DOI: 10.1002/masy.200950707

Preparation of Composite Polymer Particles by Seeded Dispersion Polymerization in Ionic Liquids

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Summary: Submicron-sized monodisperse PS particles were prepared by dispersion polymerization of styrene in ionic liquids with poly(vinylpyrrolidone) as stabilizer. Seeded dispersion polymerization of MMA was subsequently carried out with PS seeds in [Bmim][BF_4] to prepare PS/PMMA composite particles. Observation of the obtained particles of ultrathin cross-sections with a scanning and transmission electron microscope revealed that no secondary nucleation occurred during the seeded dispersion polymerization and that the particles have a core-shell morphology consisting of a PS core and a PMMA shell. Successful preparation of PS/PMMA composite particles in an ionic liquid has thus been demonstrated. Moreover, PS/PAA (PS-core/PAA-shell) composite particles were prepared by seeded dispersion polymerization in [DEME][TFSI], illustrating that hydrophobic/hydrophilic composite particles can be readily prepared in the ionic liquid.

Keywords: composite polymer particle; dispersion polymerization; ionic liquid; radical polymerisation

Introduction

Ionic liquids, which are salts that melt at ambient temperature, are considered environmentally friendly solvents due to their low vapor pressures, chemical and thermal stability, and non-flammability.[1] In the field of polymer chemistry, application of ionic liquids as solvents for polymerization processes is gradually receiving increased attention to replace conventional organic solvents.[2–10] It has been reported that radical polymerization in ionic liquids provided higher polymerization rates and higher molecular weights than in the bulk or organic solvents (homogeneous systems) due to a reduced termination rate because of high viscosity of the ionic liquids,[11–15] and also as a result of an increase in the propagation rate coefficients in some cases.[12] A number of studies on heterogeneous systems in ionic liquids have also been reported. Conducting polymer (polypyrrole nanoparticles) were synthesized by chemical oxidative polymerization in an ionic liquid.[16] Anodic oxidation electropolymerization of 3,4-ethylenedioxythiophene was carried out in ionic liquid microemulsions.[17] Poly(para-phenylenevinylene) particles were prepared by evaporation of water from the solution containinng polymer and an ionic liquid as a poor solvent.[10] Colloidal stability of bare and poly(methyl methacrylate)-grafted silica nanoparticles in an ionic liquid was also studied from both experimental and theoretical viewpoints.[18] Moreover, in order to avoid the use of organic volatile compounds, living cationic ring opening polymerization of 2-ethyl-2-oxazoline was carried out in an ionic liquid by microwave irradiation.[19]

Recently we succeeded in preparing polystyrene (PS) particles by dispersion polymerization in an ionic liquid, diethyl(2-methoxyethyl)methylammonium bis(trifluoromethanesulfonyl)imide ([DEME][TFSI])

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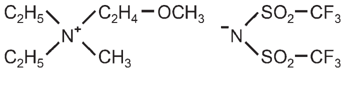
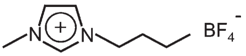
with a radical initiator at 70 °C, for the first time.[20] The particle size and its distribution in ionic liquids could be controlled in a manner similar to that in organic solvents. Moreover, we succeeded in producing PS particles by thermal polymerization in the absence of a radical initiator at 130 °C in [DEME][TFSI] using a conventional reactor (not autoclave) utilizing the advantages of non-volatility and thermal stability of the ionic liquid.

The polarity and solvent power of ionic liquids, which can be easily tuned by changing the counter-anions, are quite different from water and organic solvents. It is possible to prepare novel types of composite polymer particles (such as hydrophilic and hydrophobic composite polymer particles) in ionic liquids because the polarity of the medium can strongly affect the morphology. Moreover, it is possible to prepare composite particles that require high polymerization temperature. We are interested in preparation of novel functional composite polymer particles in ionic liquid, and to compare the results with previous work on the preparation of functional composite polymer particles in water and organic solvents.

In this study, PS/poly(methyl methacrylate) (PMMA) and PS/poly(acrylic acid) (PAA) composite particles were prepared by seeded dispersion polymerizations of MMA and AA, respectively, in ionic liquids using PS seed particles.



