Stereocomplex Formation of Isotactic and Syndiotactic Poly(methyl methacrylate)s in Ionic Liquids Leading to Thermoreversible Ion Gels

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ABSTRACT: We found that stereoregular isotactic poly(methyl methacrylate) (*it*-PMMA) (*mm* = 97%) and syndiotactic poly(methyl methacrylate) (*st*-PMMA) (*rr* = 90%) with a narrow molecular weight distribution form a stereocomplex in ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$). The stereocomplex formation brought about the gelation of $BMIPF_6$ and was fully thermoreversible accompanied by a sol−gel transition at around the melting point of the crystalline stereocomplex in $BMIPF_6$ as evidenced by differential scanning calorimetry and polarized optical microscopy measurements of the gel. The effects of ionic liquids, the molar ratio of the *it*- and *st*-PMMAs, and the heating and cooling rates on the stereocomplex formation accompanied by gelation were also investigated. The fully thermoreversible gel in the ionic liquid with a high melting point (T_m = 175.0 °C) due to the unique stereocomplex formation may provide a new opportunity to fabricate advanced electrochemical devices.

Introduction

Stereocomplexes are unique polymer-based supramolecules composed of polymer chains with identical repeating units but different stereochemical configurations. It has been known that isotactic (*it*) and syndiotactic (*st*) poly(methyl methacrylate) (PMMA) chains assemble to form a crystalline stereocomplex with an apparent melting point in specific solvents.[1] The stereocomplex has been applied to sophisticated materials, such as ultrathin films,[2] microcellular foams,[3] dialyzers,[4] and thermoplastic elastomers.[5] Since the discovery of the PMMA stereocomplex,[6] numerous studies have been reported to elucidate the mechanism of complex formation and the structure of the stereocomplex.[1,7] Schomaker and Challa reported that the stereocomplex may be composed of double-stranded helices of *it*- and *st*-PMMAs postulated by the X-ray diffraction measurements.[8] However, the structural characteristics of the stereocomplex are still under debate. The stereocomplex formation occurs in specific organic solvents which significantly influence the complexation; in acetonitrile and *N*,*N*-dimethylformamide, stereocomplexes with high melting points efficiently form, whereas in benzene and toluene, the complexation is weak, and in noncomplexing solvents such as chloroform and dichloromethane, stereocomplexation hardly occurs.[9] Because of the rather low boiling points of the solvents, it was difficult to study the stereocomplex formation processes in solutions.

Ionic liquids (ILs) are room temperature molten salts and have widely been used as a recyclable alternative to traditional organic solvents for organic syntheses due to their nonvolatile, high polarity, ionic conductivity, and stable physical properties.[10] ILs can also be used as solvents for the radical polymerization of MMA, resulting in atactic or syndiotactic plasticized PMMA with improved thermal stability and ion gels with a high ionic conductivity when copolymerized with a cross-linking agent.[11]

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Herein, we report the highly efficient stereocomplex formation between stereoregular *it*- and *st*-PMMAs with a narrow molecular weight distribution in ILs such as 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$). We found that the stereocomplex formation resulted in thermoreversible gels in the ILs. The gelation behaviors accompanied by the stereocomplex formation were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy.

Results and Discussion

The *it*-PMMA (M_n = 21 800, M_w/M_n = 1.12, *mm* = 97%) and *st*-PMMA (M_n = 21 400, M_w/M_n = 1.14, *rr* = 90%) were prepared by the conventional living anionic polymerization of MMA in toluene at −78 °C with *t*-C_4H_9MgBr[12] and *t*-C_4H_9Li/(*n*-$C_4H_9)_3Al$[13] as initiators, respectively. PMMA samples in the ILs were prepared as follows. The *it*- and *st*-PMMAs were first dissolved in dichloromethane, and each solution was diluted with the appropriate amount of $BMIPF_6$ at room temperature. The $BMIPF_6$ solutions of the *it*- and *st*-PMMAs were obtained by evaporating the dichloromethane under vacuum at room temperature. The *it*- and *st*-PMMAs (2 wt %) were soluble in $BMIPF_6$ and formed a clear solution (Figure 1, a and b, respectively).[14] However, upon mixing the solutions at a ratio of *it*/*st* = 1/2 in unit molar base, the solution immediately became a viscous liquid and subsequently turbid and gelled within 10 min at room temperature (Figure 1c), indicating the stereocomplex formation between the *it*- and *st*-PMMAs in $BMIPF_6$.

