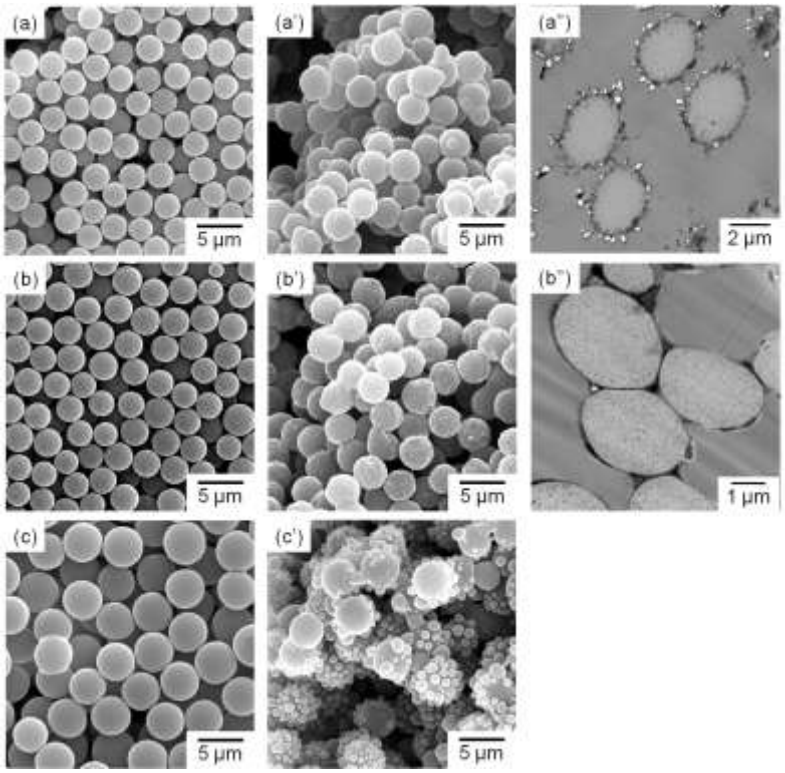


Figure 2. SEM images of PMMA, PEMA and P*t*BMA seed particles (a-c) and obtained particles after seeded dispersion polymerization of [MTMA][TFSA] (a'-c'). TEM image of ultrathin cross sections of obtained particles stained for 30 min with a 3 wt% aqueous phosphotungstic acid solution (a'', b'').

Moreover, in order to investigate the effect of solvent, the preparation of PMMA/PIL composite particles in water was carried out. The polymerization condition was changed into seeded polymerization because [MTMA][TFSA] was insoluble in water. The spreading coefficients in this system were calculated as follows: $S_{PMMA} = -9.0 < 0$, $S_{PIL} = +1.9 > 0$ and $S_{water} = -32.4 < 0$, which is expected that core-shell PMMA/PIL composite particles was obtained in batch system. As shown in Figure 3a and b, no secondly nucleated particles were observed and the diameter of the obtained particles after seeded polymerization in water was larger than that of PMMA seed particles with maintaining monodispersity. The interior structure was observed core-shell structure composed of light PMMA cores surrounded by dark PIL shells (Figure 3c). This result indicated that PMMA/PIL composite particles with core-shell morphology were prepared in batch system.

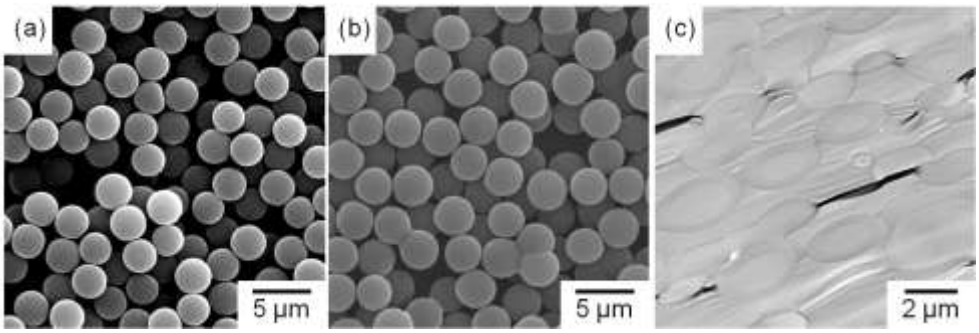


Figure 3. SEM photographs of PMMA seed particles (a) and obtained particles prepared by seeded polymerization of [MTMA][TFSA] in water (b) and TEM photograph of ultrathin cross sections of PMMA/Poly([MTMA][TFSA]) composite particles stained for 30 min with a 3 wt % aqueous phosphotungstic acid solution (c)

Property modification of PIL composite particles utilizing anion exchange

We have reported that the PIL composite particles exhibited the property of ionic liquid because they could be observed by SEM without coating.[37] To modify the additional property, anion exchange reaction with core-shell PMMA/PIL composite particles was carried

out and their functionality was investigated. The property design is important in the case of utilizing composite particles in various fields. When anion exchange between PIL composite particles and [Bmim][$FeCl_4$] was carried out to modify the magnetism, polymer was dissolved in the medium. To prevent polymer from dissolving after anion exchange, the preparation of PIL composite particles with cross-linked PIL shell by seeded polymerization was carried out. However, the formation of secondly nucleated particles was observed after polymerization and no composite particles were obtained. Contrarily, when seeded dispersion polymerization of MMA and EGDM with PIL seed particles was carried out, the composite particles composed of PIL core and P(MMA-EGDM) shell was successfully prepared (Figure 4).

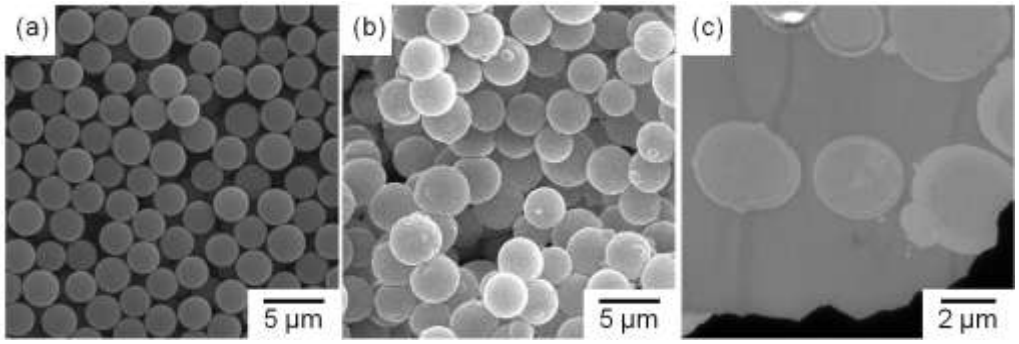


Figure 4. SEM images of PIL seed particles (a) and particles prepared by seeded dispersion copolymerization of MMA and EGDM (b). TEM image of ultrathin cross sections of the obtained particles stained for 30 min with 3 wt% aqueous phosphotungstic acid solution (c).

To confirm whether the obtained PIL composite particles maintained the property of ionic liquid, anion exchange reaction was carried out in LiBr ethanol solution. Figures 5a shows SEM image of PIL/P(MMA-EGDM) composite particles after anion exchange in LiBr ethanol solution at room temperature for 24 h. Although some composite particles after anion exchange have dent, most of the obtained particles have maintained spherical. This is

indicated that PIL-core might be eluted into ethanol media because poly([MTMA]Br) (PIL[Br]) can be soluble in ethanol, resulting that P(MMA-EGDM)-shell should have dent. When the obtained particles after anion exchange was confirmed by the FT-IR (bottom of Figure 5), the obtained particle had no peaks at 1355 cm^{-1} which is attributed to the $S(=O)_2$ of TFSA anion, indicating that TFSA anion was replaced with Br anion. When ultrathin cross-sections of PIL[Br]/P(MMA-EGDM) particles were observed by TEM, PIL[Br] cores were disappeared and only P(MMA-EGDM) shells were observed (Figure 5b). This is suggested that PIL[Br] core should be dissolved in water because the ultrathin cross-sections of particles floated on the water when we prepared them, resulting that anion exchange reaction of PIL/P(MMA-EGDM) composite particles was proceeded smoothly.

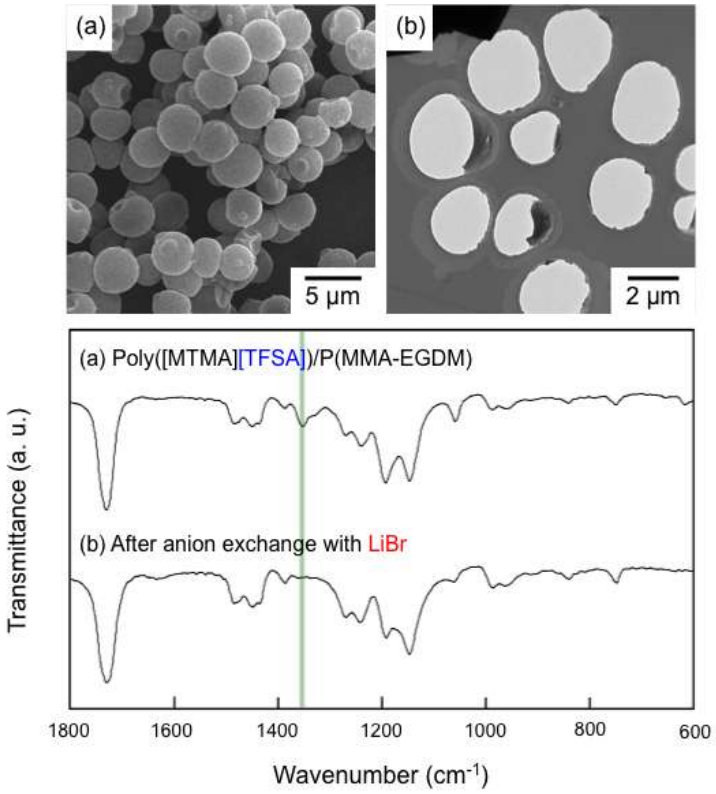


Figure 5. (Top) SEM image of PIL[Br]/P(MMA-EGDM) composite particles (a) and TEM image of ultrathin cross sections of the particles. (Bottom) FT-IR spectra of PIL/P(MMA-EGDM) composite particles before (a) and after anion exchange procedure with LiBr (b)

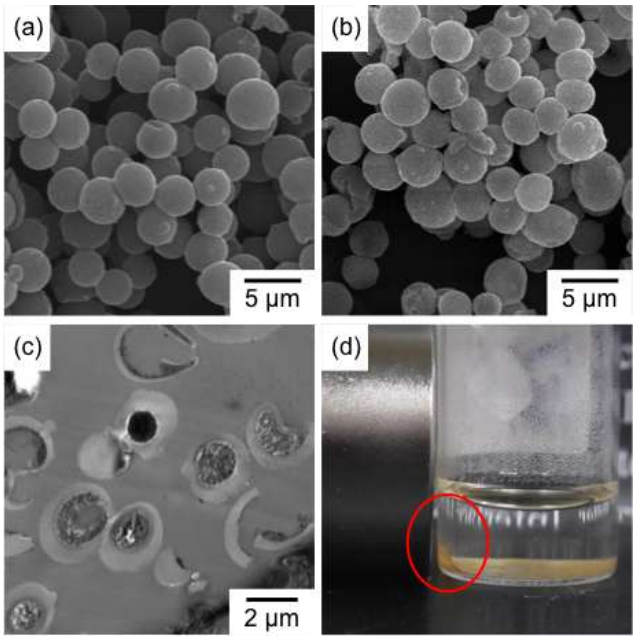


Figure 6. SEM photographs of PIL/P(MMA-EGDM) composite particles after anion exchange procedure with [Bmim][$FeCl_4$] (a) and after the reduction reaction of PIL[$FeCl_4$]/P(MMA-EGDM) particles with $NaBH_4$ (b). TEM photograph (c) of ultrathin cross sections of the particles and visual appearance (d) of the particles responding to a neodymium magnet.

To modify the paramagnetic to composite particles, anion exchange reaction was carried out using [Bmim][$FeCl_4$] which shows magnetic response. As shown in Figure 6a, the morphology of obtained particles after anion exchange reaction had no difference compared to that of composite particles before anion exchange. Although the magnetic responsiveness of the obtained particles was investigated using neodymium magnet, these particles showed no response to the magnet. To confirm whether the counter anion of PIL-core was exchanged from TFSA to $FeCl_4$ anions, the reductive reaction of Fe(III) ion in $FeCl_4$ anion was carried out with $NaBH_4$. $NaBH_4$ aqueous solution (1 wt%, 2.0 g) was added to 1 wt% poly([MTMA][$FeCl_4$])/P(MMA-EGDM) dispersion in ethanol (2.0 g) and stirred at room temperature for 12 h due to reduction of Fe(III) ion, and then the as-prepared dispersion was washed by centrifugation with ethanol. The outside structure of obtained

particles after reductive reaction maintained the initial state and Fe nanoparticles were observed inside particles (Fig. 6b and c). As shown in Figure 6d, the obtained particles showed the magnetic responsiveness, resulting that the PIL composite particles with magnetism were successfully prepared utilizing anion exchange reaction.

Conclusion

Seeded dispersion polymerization of ionic liquid monomer [MTMA][TFSA] in methanol/water mixtures with PMMA and PEMA seed particles led to the formation of polymer/PIL composite particles. On the other hand, in the case of P*t*BMA seed particles, the secondary nucleation of the PIL particles was occurred and no composite particles were obtained. We also successfully prepared core–shell PMMA/PIL composite particles with a PMMA core and a PIL shell by seeded polymerization in water media. These results suggested that the polarity of seed polymer and solvent had influence on the formation of PIL composite particles. Moreover, the functional property such as magnetism was successfully modified by anion exchange with PIL/P(MMA-EGDM) core-shell composite particles prepared by seeded dispersion copolymerization of MMA and EGDM in ethanol using PIL seed particles.

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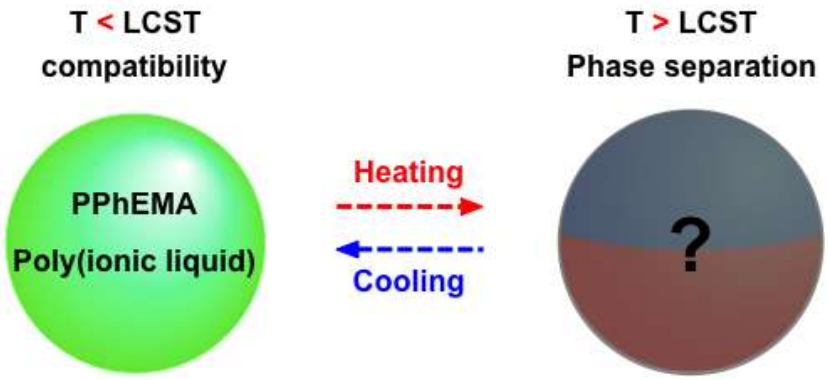
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Chapter 6

Preparation of Poly(phenylethylmethacrylate)/ Imidazolium-based Poly(ionic liquid) Composite Particles having Thermosensitive Property



Abstract: Composite particles composed of poly(2-phenylethyl methacrylate) (PPhEMA) and imidazolium-based poly(ionic liquid)s were prepared by suspension polymerization of ionic liquid monomer in the presence of PPhEMA. When 1-vinyl-3-butylimidazolium bis(trifluoromethanesulfonyl)amide ([Vbim][TFSA]) was used as ionic liquid monomer, the obtained composite particles after suspension polymerization at 70°C and 30°C had phase-separated and homogeneous structure, respectively. Their inner morphology after heat treatment was no different compared with that before heat treatment, which is indicated that PPhEMA/Poly([Vbim][TFSA]) composite particles did not exhibit lower critical solution temperature (LCST) behavior. On the other hands, the composite particles prepared by suspension polymerization of [Veim][TFSA] as ionic liquid monomer at 30°C were transformed the inner morphology from homogeneous to phase-separation by heat treatment. The morphology transformation of composite particles also had dependent on PPhEMA molecular weight.