[DEME][TFSI]



[Bmim][BF$_4$]

Experimental Part

Materials

Styrene, isobutyl methacrylate (*i*BMA), methyl methacrylate (MMA), methyl acrylate (MA), 2-hydroxyethyl methacrylate (HEMA), acrylonitrile (AN), methacrylic acid (MAA) and acrylic acid (AA) were purified by distillation under reduced pressure in nitrogen atmosphere. Reagent-grade 2.2′-azobis(4-methoxy-2,4-dimethylpentanenitrile) (V-70), 2.2′-azobis(isobutyronitrile) (AIBN) and 1.1′-azobis(cyclohexane-1-carbonitrile) (V-40) were purified by recrystallization from methanol. Poly (vinylpyrrolidone) (PVP, K-30, weight-average molecular weight 3.6×10^5) was used as received. The ionic liquids, diethyl(2-methoxyethyl)methylammonium bis(trifluoromethanesulfonyl)imide ([DEME][TFSI], provided by Nisshinbo Industries Inc., Tokyo, Japan) and 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$], Nacalai Tesque Inc., Kyoto, Japan, purity of 97% or more) were used as received.

(Seeded) Dispersion Polymerizations in Ionic Liquids

Dispersion polymerizations of styrene (0.25 g) in 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF$_4$]) or [DEME][TFSI] (2.5 g) were carried out in glass vessels at 70 °C for 24 h with magnetic stirring at 400 rpm. V-40 (in [Bmim][BF$_4$], 3.7 mg) or AIBN (in [DEME][TFSI], 2.5 mg) and PVP (12.5 mg) were used as initiator and colloidal stabilizer, respectively.

Seeded dispersion polymerizations of MMA and AA were carried out with PS seeds in [Bmim][BF$_4$] or [DEME][TFSI] at 35 and 70 °C (PS/MMA and PS/AA, 1/0.5, w/w) with V-70 (2.4 mg) and AIBN (0.6 mg) as initiators, respectively.

Particle Observation

Particles were observed by scanning electron microscopy (SEM, S-2460, Hitachi Science Systems Ltd., Ibaraki, Japan) after centrifugal washing three times with methanol, which is miscible with the ionic liquids. The number-average diameter (D_n) and coefficient of variation (C_v) were determined by a transmission electron microscopy (TEM, JEM-1230, JEOL Ltd., Tokyo, Japan) using Macintosh computer image software (MacSCOPE, Mitani Co. Ltd., Fukui Japan). Cross-sections were prepared as follows: The dried polymer particles were stained with RuO_4 vapor at room temperature for 30 min in the presence of 1% RuO4 solution, then dispersed in an epoxy matrix, cured at room temperature for 24 h, and microtomed.

Characterization

Monomer conversions were measured gravimetrically. Molecular weights (MW) and molecular weight distributions (MWD) were obtained by gel permeation chromatography (GPC) using two poly(styrene-divinylbenzene) gel columns (Tosoh Corporation, TSK gel GMHHR-H 7.8 mm i.d. × 30 cm) with THF as eluent at a flow rate of 1.0 mL/min employing refractive index (RI) detection (Tosoh). The columns were calibrated with six linear PS samples (1.05×10^3–5.48×10^6, $M_w/M_n = 1.01$–1.15).

The weight ratios of PS/PMMA in the composite particles were determined by ^1H NMR. The ^1H NMR measurements were carried out with a Bruker Avance 500 MHz spectrometer at room temperature in $CDCl_3$.

Results and Discussion

Influence of the Ionic Liquid

In a dispersion polymerization, the monomer, initiator, and colloidal stabilizer are soluble in the medium, but the obtained polymer is insoluble. The solubilities of monomer and polymer are important for dispersion polymerization in ionic liquids. Many vinyl monomers are soluble in ionic liquids, but the solubility of polymer in ionic liquids is complex and cannot be readily predicted.[21] In order to investigate the suitability of various monomer/polymer/ionic liquid combinations, preliminary solution/precipitation polymerizations using the ionic liquids $[Bmim][BF_4]$ and [DEME][TFSI] were conducted to estimate whether phase separation occurred before or after the polymerization. The results obtained were shown in Table 1.

Table 1.
Polymer[a] solubility[b] in ionic liquids.