The stereocomplex formation in $BMIPF_6$ was then studied by DSC using highly concentrated samples. Figure 2a shows the DSC thermograms of *it*-PMMA in $BMIPF_6$ (30 wt %). The sample sealed in an aluminum pan was first heated to 200 °C for 1 min to remove any residual thermal history. The DSC thermograms were recorded upon cooling from 200 to 0 °C (i in Figure 2a) followed by heating from 0 to 200 °C (ii) at a cooling or heating rate of 10 °C/min. $BMIPF_6$ showed no transi-

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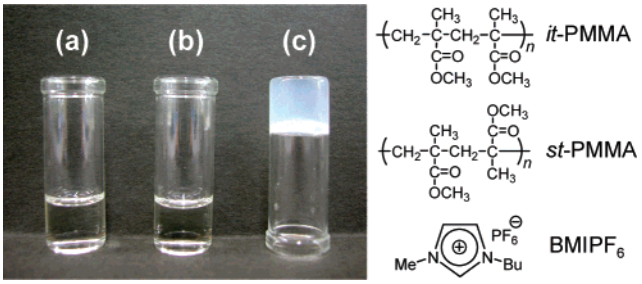


Figure 1. Photograph of *it*-PMMA (a), *st*-PMMA (b), and their stereocomplex (*it*/*st* = 1/2 in unit molar base) (c) in $BMIPF_6$. The polymer concentrations are 2 wt %.

tions under the same conditions. The DSC thermogram during the heating process showed a small endothermic peak (heat of melting (ΔH_m) = 5.3 J/g, based on a unit weight of the polymer) at ca. 60 °C. After annealing the sample at 25 °C for 24 h, it became a gel and exhibited a large endothermic peak (ΔH_m = 30.9 J/g) at 63.6 °C corresponding to the melting point (T_m) of the *it*-PMMA in $BMIPF_6$ (iii in Figure 2a). The results indicate that *it*-PMMA crystallizes very slowly in $BMIPF_6$. On the other hand, *st*-PMMA showed no thermic peak in the DSC measurements during the cooling and heating processes (Figure 2b).

Figure 2c shows the DSC thermograms of a blend of the *it*- and *st*-PMMAs (*it*/*st* = 1/2) in $BMIPF_6$ (30 wt %). The sample was prepared in a similar way to yield a stereocomplex gel. The DSC thermograms showed a sharp exothermic peak (heat of crystallization (ΔH_c) = 40.5 J/g) at 128.0 °C and a sharp endothermic peak (ΔH_m = 41.6 J/g) at 175.0 °C during the cooling and heating processes, respectively. The exothermic and endothermic peaks correspond to the crystallization and melting of the stereocomplex, respectively. The T_m and ΔH_m did not change after annealing the sample at 130 °C for 24 h, suggesting that the stereocomplexation in $BMIPF_6$ can rapidly reach an equilibrium at the cooling rate of 10 °C/min.

Visual inspection of the sample clearly indicated that the sol−gel transformation occurred at around the T_m and T_c during the heating and cooling processes, respectively. We note that the T_m of the stereocomplex in $BMIPF_6$ (175.0 °C) is considerably high despite the existence of solvents. A similar gelation has also been reported for a blend of the *it*- and *st*-PMMAs (*it*/*st* = 1/1) in *o*-xylene.[15] However, quantitative analysis of the T_m in the gel was difficult due to vaporization of the solvent, and the T_m values of the stereocomplex in *o*-xylene at high total polymer concentrations (30−50 wt %) were reported to be ca. 150 °C, which was lower than that in $BMIPF_6$.

Variations in the counteranions of ILs significantly affected the stereocomplex formation. The *it*- and *st*-PMMAs that dissolved in 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMITFSI) also formed stereocomplexes. However, the T_c and T_m values