Introduction

Thermosensitive polymers are polymers that is drastically changed the solubility in a solvent with increasing or decreasing the temperature.[1-4] Poly(*N*-isopropyl acrylamide) (PNIPAM), which is typical thermosensitive polymer, is soluble in water below 32˚C and insoluble above 32˚C. This behavior in polymer solution is called as lower critical solution temperature (LCST)-type phase transition behavior.[5-7] Generally, when a polymer is mixed in a solvent, the change in Gibbs free energy (ΔG_{mix}) is represented as $\Delta H_{mix} - T\Delta S_{mix}$ (ΔH: enthalpy, ΔS: entropy) and polymer can be dissolved in the case of negative ΔG_{mix}. When polymer solution exhibits LCST-type phase transition behavior, ΔS_{mix} exhibited the negative value, which are uncommon phenomenon and a key factor because the value of ΔG_{mix} is increased toward positive with increasing temperature.[8] Such thermosensitive polymers have attracted attention as biochemical and medical materials.[9-12]

The LCST-type phase transition behavior can be observed in water as well as ionic liquids. Ionic liquids are organic molten salts at room temperature and used as environmental-friendly media due to nonflammability, high thermal stability, and low vapor pressure in various fields.[13-26] Watanabe groups have reported that poly(benzyl methacrylate) and its derivative exhibited LCST-type phase transition behavior in imidazolium-based ionic liquid (1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide: [Bmim][TFSA]) and their phase separation mechanism.[27-30] They also reported the preparation of thermosensitive gel particles in ionic liquids, in which the gel particles exhibited volume transition behavior around LCST.[27] Recently, we have investigated the synthesis of free-standing thermosensitive composite gel particles including the ionic liquid by seeded polymerization.[31] The ionic liquid in composite gel particles around LCST was transferred from poly(2-phenylethyl methacrylate) (PPhEMA) phase to poly(methyl methacrylate)

(PMMA) phase, resulting volume transition behavior was observed in water, air and under vacuum.

Until now, the main research object on LCST has been the investigation of phase transition behavior between polymer and solvent. When the other phase is not solvent but polymer, that is polymer blend system, it is much interesting whether the LCST behavior is exhibited. Generally, most of polymer blends is occurred phase separation because different polymer chains is immiscible. The partial polymer blends has compatible at low temperature and immiscible at high temperature, which is LCST behavior.[32,33] However, the combination of polymer blends with LCST behavior has limited.

We tried to prepare polymer/PIL composite particles with LCST behavior by suspension polymerization of imidazolium-based ionic liquid monomer in the presence of PPhEMA homopolymer. Watanage group has reported that LCST of PPhEMA in [Bmim][TFSA] is 118°C previously. In this research, 1-vinyl-3-butylimidazolium bis(trifluoromethanesulfonyl)amide ([Vbim][TFSA]) with a similar molecular structure to [Bmim][TFSA] was used as ionic liquid monomer. We expect that LCST between PPhEMA and PIL would be decreased below 100°C because ΔS is more negative due to entanglement between polymer chains, and LCST behavior of composite polymer would be observed in water. Moreover, the effects of molecular weight and structure of PIL on the preparation of composite particles are investigated.

Experimental Section

Materials

PhEMA (Polysciences, Inc., Pennsylvania, USA), vinyl toluene (VT; Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) (mixture of meta and para isomers), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70; Wako Pure Chemical Industries, Ltd., Osaka, Japan), poly(vinyl alcohol) (PVA; Nippon Synthetic Chemical, Osaka, Japan) (Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%), *n*-butylbromide, 1-ethylbromide, 1-vinylimidazole (Nakalai Tesque Inc., Kyoto, Japan), lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) (99.7%, Kanto Chemical Co., Inc.) were used as received. *n*-Butyl methacrylate (*n*BMA; Nakalai Tesque Inc., Kyoto, Japan) were distilled under reduced pressure in a nitrogen atmosphere. Reagent grade 2,2′-azobis(isobutyronitrile) (AIBN) was purified by recrystallization in methanol. Water used in all experiments was obtained from the Erix®UV (Millipore, Japan) purification system and had a resistivity of 18.2 MΩ cm.

Preparation of ionic liquid monomers

A typical synthesis of different imidazolium-based ionic liquid monomers was carried out as reported in previous papers.[34] First, [Vbim]Br was prepared with *n*-butylbromide and 1-vinylimidazole. *n*-Butylbromide (0.15 mol) was dropped into 1-vinylimidazole (0.13 mol) under vigorous stirring. The mixture was poured into glass tubes and degassed using several vacuum/N_2 cycles, and then sealed glass tubes were reacted in an oil bath at 100 °C for 20 h at 60 cycles min^{-1}. The product was obtained as high viscous and brownish-red liquid, washed three times with ethyl acetate and then dried under vacuum. After the obtained [Vbim]Br (0.11 mol) was dissolved in water, the aqueous

solution of Li[TFSA] (0.12 mol) was added into [Vbim]Br aqueous solution under vigorous stirring. After the phase separation gradually occurred, the lower oily layer was collected, washed five times with distilled water and then dried under vacuum. [Vbim][TFSA] was obtained as brownish-red liquid. The synthesis procedure of 1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide ([Veim][TFSA]) was carried out under the same condition except for the preparation of [Veim]Br with 1-ethylbromide and 1-vinylimidazole in methanol at 40˚C overnight.

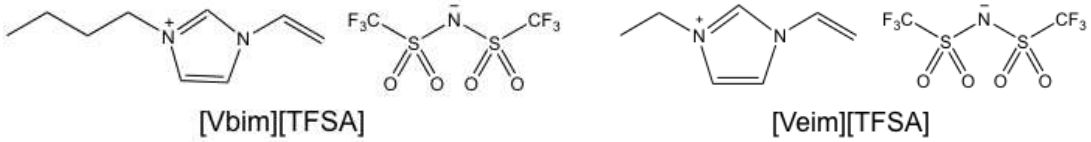


Figure 1. Structure of ionic liquid monomers

Preparation of PhEMA homopolymer by solution polymerization

The typical procedure was as follows: A homogeneous solution of PhEMA (5.0 g), toluene (5.0 g), and AIBN (0.05 g) was poured into glass tubes and degassed using several vacuum/N_2 cycles, and then sealed glass tubes. The polymerization was carried out at 60˚C for 12 h with shaking the glass tube horizontally at 80 cycles min^{-1}. The product was precipitated in hexane to remove the residual monomer and subsequently dried under vacuum at room temperature.

Measurement of LCST between PPhEMA and ionic liquid monomer

PPhEMA (0.1 g) was dissolved in ionic liquid monomer (0.3 g) and THF (1.0 g) mixtures, and then THF was evaporated slowly from mixture at room temperature overnight, resulting homogeneous solution consisted of ionic liquid monomer and PPhEMA was

prepared. Transmittance of this solutions was measured at 500 nm using a UV-2500 UV-vis spectrophotometer (Shimazu Corporation, Kyoto, Japan) with a heating rate of 0.4°C min^{-1}. The LCST was defined as the temperature at which the transmittance reached 50%.

Preparation of PPhEMA/PIL composite particles by suspension polymerization

The PPhEMA/imidazolium-based PIL composite particles were prepared by suspension polymerization. A typical procedure is described below. PPhEMA (0.1 g) was dissolved in ionic liquid monomer (0.3 g) and THF (1.0 g) mixtures. After THF was evaporated slowly at room temperature overnight, homogeneous solution consisted of ionic liquid monomer and PPhEMA was obtained. V-70 or AIBN (3.0 mg) was dissolved in the obtained monomer solution, and the homogeneous oil phase was poured into PVA aqueous solution (1.0 wt%, 3.0 g), homogenized at 4000 rpm for 3 min. The obtained suspension was added to a glass tube, degassed using several vacuum/N_2 cycles, and then sealed. The sealed glass tube was placed in water bath at 30 or 70°C for 24 h with shaking at 80 cycles min^{-1}. After polymerization, the obtained emulsion was diluted, added to a glass tube again, and then carried out heat treatment at appropriate temperature for 24 h. The composite particles were observed using an optical microscope (Nikon ECLIPSE 80i and Nikon MICROPHOT-FXA, Nikon Corporation, Tokyo, Japan).

Results and Discussion

To investigate whether PPhEMA in [Vbim][TFSA] exhibits LCST behavior, the transmittance of monomer solution was measured by uv-vis spectrophotometer.

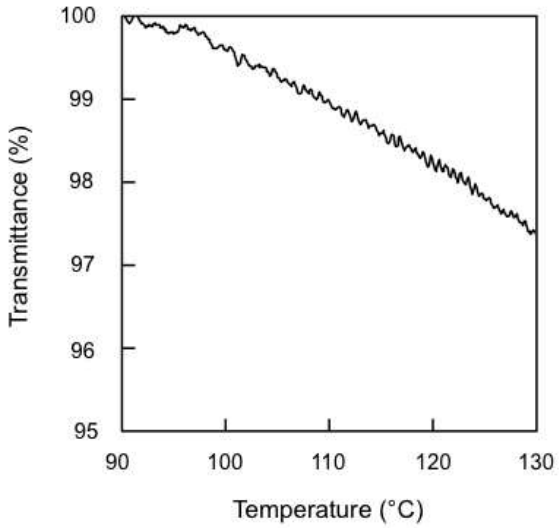


Figure 2. Measurement of transmittance (500 nm) as a function of temperature (0.4°C min^{-1}) of [Vbim][TFSA] solution of PPhEMA

As shown in Figure 2, the transmittance at 500 nm was slightly decreased over 100°C. However, it was difficult to observe the LCST on this system because the measurement temperature was limited at 130°C. It is expected the possibility that PPhEMA in [Vbim][TFSA] has LCST behavior over 130°C. On the other hands, each polymer was dissolved in THF and then the polymer blend film was prepared by evaporation of the THF at room temperature on the slide glass. The obtained blend film was switched from transparent to opaque by heat treatment at 150°C for 30 min (Fig. 3). Previously, we have reported that LCST (65°C) of gel particles including [Bmim][TFSA] dispersed in water was shifted to lower temperature compared to bulk state (98°C).[31] In this system, when PPhEMA/Poly([Vbim][TFSA]) composite polymer is heat-treated in water, the decrease of LCST might be observed.

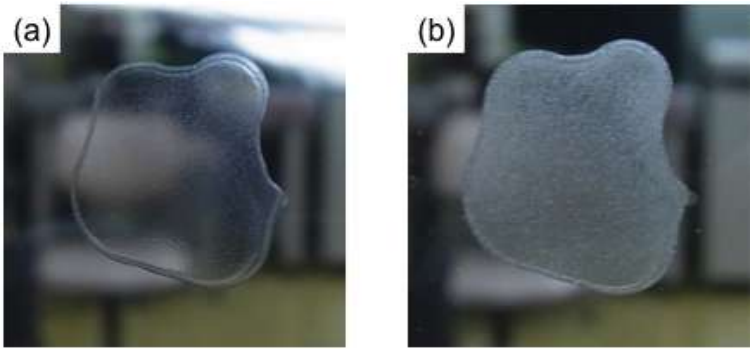


Figure 3. Visual appearances of polymer blend film composed of poly([Vbim][TFSA]) and PPhEMA at *r.t.* (a) and after heat treatment at 150°C (b)

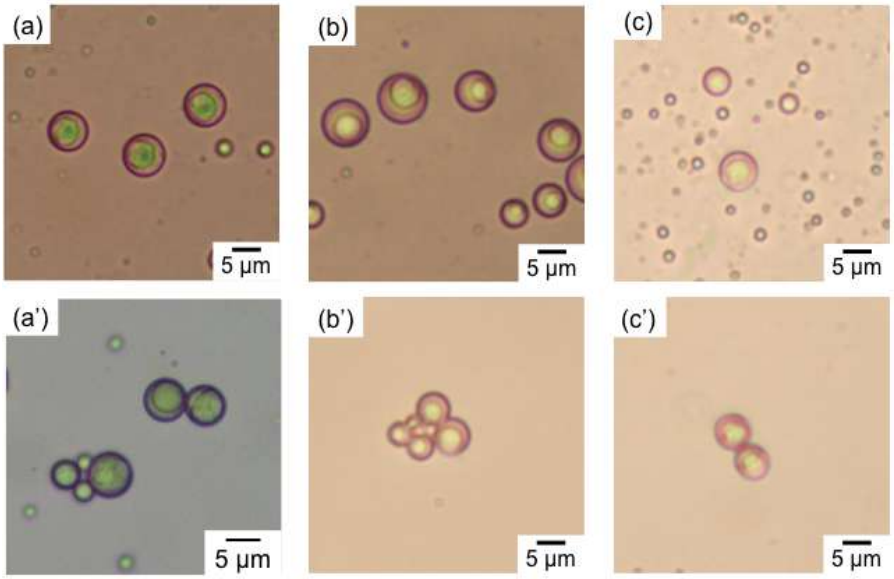


Figure 4. Optical micrographs of P(PhEMA-X) (X; (b, b') VT (15 mol%), (c, c') BMA (10 mol%))/Poly([Vbim][TFSA]) composite particles by suspension polymerization at 70˚C. Observation temperature: (a, b, c) *r.t.*, (a', b', c') after heat treatment at 150˚C for 60 h.

Figure 4 shows the optical micrographs of PPhEMA/Poly([Vbim][TFSA] composite particles prepared by suspension polymerization of [Vbim][TFSA] at 70°C before and after heat treatment at 150°C for 60 h. The obtained particles were already phase-separated, and the morphology of composite particles after heat treatment was nearly unchanged. This result is indicated the possibility of shift in the LCST between PPhEMA

and Poly([Vbim][TFSA]). In order to change the LCST, composite particles using PPhEMA-based copolymer (VT, 15 mol% based on PhEMA; *n*BMA, 10 mol% based on PhEMA) was prepared and then heat-treated. However, both of composite particles had similar morphology before and after heat treatment.

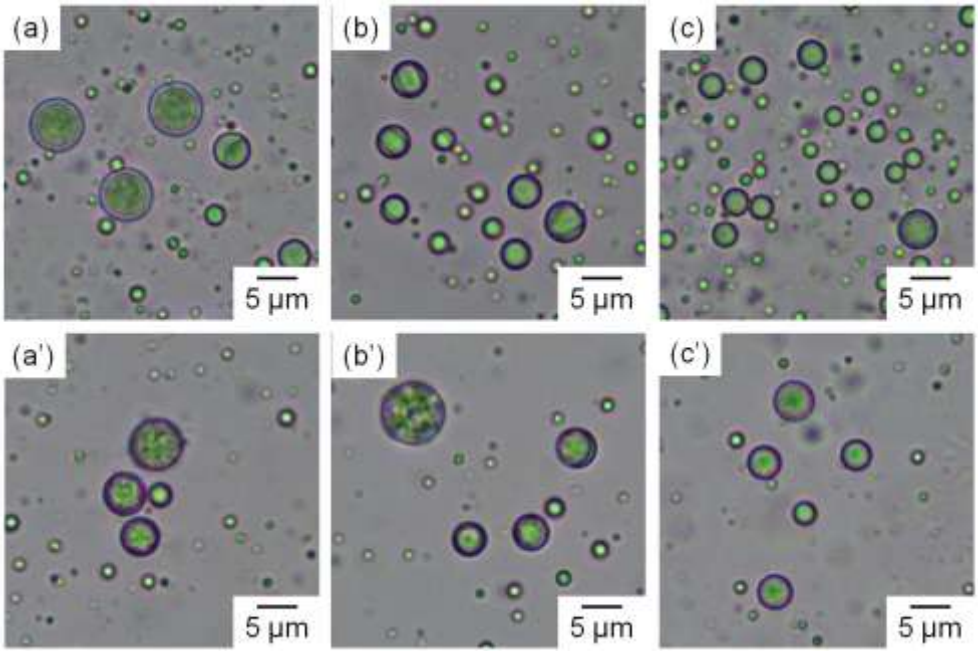


Figure 5. Optical micrographs of P(PhEMA-X) (X; (b, b') VT (15 mol%), (c, c') BMA (10 mol%))/Poly([Vbim][TFSA]) composite particles by suspension polymerization at 30˚C. Observation temperature: (a, b, c) *r.t.*, (a', b', c') after heat treatment at 70˚C for overnight.

While suspension polymerization of [Vbim][TFSA] was proceeded at 70°C, it is possible that PPhEMA phase and poly([Vbim][TFSA]) phase were separated because polymerization temperature was already above LCST on this system. To investigate effect of temperature on the preparation of composite particles, polymerization temperature was changed to 30°C and heat treatment of obtained particles was carried out at 70°C. Although the inner structure of obtained particles was somewhat homogeneous, heat treatment at 70°C for 24 h provided no significant change for morphology of composite particles (Figure 5).