IL	$[Bmim][BF_4]$		[DEME][TFSI]	
	monomer	polymer	monomer	polymer
St	○	×	○	×
*i*BMA	○	△	○	△
MMA	○	△	○	○
MA	○	○	○	○
HEMA	○	△	○	×
AN	○	×	○	×
MAA	△	△	○	×
AA	○	×	○	×

[a] Polymerization was carried out with 10 wt% monomer and 0.1 wt% AIBN (re. to IL) at 70°C for 24 h

[b] ○: soluble, △: partially soluble/swelling, ×: insoluble

Abbreviations: *i*BMA, *i*butyl methacrylate; MMA, methyl methacrylate; MA, methyl acrylate; HEMA, 2-hydroxyethyl methacrylate; AN, acrylonitrile; MAA methacrylic acid; AA, acrylic acid

$[Bmim][BF_4]$ is more hydrophilic than [DEME][TFSI] and miscible with water. In order to check the influence of the ionic nature liquid on dispersion polymerization, the polymerization of styrene in $[Bmim][BF_4]$ was carried out under the same conditions as for the [DEME][TFSI] system described in a previous paper.[20] Figure 1 shows SEM photographs of PS particles prepared by dispersion polymerization in [DEME][TFSI] and $[Bmim][BF_4]$ at various PVP concentrations. In the $[Bmim][BF_4]$ system, submicron-sized PS particles can be clearly observed and the particle size can be controlled by changing the PVP concentration, similar to the case of [DEME][TFSI]. However, unlike for [DEME][TFSI], the particle surfaces were somewhat rough when using $[Bmim][BF_4]$. This may be caused by differences in partition of styrene between the PS particles and ionic liquid and in critical chain length of PS in the medium.[22,23] The number-average molecular weight (M_n) of PS prepared in ionic liquid ($M_n = 4.5$ and 5.0×10^4, in $[Bmim][BF_4]$ and [DEME][TFSI], respectively) was higher than in ethanol ($M_n = 2.4 \times 10^4$). There are two likely explanations for the decrease in molecular

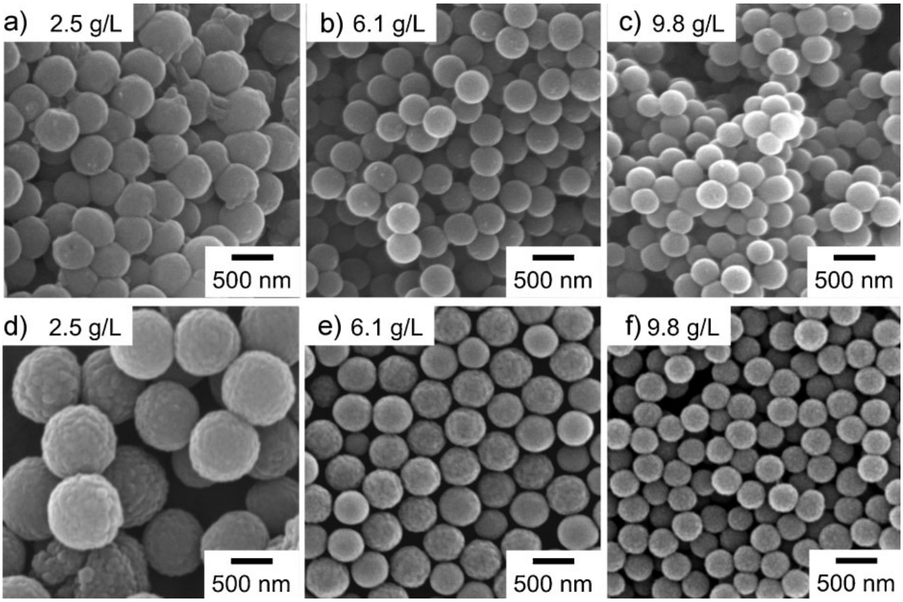


Figure 1.
SEM photographs of PS particles prepared by dispersion polymerizations at 70 °C in [DEME][TFSI] (a, b, c) and [Bmim][BF_4] (d, e, f) with various PVP concentrations (g/L): (a, d) 2.5; (b, e) 6.1; (c, f) 9.8.

weight in ethanol: (i) Chain transfer to ethanol. If chain transfer to ethanol is the main end-forming event in the ethanol system, M_n will be close to 2.4×10^4 g/mol (based on [styrene] = 1.2 mol/L, [ethanol] = 15 mol/L and chain transfer constant = 1.32×10^{-4} at 60 °C,[24] *i.e.* degree of polymn = $k_p[\mathrm{St}]/k_{tr}[\mathrm{ethanol}]$), which is comparable to the experimental molecular weight. (ii) The termination rate coefficient is lower in ionic liquids than in conventional organic solvents due to the high viscosity of the former,[11,12,14] which would cause the molecular weight to be lower in ethanol.

Figure 2 shows conversion-time plots for the dispersion polymerizations. In the case of [DEME][TFSI], the polymerization proceeded smoothly with the conversion reaching 80% in 6 h and 90% in 24 h. The rate of polymerization was higher than in the corresponding dispersion polymerization in ethanol. It is known that radical polymerization in homogeneous systems proceeds more rapidly in ionic liquids than in organic solvents.[11] A reason could be the reduced termination rate in the ionic liquid due to their high viscosities ([DEME][TFSI]: 120 mPa · s at 20 °C). However, in the case of the other ionic liquid, [Bmim][BF_4] (118 mPa · s at 20 °C), which has a similar viscosity as [DEME][TFSI], the polymerization rate was almost the same as for the ethanol system. This implies that the differences in

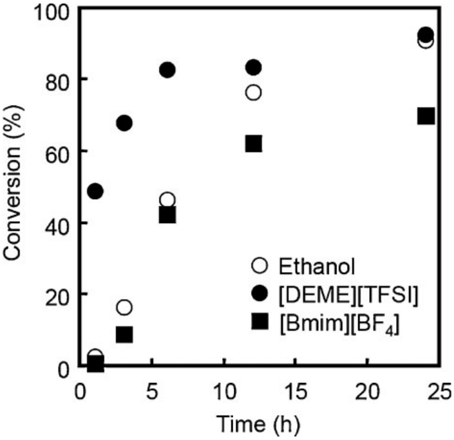


Figure 2.
Conversion vs time plots for dispersion polymerizations of styrene in ethanol (○), [DEME][TFSI] (●) and [Bmim][TFSI] (■) with [AIBN] = 7.5 mmol/L and [styrene] = 1.2 mol/L at 70 °C.

polymerization rates cannot be rationalized only in terms of viscosity differences. It has been reported that the propagation rate coefficients are higher in ionic liquids than in organic solvents.[12] Beuermann et al. reported that the propagation rate coefficients of MMA and glycidyl methacrylate were enhanced in [Bmim][BF_4],[25] due to lowering of the activation energy for propagation upon gradually replacing monomer molecules by ionic liquid species. The high polarity of the ionic liquid affects the structure of the transition state for the polar methacrylate monomer. In the present work, it is likely that the propagation rate was not enhanced in [Bmim][BF_4] because styrene is non-polar and thus interaction with the hydrophilic ionic liquid would be limited. However, these considerations on the propagation rate (k_p) cannot explain why the polymerization rate in [DEME][TFSI] was higher than in ethanol. Overall, it thus appears that the conversion-time data in Figure 2 cannot be explained simply based on current understanding of propagation and termination rates in homogeneous systems, and it may be that factors associated with the heterogeneity of the systems also influence the polymerization rate.

PS/PMMA Composite Particles

Both styrene and MMA are soluble in [Bmim][BF_4], whereas PS is insoluble. PMMA swells with [Bmim][BF_4] at 70 °C (Table 1), but is insoluble at 35 °C, which indicates that the preparation of PS/PMMA composite particles in this ionic liquid should be possible. Seeded dispersion polymerization of MMA was subsequently carried out in [Bmim][BF_4] at 35 °C for 24 h with PS seeds prepared by dispersion polymerization in [Bmim][BF_4].

Figures 3a and b show SEM photographs of PS particles obtained in the dispersion polymerizations. In the first step (Figure 3a), comparatively monodisperse PS particles of approximately 600 nm in diameter were obtained. These PS particles were then used as seeds in the second step. The diameter of the particles prepared by seeded dispersion polymerization was larger than that of the seed particles, and the particle size distribution was comparatively narrow. The SEM photograph (Figure 3b) also revealed that no secondary nucleation occurred during the seeded dispersion polymerization, indicating that the seeded growth proceeded smoothly. The composition of the particles was estimated by ^1H NMR: the weight ratio of PS/PMMA was 1/0.42, consistent with the diameter increase during the seeded polymerization.