These results indicated that the alkyl chain length of ionic liquid monomer was increased with proceeding polymerization, resulting that it was difficult to observe LCST behavior of PPhEMA/Poly([Vbim][TFSA]) composite particles dispersed in water. The similar phenomenon was reported by Watanabe group, in which LCST of PPhEMA in imidazolium-based ionic liquid was dependent on alkyl chain length.[29]

Effect of structure of ionic liquid monomer

When the alkyl chain length of ionic liquid was short, LCST of PPhEMA in ionic liquid was decreased as reported by Watanabe.[29] To investigate the effect of ionic-liquid-monomer structure, the preparation of composite particles by suspension polymerization was carried out using 1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide ([Veim][TFSA]) as ionic liquid monomer. Before polymerization, the transmittance of [Veim][TFSA] solution dissolved PPhEMA as function of temperature was investigated. The transmittance was decreased drastically around 90°C, which is indicated PPhEMA exhibited LCST behavior in [Veim][TFSA] (Fig. 6).

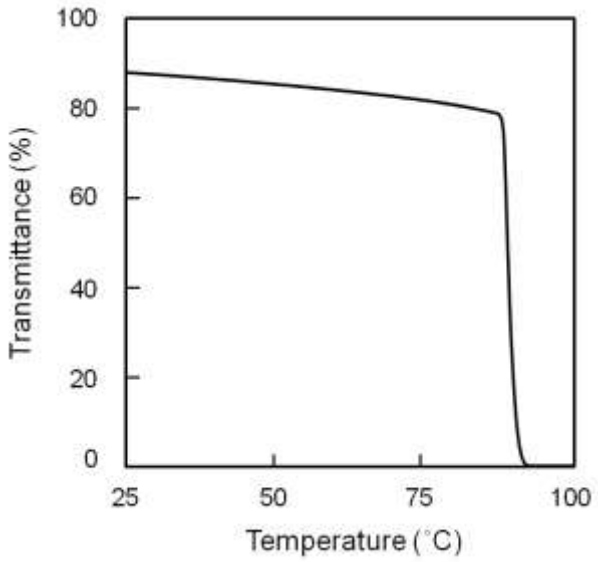


Figure 6. Measurement of transmittance (500 nm) as functions of temperature (0.4 ˚C/min) of PPhEMA/[Veim][TFSA] (w/w = 25/75)

When suspension polymerization of [Veim][TFSA] droplets dissolved PPhEMA (M_n = 35000) was carried out at 30 and 70°C, both of composite particles with homogeneous inner structure were obtained. The inner structure of the composite particles polymerized at 70°C remained even after heat treatment at 150°C. On the other hands, when composite particles prepared by suspension polymerization at 30°C was heat-treated at 70°C for 24 h, phase separation was clearly observed inside composite particles (Fig. 7a, b). Moreover, the inner structure of composite particles became unclear by additional heat treatment at 60°C, which is temperature around Tg of Poly([Veim][TFSA]), for 24 h (Fig. 7c). This result suggested that PPhEMA/Poly([Veim][TFSA] composite particles exhibited the LCST behavior, resulting thermosensitive composite particles were successfully prepared.

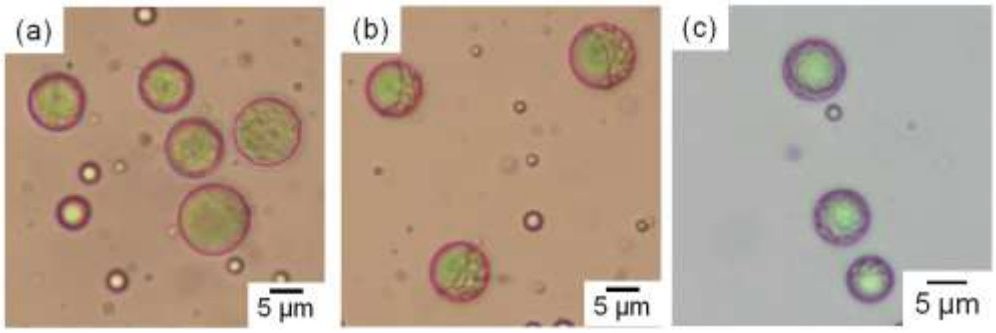


Figure 7. Optical micrographs of PPhEMA/Poly([Veim][TFSA]) composite particles by suspension polymerization at 30˚C (a), after heat treatment at 70˚C for 24 h (b), and after additional heat treatment at 60˚C for 24 h (c).

Effect of PPhEMA molecular weight on LCST behavior of composite particles

When the mobility of polymer chain is increased, LCST behavior of composite particles should be easily observed. The preparation of PPhEMA/Poly([Veim][TFSA]) composite particles was carried out using PPhEMA of various molecular weight (M_n = 10000, 15000, 35000, 80000). Figure 8 shows the optical micrographs of obtained particles before and after heat treatment at 70°C for 24 h. The inner structure of composite particles

obtained after each polymerization had homogeneous. After heat treatment of composite particles using low molecular weight PPhEMA (M_n = 10000, 15000), their inner structure was observed no difference. On the other hands, when using high molecular weight PPhEMA (M_n = 80000), the domains were observed inside composite particles instead of phase-separation between polymer phases. This is really interesting phenomenon and the formation mechanism will be investigated in the future. These results indicated that structure transformation between PPhEMA and Poly([Veim][TFSA]) by heat treatment was depend on molecular weight of PPhEMA.

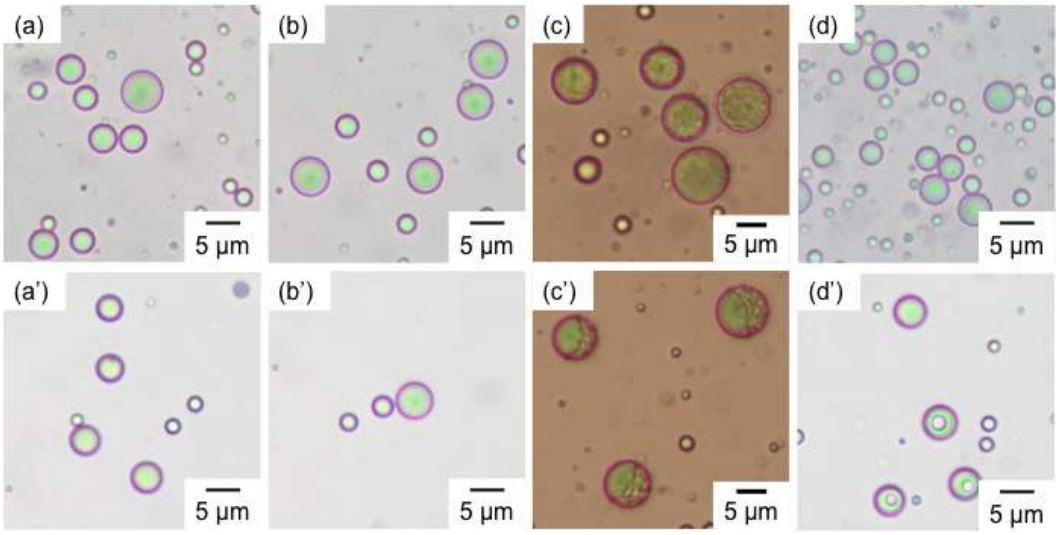


Figure 8. Optical micrographs of PPhEMA/Poly([Veim][TFSA]) composite particles before (a-d) and after (a'-d') heat treatment at 70°C for 24 h. Molecular weight of PPhEMA: (a, a') 10000; (b, b') 15000; (c, c') 35000; (d, d') 80000.

Conclusion

When composite particles were prepared by suspension polymerization using [Vbim][TFSA], the morphologies of obtained particles had phase-separation (at 70°C) and homogeneous (at 30°C), respectively. After heat treatment, both of composite particles had no different structure compared with morphology of composite particles before heat treatment. This is suggested that LCST behavior of PPhEMA/Poly([Vbim][TFSA]) composite particles was not observed. In the case of composite particles with [Veim][TFSA], the obtained particles after suspension polymerization at 30°C had homogeneous morphology. Their inner morphology was phase-separated after heat treatment at 70°C, and then the boundary between PPhEMA and PIL phases was unclear after heat treatment at 60°C. This result indicated that polymer/PIL composite particles with thermosensitive property were successfully prepared. Moreover, the inner structure transformation of PPhEMA/Poly([Veim][TFSA]) composite particles by temperature was depend on molecular weight of PPhEMA.

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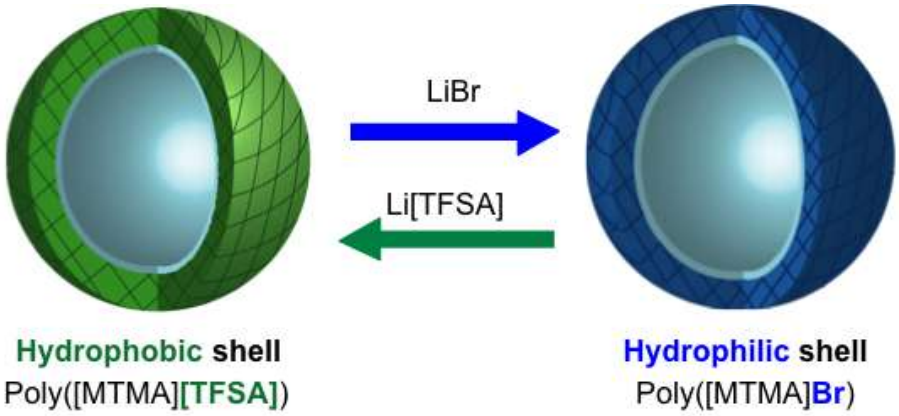
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Chapter 7

Preparation of Poly(ionic liquid) Hollow Particles with Switchable Property by Suspension Polymerization



Abstract: The preparation of micrometer-sized poly(ionic liquid) hollow particles were carried out by suspension polymerization of ionic liquid monomer and cross-linker utilizing the self-assembling of phase-separated polymer (SaPSeP) method. At optimum condition, poly(ionic liquid) hollow particles with smooth surface were successfully prepared. The obtained particles have switchable property between hydrophilic and hydrophobic by anion exchange process. Moreover, the water-soluble fluorescent material was encapsulated inside hollow particles utilizing this property.

Introduction

Polymer particles having hollow structure have been applied in various industrial fields such as cosmetic, catalysis and medical products.[1-4] Such a hollow polymer particles were prepared by various methods such as layer-by-layer assembly, interfacial polymerization on the surface of droplets, and template method.[5-10] Previously, we have reported the synthesis method of hollow polymer particles by suspension polymerization, which is named the Self-assembling of Phase-Separated Polymer (SaPSeP) method.[11,12] Moreover, we have demonstrated this formation mechanism in detail and capsule particles encapsulated various materials were successfully prepared by this method.[13-16] However, the encapsulated materials should be determined before polymerization by SaPSeP method, and it is impossible to replace them to other materials inside capsule particles obtained after polymerization. Whenever the encapsulated materials of capsule particles prepared by SaPSeP method was altered, it has a need for the review of synthesis condition. To solve this problem, it is required that the hollow particles after polymerization can be introduced the objective afterward, which is expected the further application because various materials can be encapsulated in one hollow particles.

Ionic liquids are one of the organic salt, which is defined as molten slats below 100°C. They have various functional properties such as nonflammability, low vapor pressure, ionic conductivity, and CO_2 solubility. Due to these properties, they have been reported many researches on application for synthesis media as well as functional materials.[17-30] We have demonstrated the preparation of poly(ionic liquid) (PIL) particles by dispersion polymerization of ionic liquid monomer [2-(methacryloyloxy)ethyl]trimethylammonium bis(trifluoromethanesulfonyl)amide ([MTMA][TFSA]) in methanol and ethanol with poly(vinylpyrrolidone) (PVP) as a

stabilizer.[31] In this report, PIL particles were dissolved in an ethanolic LiBr solution and then PIL was precipitated by addition of Li[TFSA] in the solution. This phenomenon was happened by anion exchange between PIL and salt anions, which was suggested that the property of PIL could be changed instantaneously between hydrophobic and hydrophilic.

In ***Chapter 7***, preparation of PIL hollow particles having switchable property was demonstrated. Moreover, the reserve and release behavior of water-soluble fluorescent material inside hollow structure were investigated utilizing anion exchange.

Experimental Section

Materials

Ethylene glycol dimethacrylate (EGDM; Nacalai Tesque, Inc., Kyoto, Japan) was washed with an aqueous 1 mol L^{-1} sodium hydroxide solution and then purified water to remove any polymerization inhibitors. *n*-Butyl methacrylate (Nacalai Tesque, Inc., Kyoto, Japan) was purified via distillation under reduced pressure in a N_2 atmosphere. Benzoyl peroxide (BPO; Nacalai Tesque, Inc., Kyoto, Japan) and 2,2'-azobis(isobutylnitrile) (AIBN; Nakalai Tesque Inc., Kyoto, Japan) were purified via recrystallization. Poly(vinyl alcohol) (PVA; Nippon Synthetic Chemical Ind. Co., Ltd., Osaka, Japan; Gohsenol GH-17: degree of polymerization, 1700; degree of saponification, 88%), *n*-butyl acetate, toluene, ethanol, Rhodamine B (Nakalai Tesque Inc., Kyoto, Japan), lithium bromide (LiBr) (99%, Aldrich), [2-(methacryloyloxy)ethyl]trimethylammonium chloride ([MTMA]Cl) solution (80 wt % in water, Aldrich), and lithium bis- (trifluoromethanesulfonyl)amide (Li[TFSA]) (99.7%, Kanto ChemicalCo., Inc.) were used as received. The water used in all the experiments was obtained from an ErixUV (Millipore, Japan) purification system and had a resistivity of 18.2 MΩ cm.

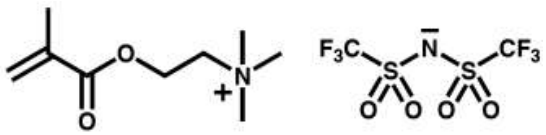
Preparation of Poly(n-butyl methacrylate) (P*n*BMA)

Poly(*n*-butyl methacrylate) (P*n*BMA) was prepared by solution polymerizations as follows. BMA (5 g) was dissolved in toluene (5 g) with AIBN (0.05 mg) as initiator and then solution polymerization was carried out in a sealed glass tube under a N_2 atmosphere at 70 °C for 12 h. The tube was shaken horizontally at 80 cycles/min (3-cm strokes). The obtained solution was purified by reprecipitation into methanol and dried under reduced pressure. The weight (number)-average molecular weight PBMA was 7.4×10^5 (3.3×10^5), measured by

gel permeation chromatography (Tosoh Corp., TSK gel GMHHR-H, 7.8 mm i.d. × 30 cm) with the calibration being obtained using polystyrene standards with tetrahydrofuran as the solvent.

Preparation of Poly(ionic liquid) Hollow Particles

The ionic liquid monomer [MTMA][TFSA] was synthesized by mixing aqueous solutions of [MTMA]Cl and Li[TFSA] as published previously.[31] Homogeneous oil phase consisted of [MTMA][TFSA] (ionic liquid monomer; 0.5-0.99 g), EGDM (cross-linker; 0.5-0.01 g), BPO (initiator; 0.04 g), P*n*BMA (accelerator; 0.01-0.1 mg), and *n*-butyl acetate (1.0 g) and 0.3 wt% PVA aqueous solution (20 g) was homogenized at 2000 rpm for 3 min and then 6000 rpm for 3 min using a NISSEI ABM-2 homogenizer. Suspension polymerizations were carried out at 70 °C for 15 h under a N_2 atmosphere in sealed glass tubes with shaking horizontally at 80 cycles min^{-1} (3 cm strokes). After polymerization, the obtained emulsions were washed with water to remove excess PVA, washed with ethanol to remove *n*-butyl acetate via centrifugation, and then the disperse phase was replaced with water.



[MTMA][TFSA]

Anion Exchange of Poly(ionic liquid) Hollow Particles with LiBr

The ethanol dispersion of poly([MTMA][TFSA]-EGDM) hollow particles (w/w = 7/3) [particles (0.1 g) and ethanol (4 g)] was added to the ethanol solution (20 g) of LiBr (4 g). The mixture was mildly stirred at room temperature for 24 h to change their counter anions from TFSA to Br anions. To remove residual salts, the as-prepared dispersion was washed by centrifugation 10 times with ethanol.

Contact Angle Measurements of Poly(ionic liquid) Films

The contact angle of water on the films was measured using a DropMaster 300 (Kyowa Interface Science, Saitama, Japan) instrument at room temperature. The poly([MTMA][TFSA]-EGDM) film (7/3, w/w) was prepared by bulk polymerization between PTFE sheets at 70 °C for 24 h. To prepare poly([MTMA]Br-EGDM) film, the poly([MTMA][TFSA]-EGDM) film was immersed in high concentration ethanol of LiBr for 24h. After then, the obtained film was washed with ethanol to remove residual salts.

Observation of encapsulation of Rhodamine B into Poly(ionic liquid) Hollow Particles and its Release

The water dispersions of poly([MTMA][TFSA]-EGDM) and poly([MTMA]Br-EGDM) hollow particles (w/w = 7/3) [particles (0.05 g) and water (2 g)] were added to Rhodamine B (Rh.B) aqueous solution (~2.0 $\times 10^{-5}$ mmol L^{-1}). In the system using poly([MTMA]Br-EGDM) hollow particles, the Rh.B aqueous dispersion was added to the aqueous solution (20 g) of Li[TFSA] (4 g). The mixture was mildly stirred at room temperature for 24 h to re-exchange the counter anion from Br to TFSA anions. To remove residual salt, the dispersion was washed by centrifugation 10 times with water. Moreover, Rh. B was released from hollow particles after washing another 10 times with water. To observe Rh.B inside hollow particles, they were observed using a C2si confocal laser scanning microscope (CLSM, Nikon Corp., Tokyo, Japan) with excitation by a He-Ne laser at 543 nm and an emission bandpass of 552−617 nm.

Characterization

The morphology of PIL hollow particles was observed with an optical microscope (ECLIPSE 80i, Nikon Corp., Tokyo, Japan) and scanning electron microscopy (SEM, JSM-6510, JEOL, Tokyo, Japan) studies of the particles coated with platinum. Transmission electron microscopy (TEM, JEM-1230, JEOL, Tokyo, Japan) characterization was performed at 100 kV. To observe the interior morphology of the hollow particles, dry samples were embedded in an epoxy matrix, cured at room temperature overnight, and subsequently microtomed. Qualitative analyses of the products were conducted on a Fourier transform-infrared spectrometer (FT-IR, FT/IR-6200, JASCO, Tokyo, Japan) using the pressed KBr pellet technique.

Results and Discussion

Preparation of hollow PIL particles by suspension polymerization

When suspension polymerization utilizing the SaPSeP method was carried out, toluene has been used as oil phase as reported previously. However, [MTMA][TFSA] was insoluble in toluene. In SaPSeP method, oil phase should be required to dissolve monomer and precipitate polymer. When solubility experiments of [MTMA][TFSA] and poly([MTMA][TFSA]) were performed, n-Butyl acetate is suitable for this system. Suspension polymerization utilizing the SaPSeP method was carried out using [MTMA][TFSA]/EGDM/AIBN/P*n*BMA/ *n*-butyl acetate droplets which is prepared using a homogenizer. Figure 1 shows optical micrographs and SEM photographs of obtained particles after polymerization in various P*n*BMA concentration systems. Below 5 wt% P*n*BMA concentration, the obtained particles have a microporous structure because the phase-separation of polymer (oligomer) inside the oil droplets at early stage of polymerization was delayed and then adsorption of oligomer toward interface between oil and water phases was insufficient. On the other hands, at 10 wt% P*n*BMA concentration, the obtained particles was spherical with smooth surface. In order to observe their inner structure, SEM observation of obtained particles fractured by rubbing with a spatula after drying on an aluminum plate and TEM observation of microtomed sections of obtained particles were performed. As shown in Figure 2, the inner structure of obtained particles has hollow structure, resulting that PIL hollow particles were successfully prepared. Moreover, when conversion was calculated by comparison of the shell thickness of obtained particles with theoretical shell thickness using 15μm-sized hollow PIL particles, experimental value (1.60 μm) was close to theoretical value (1.66 μm), which is indicated that polymerization was complete.

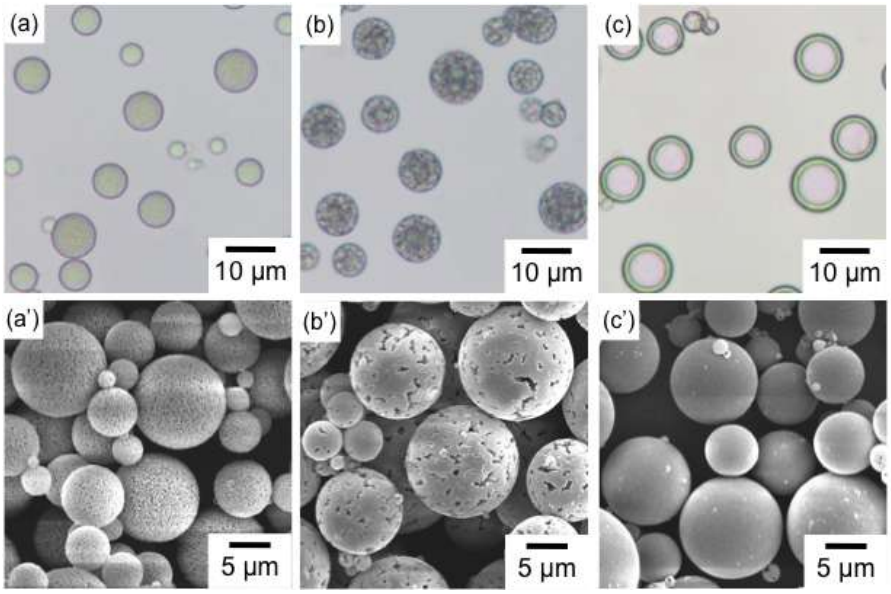


Figure 1. Optical micrographs (a-c) and SEM photographs (a'-c') of obtained particles prepared by suspension polymerizations of droplets for [MTMA][TFSA]/EGDM/PBMA/n-butyl acetate (w/w/w/w, (a, a') 0.5/0.5/0.01/1; (b, b') 0.5/0.5/0.05/1; (c, c') 0.5/0.5/0.1/1) utilizing the SaPSeP method

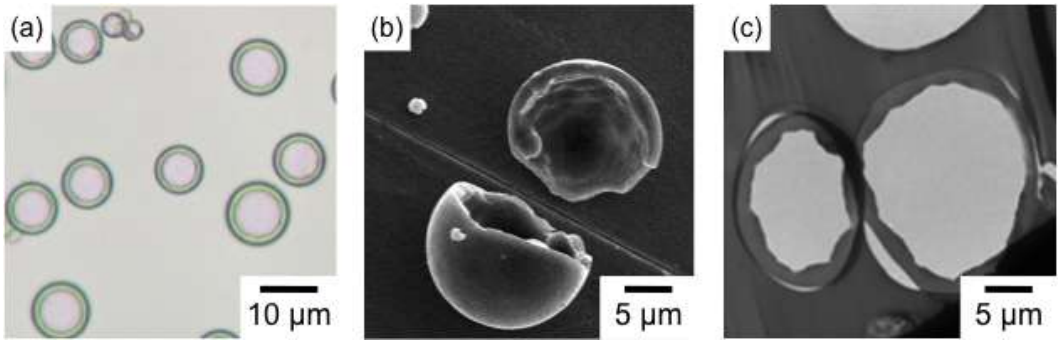


Figure 2. Optical micrograph (a) and SEM photograph (b) of obtained particles prepared by suspension polymerization of [MTMA][TFSA]/EGDM/PBMA/n-butyl acetate (0.5/0.5/0.1/1, w/w/w/w) droplets and TEM photograph (c) of ultrathin cross-sections of the obtained particles

Observation of property transformation of PIL hollow particles by anion exchange

When the property transformation of PIL hollow particles utilizing anion exchange is observed, the phenomenon should be observed dramatically in the case of PIL hollow particles with high PIL composition. Suspension polymerizations utilizing the SaPSeP

method were carried out with various [MTMA][TFSA]/EGDM ratios. In the case of above 80 wt% [MTMA][TFSA] concentrations, the obtained particles have a dent because of low cross-link density (Fig 3c, d). Below 70 wt% [MTMA][TFSA] concentration systems, PIL hollow particles with smooth surface were obtained (Fig. 3a, b).

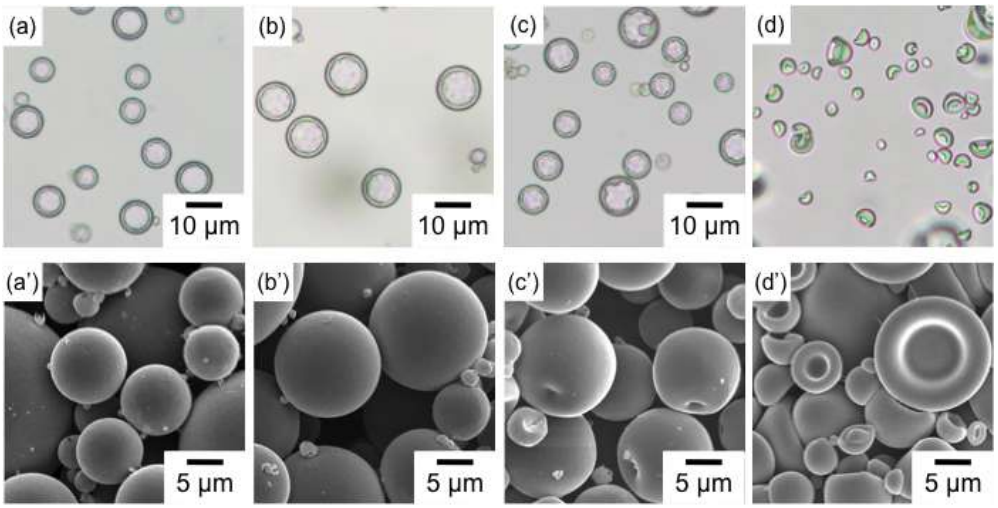


Figure 3. Optical micrographs (a-d) and SEM photographs (a'-d') of obtained particles prepared by suspension polymerizations of droplets for [MTMA][TFSA]/EGDM/PBMA/n-butyl acetate (w/w/w/w, (a, a') 0.6/0.4/0.1/1; (b, b') 0.7/0.3/0.1/1; (c, c') 0.8/0.2/0.1/1; (d, d') 0.99/0.01/0.1/1)

In order to change the property of PIL hollow particles, anion exchange reaction was carried out using PIL hollow particles ([MTMA][TFSA]/EGDM (w/w) = 70/30) in excess amount of LiBr ethanol solution. The obtained particles after anion exchange reaction have maintained hollow structure. Although the difference of morphology such as swelling was not observed because of high cross-link density, FT-IR analysis showed the disappearance of peak attributed to $S(=O)_2$ of [TFSA] by replacement from [TFSA] to Br (Fig. 4). This result suggested the procedure of anion exchange of PIL hollow particles.

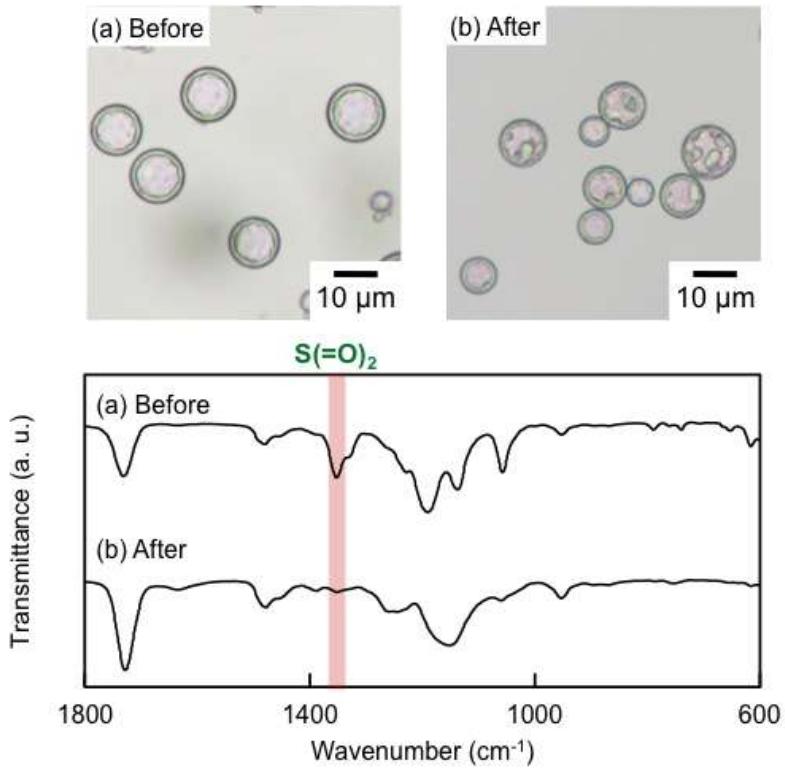


Figure 4. Optical micrographs (above) and FT-IR spectra (below) of hollow Poly([MTMA][TFSA]-EGDM)/PBMA composite particles ([MTMA][TFSA]/EGDM, w/w, 70/30) before (a) and after (b) treatment of LiBr/ethanol

Moreover, in order to investigate the property transformation by anion exchange, contact angle was measured using polymer film with same composition as PIL hollow particles. As shown in Figure 5, contact angle of polymer film before and after anion exchange was 100° and 50°, respectively. This is indicated that the property of PIL hollow particles was varied from hydrophobic to hydrophilic utilizing anion exchange process.

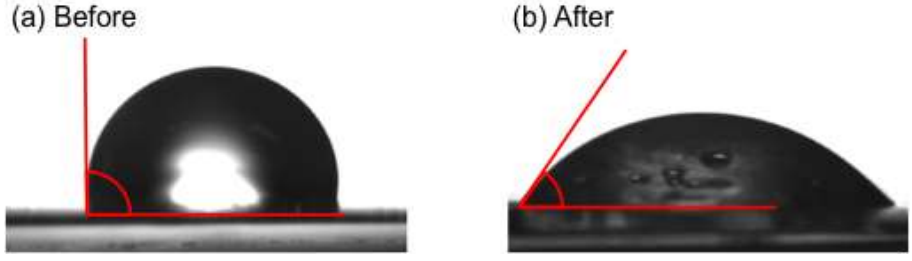


Figure 5. Visual images of the water contact angle on (a) P([MTMA][TFSA]-EGDM) film and (b) P([MTMA]Br-EGDM) film

In order to investigate the difference of penetration behavior of the water–soluble materials into hollow structure of obtained particles, PIL hollow particles before and after anion exchange were added to Rh. B aqueous solution. Figure 6 shows optical and confocal laser scanning micrographs of these particles in Rh. B aqueous solution. The PIL hollow particles having hydrophobic shell were prevented Rh. B from penetrating into hollow structure. On the other hands, Rh. B aqueous solution was penetrated into PIL hollow particles after anion exchange. These results indicated that it is possible for water–soluble material to come into hollow structure of obtained particles after anion exchange.

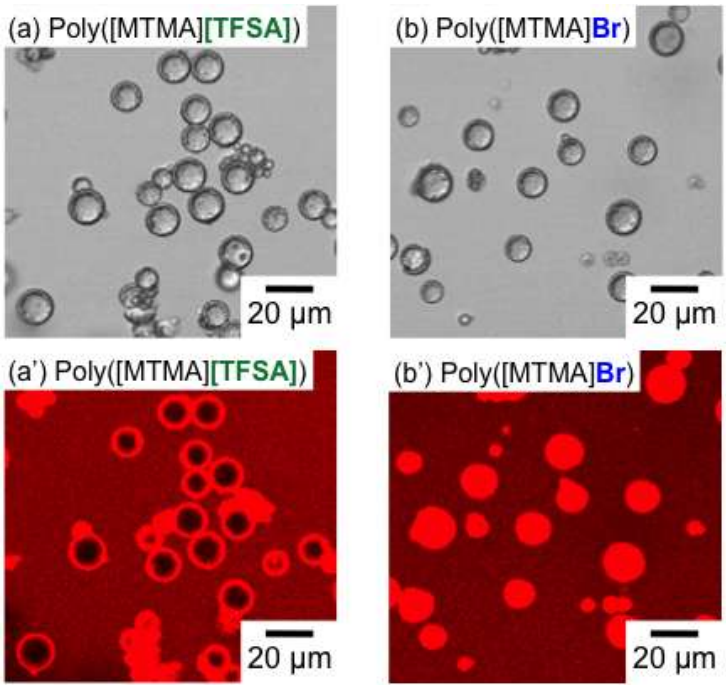


Figure 6. Optical micrographs (a, b) and confocal laser scanning microscopy (CLSM) images (a', b') of hollow P([MTMA][TFSA]-EGDM)/PBMA (a, a') and P([MTMA]Br-EGDM)/PBMA (b, b') composite particles dispersed in RhB aq.