Figure 3c shows TEM photographs of ultrathin cross-sections of the composite particles, stained with RuO_4 vapour for 30 min. RuO_4 stains PS, but not PMMA. It is evident that the particles consisting of a PS core and a PMMA shell have core-shell morphology. Although the morphology was not distinct, the results indicate that PS/PMMA composite particles were produced in ionic liquid.

PS/PAA Composite Particles

It is generally difficult to prepare composite particles comprising both hydrophilic and hydrophobic polymers using water or

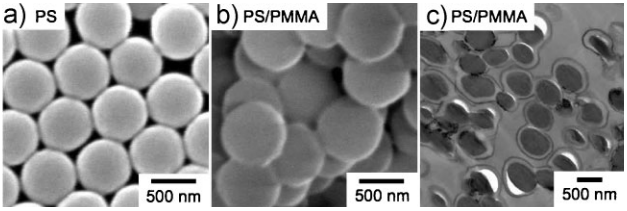


Figure 3.

SEM photographs of PS seed particles (a) and PS/PMMA composite particles (b) prepared by seeded dispersion polymerization of MMA at 35 °C using seed particles in [Bmim][BF_4] and TEM photograph of ultrathin cross sections (c) stained with RuO_4 vapor for 30 min.

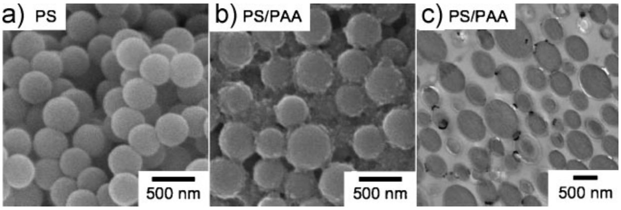


Figure 4.
SEM photographs of PS seed particles (a) and PS/PAA composite particles (b) prepared by seeded dispersion polymerization of AA at 70 °C in [DEME][TFSI], and TEM photograph of ultrathin cross sections (c) stained with RuO_4 vapour for 30 min.

common organic solvents. Both styrene and AA are soluble in [DEME][TFSI], but polystyrene and PAA are insoluble (Table 1). It was therefore expected that the hydrophobic/hydrophilic PS/PAA composite particles could be prepared in [DEME][TFSI].

Figure 4 shows a SEM photograph of the PS seed particles and the particles obtained by seeded dispersion polymerization, as well as a TEM photograph of ultrathin cross-sections stained with RuO_4 vapor (RuO_4 stains PS, but not PAA) of the particles obtained in the seeded dispersion polymerization. The PS seed particles were monodisperse with smooth surfaces; their diameter was approximately 350 nm (Figure 4a). The SEM photograph of the particles obtained from the seeded dispersion polymerization shows that the particles were larger and that the particle size distribution was relatively broad (Figure 4b) indicating that the seeded polymerization did not proceed successfully and that aggregation of seed particles may have occurred to some extent. Although some smaller particles were also visible indicating secondary nucleation, the TEM photograph (Figure 4c) of ultrathin cross-sections of them clearly indicates that the particles have a PS-core and PAA shell. PS/PAA composite particles, *i.e.* those comprising both hydrophobic and hydrophilic polymers, were thus successfully prepared.

The present results illustrate how ionic liquids can be effectively used to prepare composite polymer particles comprising both hydrophilic and hydrophobic polymers with morphologies that are difficult to obtain by more conventional means. The composite particles described in this study further expand the utility of ionic liquids as heterogeneous polymerization media for preparation of unique polymer particles that are not accessible using traditional polymerization solvents or water.

Acknowledgements: This work was partially supported by grant-in-aid for scientific research (grant 19750097) from the Japan Society for the Promotion of Science (JSPS). The authors would like to thank the Nisshinbo Industries Inc. for supplying [DEME][TFSI]. The authors are grateful to Dr. Per B. Zetterlund (Kobe University) for assistance during the preparation of this manuscript.

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