Moreover, anion exchange reaction of hydrophilic PIL hollow particles with Rh. B inside particles was carried out using Li[TFSA] aqueous solution to maintain Rh. B inside PIL hollow particles. When hydrophilic PIL hollow particles with Rh. B inside particles were washed with water, fluorescence intensity of hollow part was decreased because Rh. B

was eluted to water phase, although the shell of PIL hollow particles showed fluorescence because of Rh. B adsorption on the shell. On the other hands, PIL hollow particles, which were returned to hydrophobic by anion exchange, have been retained Rh. B inside the hollow structure and fluorescence intensity has remained. These results suggested that PIL hollow particles could be controlled the release of internal materials.

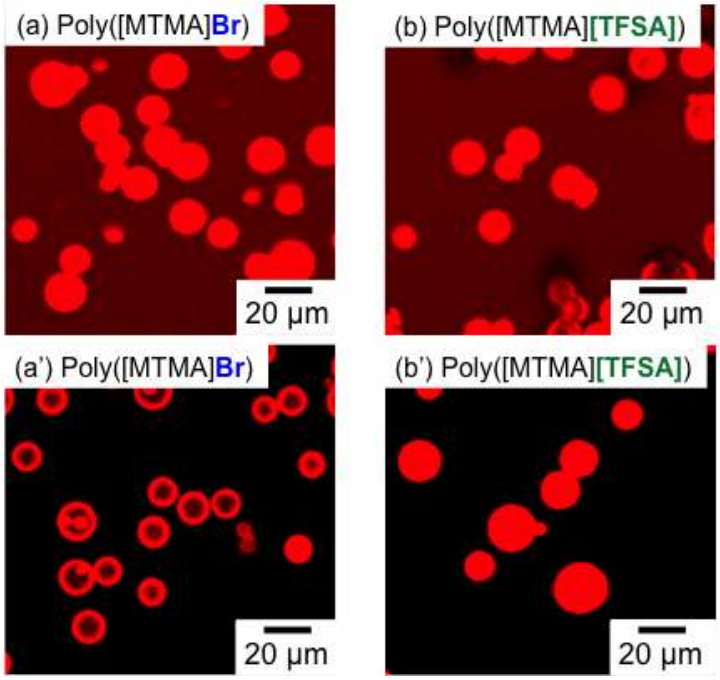


Figure 7. CLSM images of hollow P([MTMA]Br-EGDM)/PBMA (a, a') and P([MTMA][TFSA]-EGDM)/PBMA (b, b') composite particles dispersed in RhB aq. before (a) and after (b) in Li[TFSA] aq. treatment, and the hollow composite particles after washing 10 times with water (a', b')

Next, CLSM observation of hydrophobic and hydrophilic PIL hollow particles in non-aqueous solvent was performed to investigate the factor on penetration behavior of fluorescent materials into hollow structure. Figure 8 shows CLSM images of hydrophobic and hydrophilic PIL hollow particle in various solvents dissolving Nile red as fluorescent material. The penetration of fluorescent materials was occurred in DMSO and acetonitrile using hydrophobic PIL hollow particles. In the case of using hydrophilic PIL hollow

particles, the penetration of fluorescent materials was occurred in ethanol and acetonitrile. These results are indicated that solvent has effect on penetration behavior of fluorescent materials into hollow structure, which was based on solubility of PIL homopolymer in each solvent. In other words, when effective solvent for PIL homopolymer was used, fluorescent material could be penetrated into hollow structure. In ineffective solvent for PIL, polymer shell was prevented fluorescent material from penetrating into hollow structure. Actually, penetration of Nile red was not observed because toluene is ineffective solvent for both polymers (Fig. 8d, d').

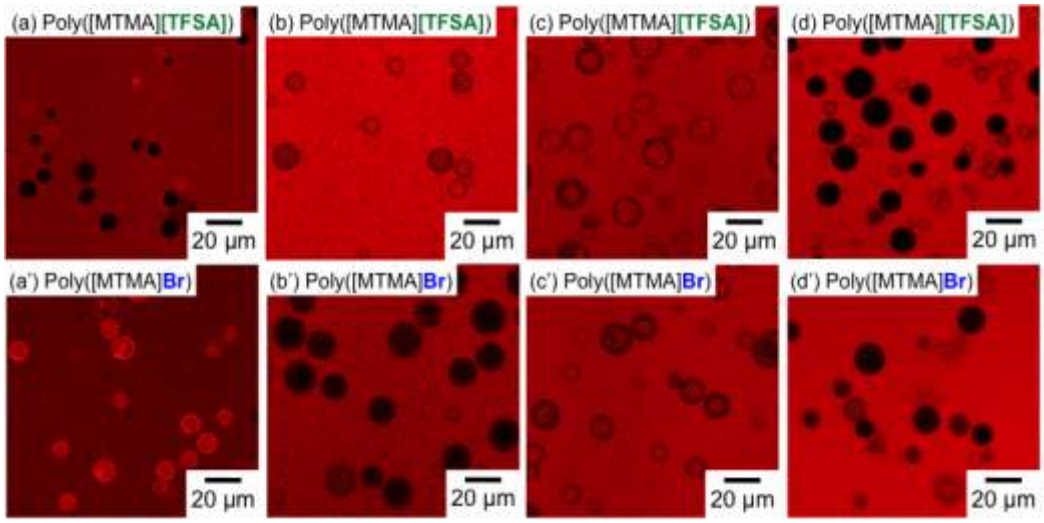


Figure 8. CLSM images of P([MTMA][TFSA]-EGDM)/PBMA (a-d) and P([MTMA]Br-EGDM)/PBMA (a'-d') hollow composite particles dispersed in various solvents dissolving Nile red. Solvents: (a, a') ethanol; (b, b') DMSO; (c, c') acetonitrile; (d, d') toluene.

These results suggested that PIL hollow particles could be control the release behavior of internal materials in water as well as non-aqueous solvent. Such a PIL hollow particles are expected to be applied in various fields because it is possible to encapsulate various materials.

Conclusion

The preparation of hollow particles having PIL shell was succeeded by suspension polymerization utilizing the SaPSeP method. The obtained PIL hollow particles could be altered between hydrophobic and hydrophilic by anion exchange. The water-soluble material was penetrated into hollow structure of hydrophilic PIL hollow particles, and then capsulated in hydrophobic PIL hollow particles obtained by further anion exchange. Moreover, the penetration behavior of materials encapsulated into hollow structure was dependent on dispersive solvent, which was occurred only in effective solvent for PIL. This result indicated the possibility that PIL hollow particles could be controlled the release of internal materials in any solvents.

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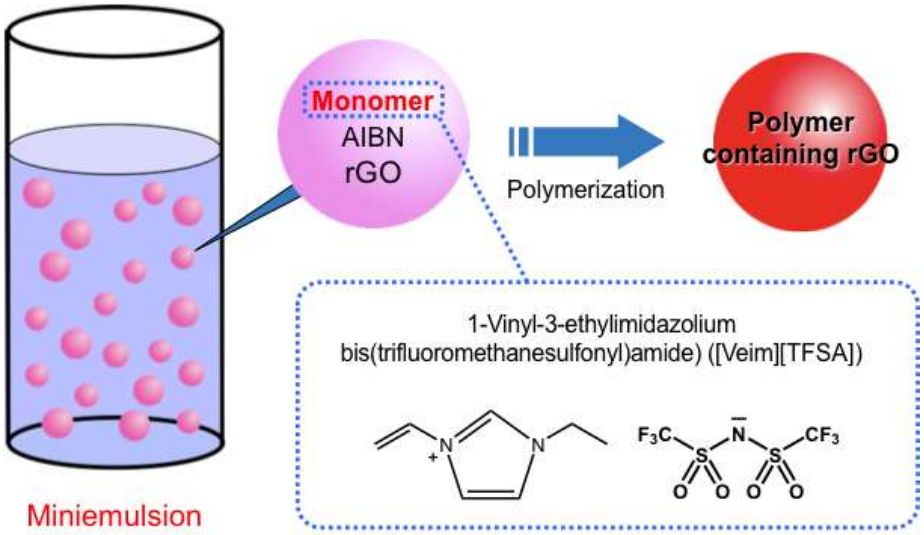
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Chapter 8

Preparation of Polymer Particles Containing Reduced Graphene Oxide using Ionic Liquid Monomer



Abstract: The preparation of polymer particles containing reduced graphene oxide (rGO) was carried out by miniemulsion polymerization using ionic liquid monomer, 1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide ([Veim][TFSA]). The rGO dispersion in [Veim][TFSA] was stable, which was maintained stability in Tween 80 aqueous solution. After miniemulsion polymerization, the stable emulsion was obtained without precipitation of rGO. The diameter of obtained particles was around 400 nm by TEM and DLS measurement. Althuogh rGO was not observed inside and outside particles by TEM, the sample after acetone treatment of emulsion was detected particle size around 30 nm with DLS. This is suggested that the polymer particles containing rGO were successfully prepared.

Introduction

Graphene is an allotrope of carbon and nanosheet with thickness of one carbon atomic layer. It has various remarkable properties, including great conductivity, optical, thermal, and mechanical properties.[1-6] Although graphene has been prepared by various methods such as mechanically exfoliation of graphite[1,7], chemical vapor deposition (CVD) method on copper substrate[8-10], the common synthetic method is reduction of graphene oxide because of high productivity compared to other synthetic methods.[11,12] Graphene and reduced graphene oxide (rGO) have attracted much attention for functional materials in various fields due to these properties.[13-17] Graphene should be dispersed in matrix to utilize them as functional materials. Nevertheless, it is difficult to obtain well-dispersed graphene because of the formation of irreversible aggregation by Van der Waals interactions between the layers. In order to prepare graphene dispersion, various improvement strategies were reported by many researchers. In 2006, the preparation of stable rGO dispersion in water was firstly reported by Ruoff and coworkers, in which the reduction of graphene oxide modified by poly(sodium 4-styrenesulfonate) was carried out.[18] Li and Shi groups have demonstrated that the preparation of rGO dispersion in water by reduction of graphene oxide which was functionalized with pyrenebutyric acid utilizing π-π interaction.[19] The rGO dispersion also has been prepared in different organic solvents in the presence of surfactants and polymer stabilizers.[20,21]

Ionic liquids, which are composed of organic cations and anions, are molten salts at room temperature.[22-24] They have attracted attention to environmental friendly media in various synthesis fields as well as functional materials such as electrolytes, CO_2 separated membrane and dispersant of carbon nanomaterials.[25-34] Zhang and Liu group was demonstrated the stable rGO dispersion in imidazolium-based ionic liquid, which has π-π

interaction between imidazolium rings and graphene sheets, without any dispersants and preparation of polymer/graphene composite using this dispersion.[35] Moreover, the obtained composite polymers have enhanced their mechanical properties. Recently, the utilizing of poly(ionic liquid)s as dispersants of rGO and graphene sheets have also reported by some groups.[36] Suh and coworkers have demonstrated the preparation of graphene sheets modified by poly(ionic liquid) and the graphene sheets have transferred between water phase and oil phase by anion exchange of poly(ionic liquid) with stable dispersibility.[37] Although poly(ionic liquid)/rGO composite materials was prepared as bulk state, there are to date no reports on poly(ionic liquid)/rGO composites in the particles state.

In ***Chapter 8***, miniemulsion polymerization was carried out to prepare poly(ionic liquid)/rGO composite particles.

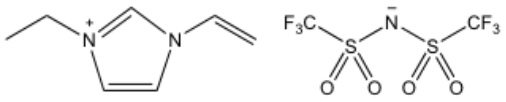
Experimental Section

Materials

Ethyl methacrylate (EMA, 99%, Aldrich) was purified by passing through a column of activated basic aluminium oxide (Ajax) to remove the inhibitor. 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich) was purified by recrystallization in methanol. Hydrazine (Sigma Aldrich), ammonia solution (28wt%), graphene nanofiber (Catalytic Materials Ltd, >98%), HCl (Ajax, 32wt%), H_2SO_4 (Ajax, 98%), H_3PO_4 (BDH Chemical), $KMnO_4$ (Ajax), H_2O_2 (Ajax, 30wt%), 1-ethylbromide, 1-vinylimidazole (Nakalai Tesque Inc., Kyoto, Japan), lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) (99.7%, Kanto Chemical Co., Inc., Japan) were used as received. Deionized water used in all experiments.

Preparation of ionic liquid monomer (1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide: [Veim][TFSA])

A typical synthesis of imidazolium-based ionic liquid monomers was carried out as reported in previous papers.[38] First, [Veim]Br was prepared with 1-ethylbromide and 1-vinylimidazole. 1-Ethylbromide (0.15 mol) was dropped into 1-vinylimidazole (0.13 mol) under vigorous stirring in methanol. The mixture was poured into Schlenk flask, degassed using several vacuum/N_2 cycles, and then reacted in water bath at 40 °C for overnight at 220 rpm. When the obtained solution was dropped into diethyl ether, white-solid material was obtained, and then dried under vacuum. After the obtained [Veim]Br (0.11 mol) was dissolved in water, the aqueous solution of Li[TFSA] (0.12 mol) was added into [Veim]Br aqueous solution under vigorous stirring. After the phase separation gradually occurred, the lower oily layer was collected, washed five times with distilled water and then dried under vacuum. [Veim][TFSA] was obtained as a bit yellow-colored liquid.



[Veim][TFSA]

Figure 1. Structure of ionic liquid monomers

Preparation of GO from graphene nanofiber

GO was prepared by the oxidation of graphite nanofibers as following previous report.[39] Briefly, 2 g of graphite was added to 250 mL of sulfuric and phosphoric acids (v/v=9/1) mixtures and then 12 g $KMnO_4$ was slowly added to the mixture in the ice bath with stirring (The temperature was kept below 10°C). The flask was placed in oil bath at 45°C for 17 h with 400 rpm to oxidize graphene nanofibers. The mixture was poured onto ice (400 g), treated with 15 mL of 30wt% H_2O_2 aqueous solution and then purified by centrifugation (8000 rpm, 8 min) with several washing cycles of 3.4wt% HCl aqueous solution (3 times), acetone (3 times) and diethyl ether (2 times). The isolated material was dried in a vacuum oven and stored in a dessicator until use, and characterized by XPS and FT-IR spectroscopy.

Preparation of reduced graphene oxide (rGO) by chemical reduction

GO dispersion (GO: 100mg, water: 100g) was prepared by ultrasonication (Digital Sonifier, model 450, Branson; 50% amplitude while on ice) for 1 h. 200μL of hydrazine and 400μL of 28wt% ammonium aqueous solution were added to the dispersion, and then chemical reduction was carried out at 95°C for 6 h with 300rpm. rGO powder was obtained after dialysis for 3 days and freeze-dry for 1 day, which was characterized by XPS.

Preparation of polymer particles incorporated rGO by miniemulsuion polymerization

rGO was added to [Veim][TFSA] and EMA mixture (various ratio) and the mixture was ultrasonicated for 5 min to prepare rGO-dispersed monomer. The oil phase dissolved AIBN (1.0g) was mixed with 1wt% Tween 80 aqueous solution (10 g), emulsified using ultrasonication at 50% amplitude for 10 min. The obtained emulsion was subsequently transferred to round-bottom Schlenk flask, sealed off with silicon rubber septum, and purged with nitrogen for 5 minutes. Miniemulsion polymerization was carried out at 60 °C for 24 h with 240 rpm.

Characterization

Hydrodynamic diameter was measured by using a Malvern ZetaSizer Nanoseries with DTS software, operating a 4 mW He–Ne laser at 633 nm at an angle of 173° at 25 °C. Reported values were based on the average of five separate measurements. FTIR spectra were recorded using a Bruker IFS66/S instrument in attenuated total reflectance (ATR) mode, using an average of 64 scans recorded between 500–4000 cm^{-1} at a resolution of 4 cm^{-1}. TEM images were obtained using a JEOL1400 transmission electron microscope at an accelerating voltage of 100 kV. The specimens were prepared by casting a drop of diluted aqueous polymerized miniemulsion onto a Formvar-coated copper grid followed by drying at room temperature. X-Ray Photoelectron spectra (XPS) were recorded using a Kratos Axis ULTRA XPS using monochromatic Al X-rays (1486.6 eV) at 225 W (15 kV, 15 mA). Survey scans were carried out over 1360–0 eV binding energy range with 1 eV steps and a dwell time of 100 ms; high resolution scans were run with 0.2 eV steps and a dwell time of 250 ms. Surface and pore analyses were carried out using Micromeritics TriStar 300 automated gas-sorption system, employing N_2 as the adsorbate, after pretreatment of the sample at 433 K for 8 h.

Results and Discussion

Preparation of GO and rGO

GO sheets were prepared by using a modified Hummer's method. The diameter of obtained GO was approximately 100 nm from DLS result and the XPS spectrum of GO shows that C:O atomic ratio was measured to 1.85:1 (Fig. 2a), which are good consistent with Per group reports.[40] After reduction of GO, the XPS spectrum of obtained materials exhibited strong peak at 284.5 eV (C1s) and weak peak at 530 eV (O2s) (Fig. 2b), and that the C:O atomic ratio was increased to 8.7. Moreover, the two energy peaks, which are attributed to ketone (C=O) groups at 287.3 eV and carboxylic (O-C=O) groups at 289.1 eV, were significantly decreased and the binding energy peak attributed to graphitic regions was increased after reduction (Fig. 3). These results are indicated that the obtained material was reduced graphene oxide (rGO).[12]

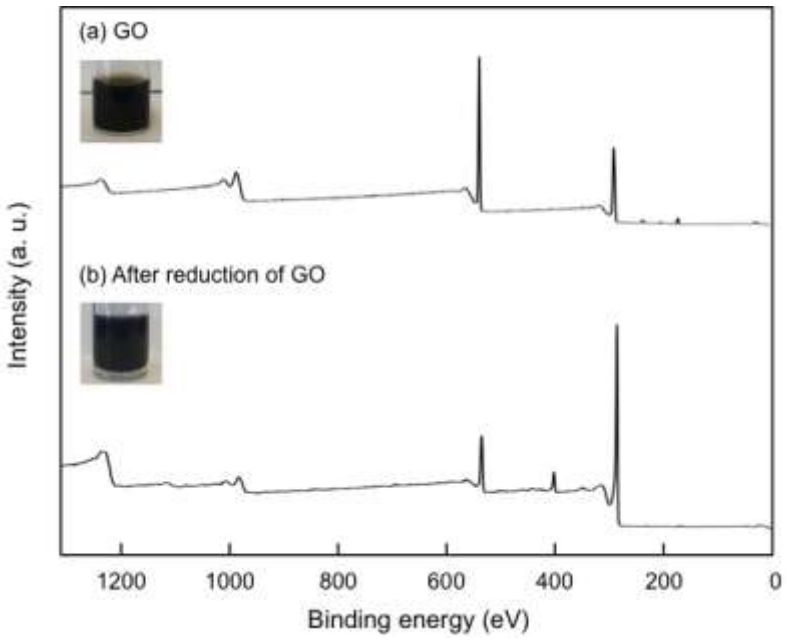


Figure 2. XPS wide scan spectra of GO (a) and obtained materials after reduction of GO (b).

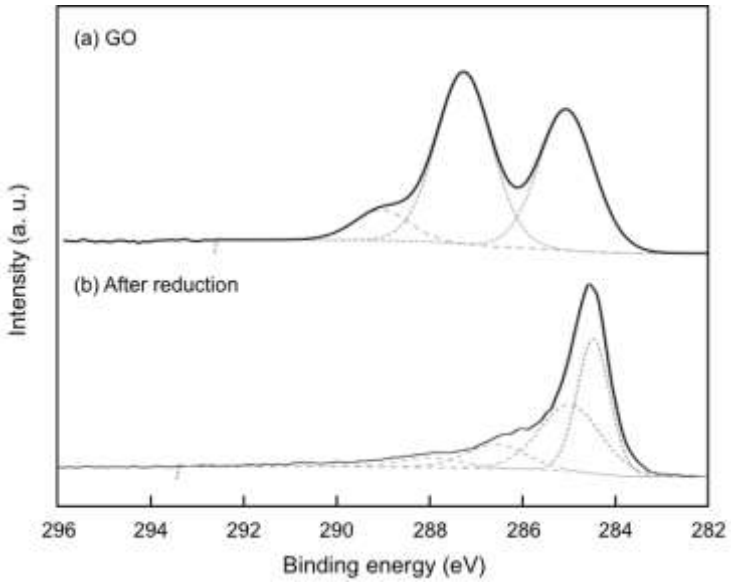


Figure 3. C1s XPS spectra of GO (a) and obtained materials after reduction of GO (b).

Preparation of polymer particles containing rGO using ionic liquid monomer

Before polymerization, the dispersibility of rGO in [Veim][TFSA] was investigated. As shown in Figure 4a, black dispersion was obtained after ultrasonication. The obtained dispersion had good stability without phase-separation in 24 h. In order to confirm the shape and size of rGO, TEM observation was carried out. TEM sample was prepared by acetone treatment on TEM grid where the dispersion was placed, because [Veim][TFSA] is soluble in acetone. As shown in Figure 4b, the diameter of obtained rGO was less than 50 nm. This results indicated that rGO was individually dispersed in [Veim][TFSA] without coaguration.

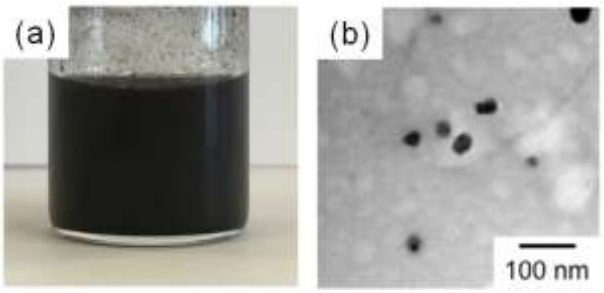


Figure 4. (a) Visual appearances of rGO dispersion in [Veim][TFSA] and (b) TEM photograph of rGO dispersion after acetone treatment on TEM grid

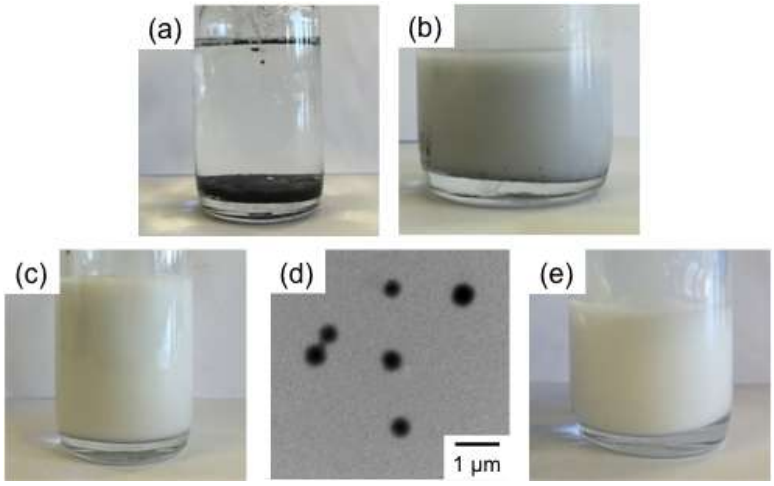


Figure 5. Visual appearances of the synthesis process of polymer particles containing rGO by miniemulsion polymerization: (a) rGO-dispersed [Veim][TFSA] in Tween 80 aq. before and (b) after ultrasonication; (c) obtained emulsion after miniemulsion polymerization and (d) TEM photograph of obtained particles; (e) emulsion prepared by emulsifier-free emulsion polymerization of styrene.

Figure 5 shows the synthesis process of poly([Veim][TFSA])/rGO composite particles. When rGO-dispersed monomer was added to 1 wt% Tween 80 aqueous solution to prepare miniemulsion, the monomer phase lied on lower layer due to high density of ionic liquid, and rGO dispersed in monomer phase maintained their stability. After ultrasonication, a milky-gray emulsion was obtained without rGO precipitation. When miniemuslion polymerization was carried out at 60°C for 24 h, stable emulsion was obtained without any coagulation. The emulsion color after polymerization was grayish compared to emulsion prepared by emulsifier-free emulsion polymerization of styrene. Although the obtained particles were spherical shape as shown in Figure 5d, rGO was not observed inside as well as outside these particles.

In order to investigate where rGO is in emulsion after polymerization, TEM observation was carried out by acetone treatment on TEM grid. It was expected that poly([Veim][TFSA]) was disappeared from TEM grid and rGO remained on TEM grid

because acetone is effective solvent for poly([Veim][TFSA]). However, the dissolving polymer was formed the film on the TEM grid, and the observation was unclear. As another way, DLS measurement was carried out using emulsion after acetone treatment, in which poly(ionic liquid) dissolved and rGO was dispersed in the solvent because poly(ionic liquid) should be interacted with rGO by π-π interaction. When emulsion before acetone treatment was measured with DLS, monomodal distribution consisting of submicrometer size (d_n = 450 nm) was detected, which is consistent with the particle diameter from TEM results. On the other hands, monomodal distribution consisting of nanometer size (d_n = 30 nm) was detected in the sample after acetone treatment. This result is suggested that nanometer-sized materials should be rGO, resulting that the poly(ionic liquid) composite particles containing rGO were successfully prepared.

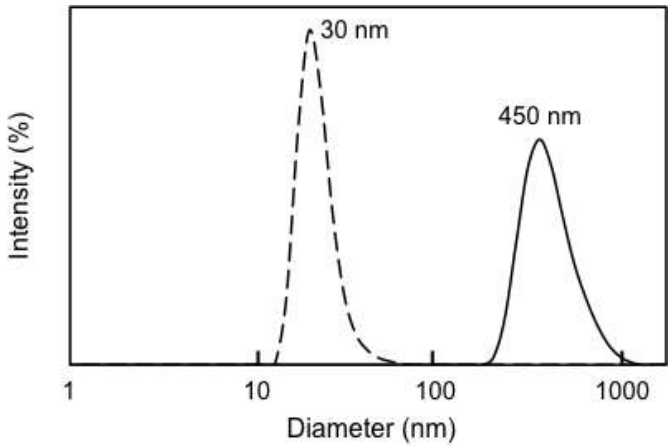


Figure 6. Number distributions of diameter of poly([Veim][TFSA]) particles containing rGO prepared by miniemulsion polymerization (line) and after acetone treatment (dash line), measured with DLS

Effect of [Veim][TFSA] on rGO dispersibility

In order to investigate the effect of ionic liquid monomer on rGO dispersibility, rGO was added to [Veim][TFSA] and EMA mixtures with various ratio, and then their dispersibility test was carried out. As shown in Figure 7, the stable black dispersions were

obtained just after ultrasonication in all systems. After 10 min, the rGO precipitation was observed in less amount of [Veim][TFSA] system. This result is indicated that the stability of rGO dispersion became low with decreasing the ratio of [Veim][TFSA], resulting that [Veim][TFSA] has important effect to stability of rGO.

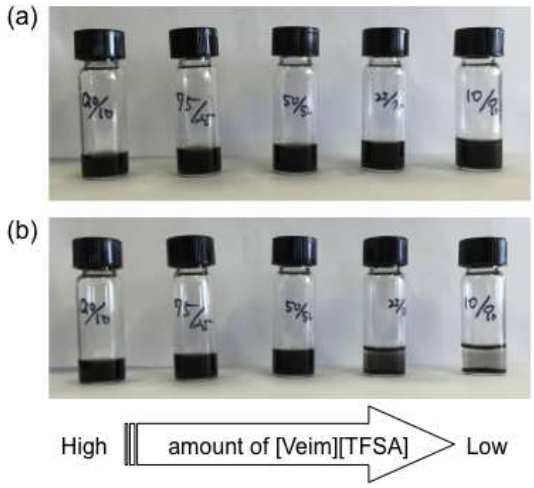


Figure 7. Visual appearances of rGO dispersion in [Veim][TFSA]/EMA mixtures (a) just after ultrasonication and (b) after 10 min

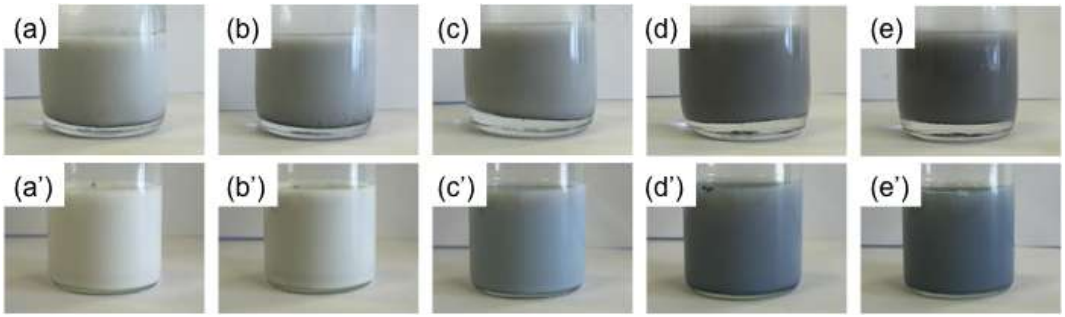


Figure 8. Visual appearances of rGO miniemulsion in [Veim][TFSA]/EMA mixtures before (above) and after polymerization (bottom). [Veim][TFSA]/EMA (w/w): (a, a') 90/10; (b, b') 75/25; (c, c') 50/50; (d, d') 25/75; (e, e') 10/90.

When rGO dispersions in [Veim][TFSA]/EMA mixtures were added to Tween 80 aqueous solution and then ultrasonicated for 5 min, the stable emulsion was obtained without rGO precipitation above high [Veim][TFSA] concentration of 75 wt% system. On the other

hands, it was observed a small amount of rGO precipitation in low [Veim][TFSA] content system (Fig. 8 above). The obtained emulsions color after polymerization were grayish in high ionic liquid monomer content, and dark deep blue in other systems because rGO was dispersed in whole sample. In high ionic liquid monomer contents systems as shown in Figure 9, the obtained particles were spherical shape and the particle size is enough to contain rGO inside the particles. In the other systems, the diameter of obtained particles was less than 50 nm although most of particles were melted by electron beams on TEM observation, which is difficult to contain rGO in the particles and rGO precipitation was occurred after polymerization.

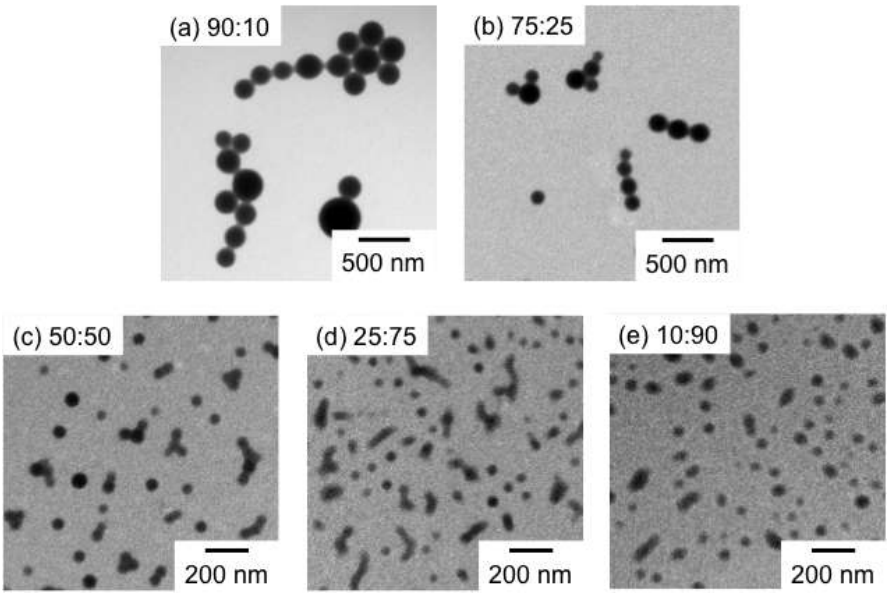


Figure 9. TEM photographs of obtained particles by miniemulsion polymerization of [Veim][TFSA]/EMA mixtures containing rGO. [Veim][TFSA]/EMA (w/w): (a) 90/10, (b) 75/25, (c) 50/50, (d) 25/75, (e) 10/90.

In order to improve the rGO stability in monomer mixtures, the material with functional groups interacted with rGO should be increased in oil phase. When rGO dispersibility test was carried out using monomer mixtures dissolved a tiny amount of

poly([Veim][TFSA]) homopolymer (0.5 and 2.5 wt% relative to monomer), the obtained dispersion after ultrasonication showed high stability (over 24 h) compared to that in the absence of PIL hopololymer (less than 1 h). After miniemulsion polymerization using these dispersions, a small amount of rGO precipitation was observed on the bottom, and the diameter of obtained particles was 80 nm and 60 nm from DLS results, respectively. These results are consistent with TEM observation (Fig. 10), and rGO should be contained inside these particles because the size of rGO was smaller than that of obtained particles.

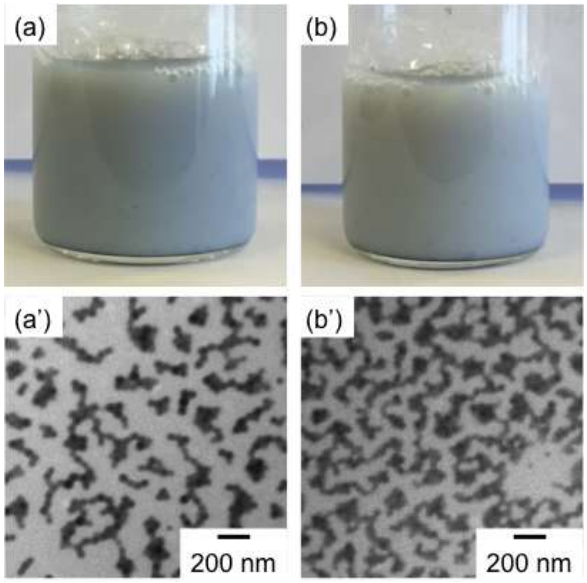


Figure 10. Visual appearances (a, b) of obtained emulsion and TEM photographs (a', b') of obtained particles by miniemulsion polymerization of [Veim][TFSA]/EMA mixtures containing rGO in the presence of poly([Veim][TFSA]) homopolymer. [Veim][TFSA]/EMA/poly([Veim][TFSA]) (w/w/w): (a, a') 1/1/0.01, (b, b') 1/1/0.05.

Conclusion

Ionic liquid monomer ([Veim][TFSA]) could be dispersed rGO without any surfactant and stabilizer, and the obtained dispersion was stable for over 24 h. The rGO in monomer phase was dispersed stably even after addition of the dispersion in Tween 80 aqueous solution, and the miniemulsion obtained after ultrasonication showed long stability. The obtained particles after miniemulsion polymerization were spherical and submicronmeter-sized with a somewhat narrow size distribution. Moreover, rGO was contained inside the particles from DLS measurement. These results are suggested that PIL particles containing rGO were successfully prepared by minemulsion polymerization. In monomer mixture system, the dispersion stability of rGO was dependent on [Veim][TFSA] concentration. The rGO stability was improved by addition of PIL homopolymer in [Veim][TFSA]/EMA mixtures.

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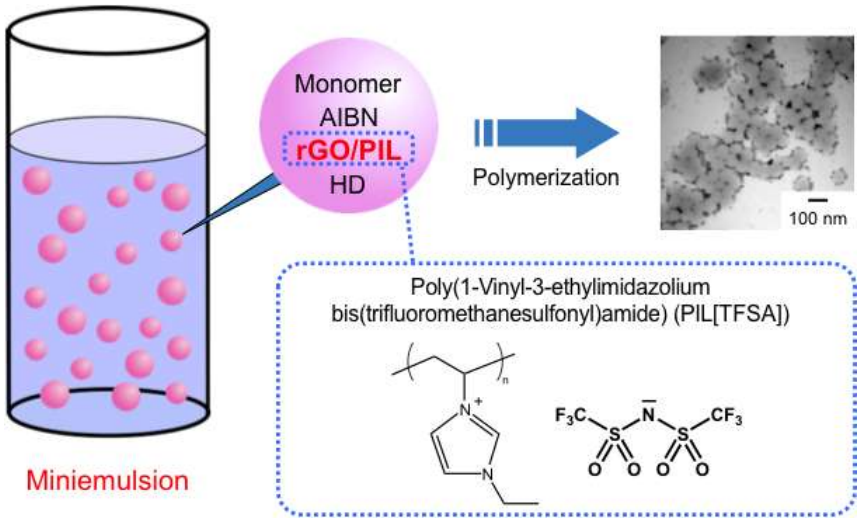
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Chapter 9

Preparation of Polymer/Reduced Graphene Oxide Composite Particles by Miniemulsion Polymerization with Poly(ionic liquid)



Abstract: Before miniemulsion polymerization, the preparation of poly(1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide) (PIL[TFSA])/rGO composite materials were carried out utilizing anion exchange process. PIL[TFSA] appear to behave as dispersant of rGO in conventional monomer. The reduction of GO was carried out in advance because desorption of PIL from GO was occurred during the reduction of GO in PIL solution. The dispersibility of obtained PIL[TFSA]/rGO composite was ineffective in any monomer because PIL[TFSA] was insoluble in monomer. PIL[TFSA]-PMMA copolymer (w/w = 70/30), which was synthesized to improve the solubility of PIL[TFSA] in monomer, was dissolved in ethyl methacrylate (EMA), and rGO was dispersed in EMA/copolymer. When minimeulsion polymerization of rGO-dispersed monomer was carried out, spherical composite particles surrounding by rGO was successfully prepared.

Introduction

Polymer particles have been used as ubiquitous applications such as coatings, adhesives, and films in industrial fields over recent decades.[1,2] Recently, the application of polymer particles have been expected as intelligent materials in sophisticated industry fields, where polymer particles are used as drug transport carrier (drug delivery system) and display material in electronic paper. In order to utilize as polymer particle state, the synthesis of one particulate with multifunctional and highly-functional property is required.

Graphene is one of carbon materials and their structure is atomically thin two-dimensional nanosheet.[3-5] In 2004, Novoselov and Geim groups have firstly reported the preparation and property of graphene, in which graphene was prepared by mechanically exfoliation of graphite.[3] Thereafter, many researchers have reported on the synthesis method and further property of graphene.[6-10] Because graphene possesses various functionalities such as great electrical, optical, thermal, and mechanical properties, they have much attracted attention as functional materials in various fields. However, when graphene is used as filler in materials to enhance their property, it is difficult to obtain well-dispersed graphene in matrix and solvent due to strong Van der Waals interactions between the layers. In order to improve the dispersibility of graphene, chemical modification of graphene and use of surfactant were reported.[11-15] Recently, imidazolium-based ionic liquid and poly(ionic liquid) prepared by polymerization of ionic liquid monomer have attracted attention as dispersant of graphene due to π-π interaction between imidazolium rings and graphene sheets.[16-18] When poly(ionic liquid) is used as dispersant of graphene, graphene dispersion was obtained in various solvent because it is possible to control the solubility of poly(ionic liquid) by anion exchange as reported by Suh and coworkers, in which graphene sheets modified by poly(ionic liquid) have transferred between water phase and oil phase by anion exchange.[18]

In previous work, we demonstrated the preparation of poly(ionic liquid) particles containing rGO by miniemulsion polymerization of rGO-dispersed ionic liquid monomer. However, the use of conventional monomer such as styrene and methyl methacrylate is required in industrial fields. In ***Chapter 9***, rGO dispersion stabilized by poly(ionic liquid) in conventional monomer was prepared. Thereafter, miniemulsion polymerization of obtained rGO-dispersed monomer was performed.

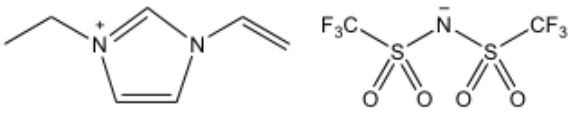
Experimental Section

Materials

Methyl methacrylate (MMA, 99%, Aldrich) and ethyl methacrylate (EMA, 99%, Aldrich) was purified by passing through a column of activated basic aluminium oxide (Ajax) to remove the inhibitor. 2,2′-azobis(isobutyronitrile) (AIBN, Aldrich) was purified by recrystallization in methanol. Hydrazine (Sigma Aldrich), ammonia solution (28wt%), graphene nanofiber (Catalytic Materials Ltd, >98%), HCl (Ajax, 32wt%), H_2SO_4 (Ajax, 98%), H_3PO_4 (BDH Chemical), $KMnO_4$ (Ajax), H_2O_2 (Ajax, 30wt%), 1-ethylbromide, 1-vinylimidazole (Nakalai Tesque Inc., Kyoto, Japan), lithium bis(trifluoromethanesulfonyl)amide (Li[TFSA]) (99.7%, Kanto Chemical Co., Inc., Japan) were used as received. Deionized water used in all experiments.

Preparation of ionic liquid monomer (1-vinyl-3-ethylimidazolium bis(trifluoromethanesulfonyl)amide: [Veim][TFSA])

A typical synthesis of imidazolium-based ionic liquid monomers was carried out as reported in previous papers.[19] First, [Veim]Br was prepared with 1-vinylimidazole and 1-ethylbromide. 1-Ethylbromide (0.15 mol) was dropped into 1-vinylimidazole (0.13 mol) under vigorous stirring in methanol. The mixture was poured into Schlenk flask, degassed using several vacuum/N_2 cycles, and then reacted in water bath at 40 °C for overnight at 220 rpm. When the obtained solution was dropped into diethyl ether, white-solid material was obtained, and then dried under vacuum. After the obtained [Veim]Br (0.11 mol) was dissolved in water, the aqueous solution of Li[TFSA] (0.12 mol) was added into [Veim]Br aqueous solution under vigorous stirring. After the phase separation gradually occurred, the lower oily layer was collected, washed five times with distilled water and then dried under vacuum. [Veim][TFSA] was obtained as a bit yellow-colored liquid.



[Veim][TFSA]

Figure 1. Structure of ionic liquid monomers

Preparation of GO from graphene nanofiber

GO was prepared by the oxidation of graphite nanofibers as following previous report.[20] Briefly, 2 g of graphite was added to 250 mL of sulfuric and phosphoric acids (v/v=9/1) mixtures and then 12 g $KMnO_4$ was slowly added to the mixture in the ice bath with stirring (The temperature was kept below 10°C). The flask was placed in oil bath at 45°C for 17 h with 400 rpm to oxidize graphene nanofibers. The mixture was poured onto ice (400 g), treated with 15 mL of 30wt% H_2O_2 aqueous solution and then purified by centrifugation (8000 rpm, 8 min) with several washing cycles of 3.4wt% HCl aqueous solution (3 times), acetone (3 times) and diethyl ether (2 times). The isolated material was dried in a vacuum oven and stored in a dessicator until use, and characterized by XPS and FT-IR spectroscopy.

Preparation of poly([Veim][TFSA]) (PIL[TFSA]) and reduced graphene oxide (rGO) composite materials

First, PIL[TFSA] solution was prepared by solution polymerization in acetone. [Veim][TFSA] (5.0 g) and AIBN (0.5 g, 10wt% based on monomer) were dissolved in acetone (10 g), transferred to round-bottom Schlenk flask, sealed off with silicon rubber septum, and purged with nitrogen for 5 minutes. Solution polymerization was carried out at 60°C for 24 h. The PIL[TFSA]/rGO and PIL[Br]/rGO composite materials were prepared as following previous report.[18]

Preparation of poly([Veim][TFSA])-co-PMMA copolymer by solution polymerization

[Veim][TFSA] (5.0 g), MMA (0.53 g), and AIBN (0.55 g, 10wt% based on monomer) were dissolved in acetone (10 g), transferred to round-bottom Schlenk flask, sealed off with silicon rubber septum, and purged with nitrogen for 5 minutes. Solution polymerization was carried out at 60°C for 24 h.

Miniemulsuion polymerization of EMA with poly([Veim][TFSA])-co-PMMA and rGO

The copolymer (4.5 mg) and AIBN (40 mg) was dissolved in EMA (1.0 g) at 60°C, and then rGO was added to EMA solution. After ultrasonication at 50% amplitude for 1 min, rGO-dispersed EMA was obtained. The dispersion was added to 1 wt% Tween 80 aqueous solution (15 g), ultrasonicated for 5 min. After that, the obtained emulsion was subsequently transferred to round-bottom Schlenk flask, sealed off with silicon rubber septum, and purged with nitrogen for 5 minutes. Miniemulsion polymerization was carried out at 60 °C for 24 h with 240 rpm.

Characterization

TEM images were obtained using a JEOL1400 transmission electron microscope at an accelerating voltage of 100 kV. The specimens were prepared by casting a drop of diluted aqueous polymerized miniemulsion onto a Formvar-coated copper grid followed by drying at room temperature. X-Ray Photoelectron spectra (XPS) were recorded using a Kratos Axis ULTRA XPS using monochromatic Al X-rays (1486.6 eV) at 225 W (15 kV, 15 mA). Survey scans were carried out over 1360–0 eV binding energy range with 1 eV steps and a dwell time of 100 ms; high resolution scans were run with 0.2 eV steps and a dwell time of 250 ms. Surface and pore analyses were carried out using Micromeritics TriStar 300 automated gas-sorption system, employing N_2 as the adsorbate, after pretreatment of the sample at 433 K for 8 h.

Results and Discussion

Preparation of PIL/rGO composite and solubility experiment

In order to be dispersed PIL/rGO composite in monomer, PIL should be hydrophobic because conventional monomer is hydrophobic. The preparation of PIL[TFSA]/rGO composite was carried out utilizing anion exchange process. When GO was ultrasonicated in PIL[TFSA] acetone solution, the stable brown dispersion was obtained. After addition of LiBr in the dispersion, the brown material was precipitated. To confirm the chemical composition of obtained materials, XPS analysis was performed. As shown in Figure 2, the spectrum exhibited two strong signals corresponding to N and Br, which is indicated PIL[Br]/GO composite materials.

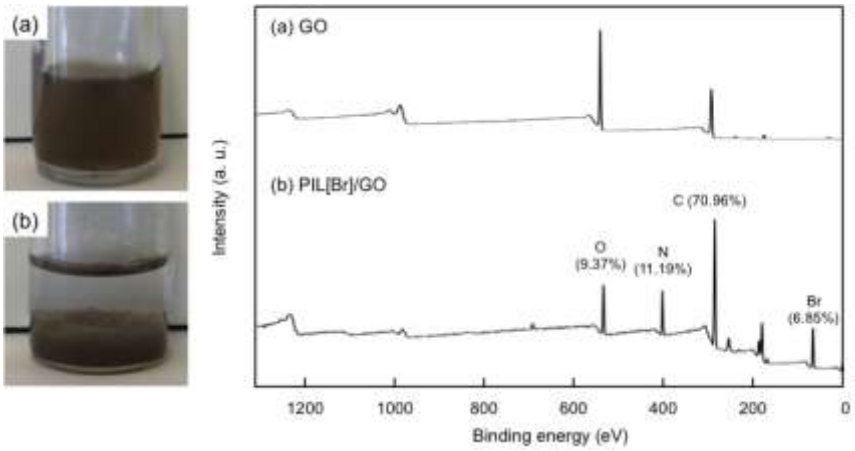


Figure 2. Visual appearances (left) of GO dispersion in PIL[TFSA] acetone solution before (a) and after (b) addition of LiBr. XPS wide scan spectra (right) of GO (a) and PIL[Br]/GO (b).

The PIL[Br]/GO was instantaneously dispersed in water, and then reduction of GO was carried out using ammonium solution and hydrazine monohydrate at 90°C. Figure 3 shows XPS spectra of PIL[Br]/GO before and after reduction. After reduction, the dispersion color was transferred to black, which is indicated that chemical reduction of GO was proceeded. Generally, the peak corresponding to oxygen should be decreased when

rGO was prepared from reduction of GO. In this system, the two kinds of peak corresponding to N and Br were deceased after reduction, which is indicated that the desorption of PIL[Br] from GO surface was occurred because of high temperature.

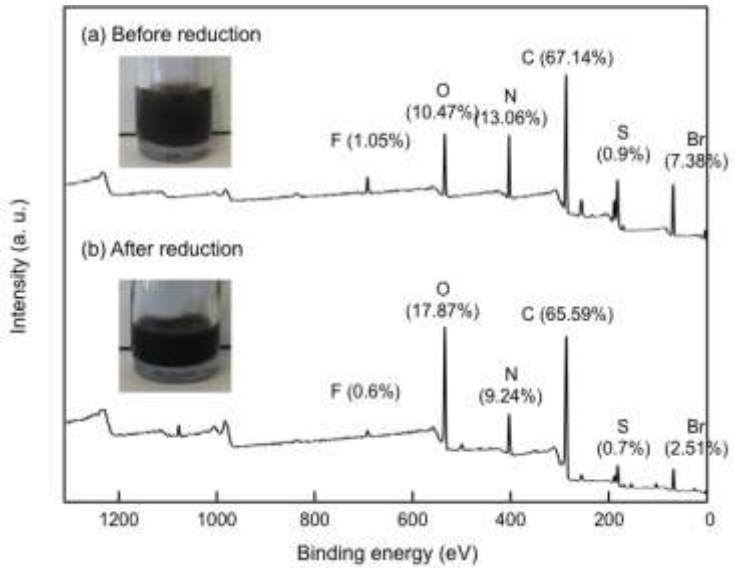


Figure 3. XPS wide scan spectra of PIL[Br]/GO before (a) and after (b) chemical reduction

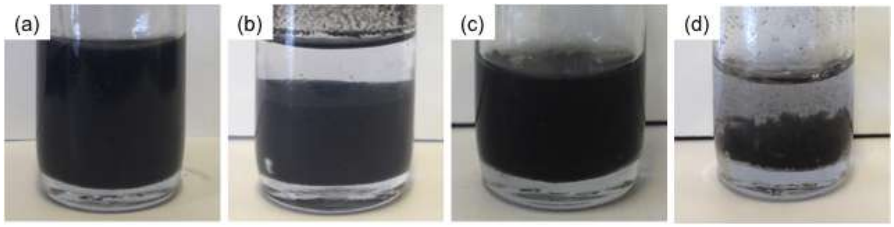


Figure 4. Visual appearances (a-d) of synthesis process of rGO/PIL[TFSA] composite materials utilizing anion exchange

In order to solve this problem, rGO was prepared in advance[21] and then the synthesis of PIL/rGO composite was carried out. Figure 4 shows the visual appearances of synthesis process of PIL[TFSA]/rGO composite materials utilizing anion exchange. rGO was well-dispersed in PIL[TFSA] acetone solution by ultrasonication for 10 min. After addition of LiBr to the dispersion, phase-separation was occurred because PIL[Br] cannot dissolve in acetone. The obtained precipitation could be dispersed instantaneously in water without

ultrasonication. When Li[TFSA] was added to the dispersion, the black precipitation was obtained.

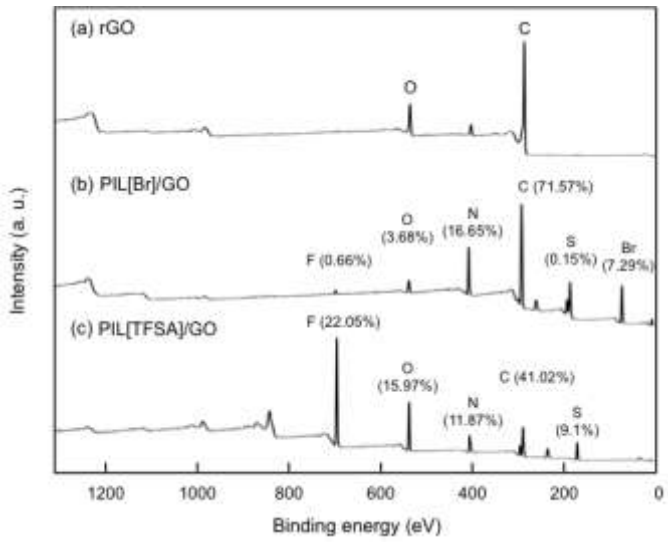


Figure 5. XPS wide scan spectra of rGO (a), PIL[Br]/rGO (b), and PIL[TFSA]/rGO (c)

When the chemical composition of materials obtained in each step was analyzed by XPS, atomic percentage of materials was significantly changed. In 1st step anion exchange process, atomic percentage of nitrogen and bromide was increased. These peaks are corresponding to PIL[Br]. After 2nd step anion exchange process, the signal corresponding to bromide was disappeared and the signals corresponding to fluorine and sulfur were appeared. These results were indicated that anion exchange was proceeded smoothly and the obtained materials were PIL[TFSA]/rGO composite.

Miniemulsion polymerization with PIL/rGO composite

Before polymerization, the dispersibility of PIL[TFSA]/rGO composite in various monomers was investigated. However, PIL[TFSA]/rGO had ineffective dispersibility in most of monomers and was swollen in MMA and EMA, which was consistent with solubility of PIL[TFSA] in any conventional monomers. When the preparation of PIL[TFSA]-PMMA

copolymer and its solubility test in various monomers were carried out in order to improve the solubility of PIL[TFSA], PIL[TFSA]-PMMA copolymer (mol/mol = 70/30) was dissolved in EMA at 60°C. rGO was dispersed in EMA/copolymer for 10 min after ultrasonication, and then miniemulsion polymerization of rGO-dispersed EMA in Tween 80 aqueous solution was carried out. After polymerization, the stable emulsion was obtained with small amount of rGO precipitation. As shown in Figure 6e, the diameter of obtained particles was around 100 nm. Moreover, the strong contrast was observed on the surrounding of particles, which should be rGO which was precipitated from inside particles. This result indicated that spherical composite polymer particles surrounding by rGO were successfully prepared instead of composite polymer particles contained rGO. The emulsion color after polymerization was similar to the sample in [Veim][TFSA]/EMA mixture system ([Veim][TFSA] content: less than 50 wt%) as described in ***Chapter 8***. When the compatibility of copolymer in monomer is improved, it should be possible to prepare composite polymer particles containing rGO using conventional monomer.

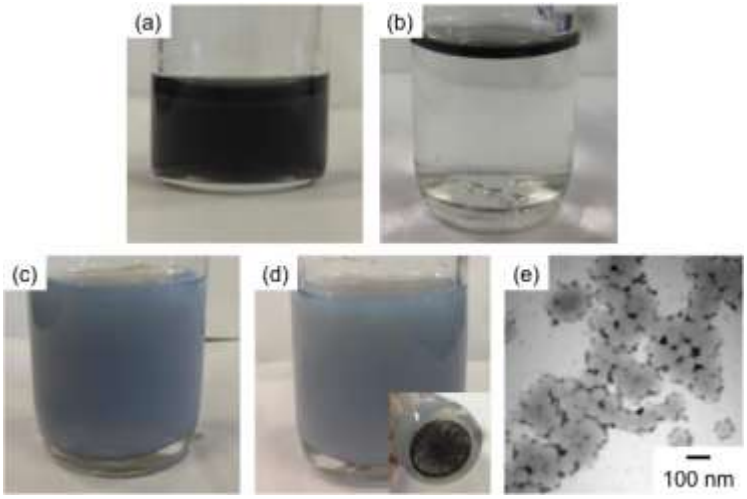


Figure 6. Visual appearances of the synthesis process of polymer particles containing rGO by miniemulsion polymerization: (a) rGO dispersion in EMA/copolymer; (b) rGO-dispersed monomer in Tween 80 aq. before and (c) after ultrasonication; (d) obtained emulsion after miniemulsion polymerization and (e) TEM photograph of obtained particles

Conclusion

PIL[TFSA]/rGO composite materials was successfully prepared utilizing anion exchange process in rGO-dispersed PIL solution. The reduction of GO should be carried out before addition to PIL solution. Otherwise, desorption of PIL from GO was occurred during the reduction of GO. However, PIL[TFSA]/rGO composite was undispersed in any monomers because of ineffective solubility of PIL[TFSA] in conventional monomer. PIL[TFSA]-PMMA copolymer (w/w = 70/30) was prepared to improve the solubility of PIL[TFSA], which was dissolved in EMA. Moreover, miniemulsion polymerization was carried out because rGO was dispersed in EMA/copolymer. The obtained particles were spherical and surrounded by rGO, resulting that the preparation of polymer/rGO composite particles was succeeded.

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Concluding remarks

The preparation of poly(ionic liquid) particles was demonstrated on the basis of fundamental knowledge about synthesis of polymer particles and ionic liquid. Basically, they could be prepared by general technique on synthesis of polymer particle. However, it should be needed some attentions when ionic materials is used.

In **Chapter 1**, poly([MTMA][TFSA]) particles were successfully prepared by dispersion polymerization at 70°C in methanol and methanol/ethanol mixtures. The particle size and distribution could be controlled by change of the PVP concentration and addition of ethanol to the medium. Furthermore, PIL particles exhibited unique properties that could be observed by SEM without coating. Solubility of PIL was easily changed by addition of LiBr and Li[TFSA]. These results suggest that PIL maintains the properties of ionic liquids.

In **Chapter 2**, specific solubility phenomenon by changing counter anion of PIL was investigated in detail. When the PIL particles dissolved in ethanol by an anion exchange mechanism, a specific solubility behavior was observed, in which the domains of the medium were generated inside the PIL particles below a salt concentration of 2.5 wt%. This solubility behavior was dependent on the salt concentration and the driving force was determined to be related to the osmotic pressure inside the PIL particles and outside (the medium).

In **Chapter 3**, preparation of poly(ionic liquid) particles was carried out by emulsion polymerization. When emulsion polymerization of [MTMA][TFSA] was conducted using ionic initiators and emulsifiers such as KPS and SDS, respectively, a stable emulsion was not obtained, and nearly all the polymer was aggregated. This result was due to anion exchange of the ionic liquid monomer with the ionic emulsifier, leading to reduced effectiveness of the

surfactant. When a nonionic initiator and emulsifier were used, submicron-sized PIL particles were successfully prepared without coagulation for the first time, and the zeta potential of the obtained particles had a high positive charge. Utilizing this surface charge, PIL particles were successfully prepared via emulsifier-free emulsion polymerization under a CO_2 atmosphere without using an ionic material. Moreover, the surface of the PIL emulsion film was relatively hydrophobic as determined by measurement of the water contact angle in the dried state. On the other hand, according to the measured retreating water contact angle, the same PIL film exhibited water wettability. Interestingly, when water was dropped on the PIL film after water on the surface had retreated completely, the PIL film was once again hydrophobic. This result suggests that surface properties of the PIL emulsion film readily switched between hydrophobic (in air) and hydrophilic (in water).

In **Chapter 4**, seeded dispersion polymerization was performed by using [MTMA][TFSA] with PS and PMMA seed particles. In the case of seeded dispersion polymerization [MTMA][TFSA] of with PS seed particles, the secondary nucleated PIL particles were observed and composite particles were not obtained. By using spreading coefficients calculated from the interfacial tensions, it was found that a thermodynamically stable morphology of the obtained particles was formation of individual particles. This result was caused by low polarity of PS. On the other hand, in the case of PMMA seed particles with a higher polarity than PS particles, composite particles having the sea-island structure were successfully prepared. Moreover, we successfully prepared PMMA/PIL composite particles having a core-shell morphology with a PMMA core and PIL shell by seeded dispersion polymerization in semi-batch system.

In **Chapter 5**, seeded dispersion polymerization of ionic liquid monomer [MTMA][TFSA] in methanol/water mixtures with PMMA and PEMA seed particles led to the formation of polymer/PIL composite particles. On the other hand, in the case of P*t*BMA seed particles, the secondary nucleation of the PIL particles was occurred and no composite particles were obtained. We also successfully prepared core–shell PMMA/PIL composite particles with a PMMA core and a PIL shell by seeded polymerization in water media. These results suggested that the polarity of seed polymer and solvent had influence on the formation of PIL composite particles. Moreover, the functional property such as magnetism was successfully modified by anion exchange with PIL/P(MMA-EGDM) core-shell composite particles prepared by seeded dispersion copolymerization of MMA and EGDM in ethanol using PIL seed particles.

In **Chapter 6**, the preparation of thermosensitive composite polymer particles composed of poly(ionic liquid) and PPhEMA was carried out. When composite particles were prepared by suspension polymerization using [Vbim][TFSA], the morphologies of obtained particles had phase-separation (at 70°C) and homogeneous (at 30°C), respectively. After heat treatment, both of composite particles had no different structure compared with morphology of composite particles before heat treatment. This is suggested that LCST behavior of PPhEMA/Poly([Vbim][TFSA]) composite particles was not observed. In the case of composite particles with [Veim][TFSA], the obtained particles after suspension polymerization at 30°C had homogeneous morphology. Their inner morphology was phase-separated after heat treatment at 70°C, and then the boundary between PPhEMA and PIL phases was unclear after heat treatment at 60°C. This result indicated that polymer/PIL composite particles with thermosensitive property were successfully prepared. Moreover,

the inner structure transformation of PPhEMA/Poly([Veim][TFSA]) composite particles by temperature was depend on molecular weight of PPhEMA.

In **Chapter 7**, preparation of hollow particles having PIL shell was succeeded by suspension polymerization utilizing the SaPSeP method. The obtained PIL hollow particles could be altered between hydrophobic and hydrophilic by anion exchange. The water-soluble material was penetrated into hollow structure of hydrophilic PIL hollow particles, and then capsulated in hydrophobic PIL hollow particles obtained by further anion exchange. Moreover, the penetration behavior of materials encapsulated into hollow structure was dependent on dispersive solvent, which was occurred only in effective solvent for PIL. This result indicated the possibility that PIL hollow particles could be controlled the release of internal materials in any solvents.

In **Chapter 8**, miniemulsion polymerization was performed to prepare polymer particles containing rGO. [Veim][TFSA] could be dispersed rGO without any surfactant and stabilizer, and the obtained dispersion was stable for over 24 h. The rGO in monomer phase was dispersed stably even after addition of the dispersion in Tween 80 aqueous solution, and the miniemulsion obtained after ultrasonication showed long stability. The obtained particles after miniemulsion polymerization were spherical and submicronmeter-sized with a somewhat narrow size distribution. Moreover, rGO was contained inside the particles from DLS measurement. These results are suggested that PIL particles containing rGO were successfully prepared by minemulsion polymerization. In monomer mixture system, the dispersion stability of rGO was dependent on [Veim][TFSA] concentration. The rGO stability was improved by addition of PIL homopolymer in [Veim][TFSA]/EMA mixtures.

In **Chapter 9**, PIL[TFSA]/rGO composite materials was successfully prepared utilizing anion exchange process in rGO-dispersed PIL solution. The reduction of GO should be carried out before addition to PIL solution. Otherwise, desorption of PIL from GO was occurred during the reduction of GO. However, PIL[TFSA]/rGO composite was undispersed in any monomers because of ineffective solubility of PIL[TFSA] in conventional monomer. PIL[TFSA]-PMMA copolymer (w/w = 70/30) was prepared to improve the solubility of PIL[TFSA], which was dissolved in EMA. Moreover, miniemulsion polymerization was carried out because rGO was dispersed in EMA/copolymer. The obtained particles were spherical and surrounded by rGO, resulting that the preparation of polymer/rGO composite particles was succeeded.

The basic and important knowledge on synthesis of poly(ionic liquid) particles should be mentioned in this dissertation. The research field on poly(ionic liquid) is still initial stage and has many things we don't understand. It has a high expectation of the further development on this field by more work.

Publication List

Chapter 1

"Preparation of Micronsized Monodisperse Poly(ionic liquid) Particles"

M. Tokuda, H. Minami, Y. Mizuta, T. Yamagami

Macromol. Rapid Commun., **33**, 1130 (2012)

Chapter 2

"Specific Solubility Behavior of Quaternary Ammonium-based Poly(Ionic Liquid) Particles by Changing the Counter Anion"

M. Tokuda, H. Minami

J. Colloid Inter. Sci., **398**, 120 (2013)

Chapter 3

"Preparation of Submicron-sized Quaternary Ammonium-based Poly(ionic liquid) Particles via Emulsion Polymerization and Switchable Responsiveness of an Emulsion Film"

M. Tokuda, T. Sanada, T. Shindo, T. Suzuki, H. Minami

Langmuir, **30**, 3406 (2014)

Chapter 4

"Preparation of Polymer/Poly(ionic liquid) Composite Particles by Seeded Dispersion Polymerization"

M. Tokuda, T. Shindo, H. Minami

Langmuir, **29**, 11284 (2013)

Chapter 5

"Effect of Polarity of Seed polymer and Solvent on the Preparation of Poly(ionic liquid) Composite Particles and Property Modification Utilizing Anion Exchange"

M. Tokuda, T. Shindo, T. Suzuki, H. Minami

In preparation

Chapter 6

"Preparation of Poly(phenylethylmethacrylate)/Imidazolium-based Poly(ionic liquid) Composite Particles having Thermosensitive Property"

M. Tokuda, T. Suzuki, H. Minami

In preparation

Chapter 7

"Preparation of Poly(ionic liquid) Hollow Particles with Switchable Property by Suspension Polymerization"

M. Tokuda, R. Nakamura, T. Suzuki, H. Minami

In preparation

Chapter 8

"Preparation of Polymer Particles Containing Reduced Graphene Oxide by Miniemulsion Polymerization using Ionic Liquid Monomer"

M. Tokuda, S. C. Thickett, H. Minami, P. B. Zetterlund

In preparation

Chapter 9

"Preparation of Polymer/Reduced Graphene Oxide Composite Particles by Miniemulsion Polymerization with Poly(ionic liquid)"

M. Tokuda, S. C. Thickett, H. Minami, P. B. Zetterlund

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