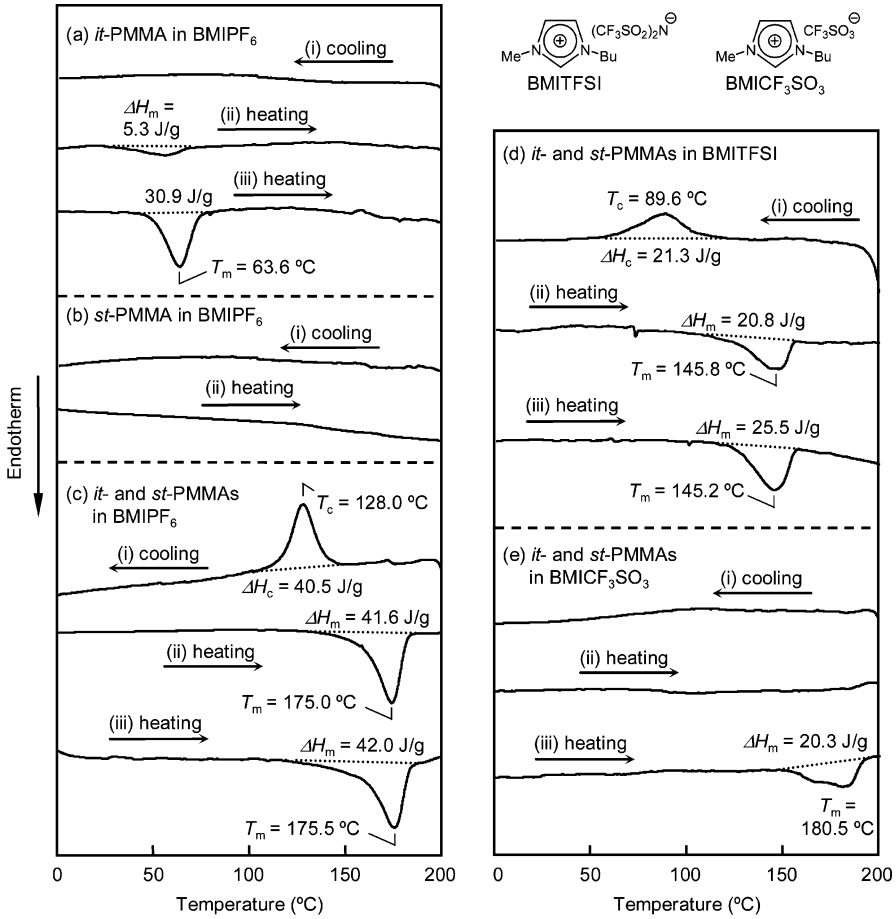


Figure 2. DSC thermograms of *it*-PMMA (a) and *st*-PMMA (b) in $BMIPF_6$ and a blend of *it*-PMMA and *st*-PMMA (*it*/*st* = 1/2 in unit molar base) in $BMIPF_6$ (c), BMITFSI (d), and $BMICF_3SO_3$ (e) at a heating or cooling rate of 10 °C/min. The total polymer concentrations were 30 wt %. The measurements were conducted after heating the samples at 200 °C for 1 min to delete the thermal histories, followed by cooling to 0 °C (i) and then heating to 200 °C (ii). The *it*-PMMA and the blends of *it*- and *st*-PMMAs were further annealed at 25 (a), 100 (d), and 130 °C (c, e) for 24 h and then heated again (iii).

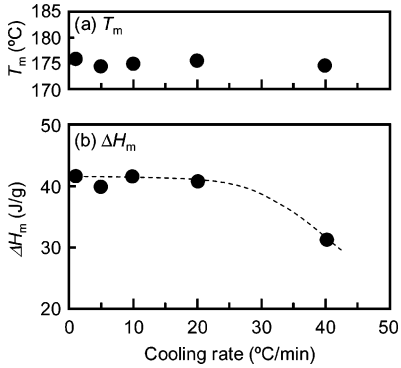


Figure 3. Changes in T_m (a) and ΔH_m (b) of a blend of *it*-PMMA and *st*-PMMA (*it*/*st* = 1/2 in unit molar base) in $BMIPF_6$ as a function of the cooling rate from the melt. The total polymer concentration was 30 wt %. The DSC measurements were conducted after cooling the sample from 200 to 0 °C at several rates followed by heating to 200 °C at the rate of 10 °C/min.

were lower and their enthalpies were smaller than those measured in $BMIPF_6$ by DSC under the same conditions (i and ii in Figure 2d). Furthermore, the ΔH_m value of the stereocomplex in BMITFSI increased when the sample was annealed at 100 °C for 24 h (iii in Figure 2d), indicating that the stereocomplex formation in BMITFSI was slower than that in $BMIPF_6$.

1-Butyl-3-methylimidazolium trifluoromethanesulfonate ($BMICF_3SO_3$) can also dissolve the *it*- and *st*-PMMAs. However, the mixed sample solution did not form a stereocomplex during the first cooling and heating processes (i and ii in Figure 2e), but they slowly formed a partial stereocomplex after annealing at 130 °C for 24 h. On the other hand, the *it*- and *st*-PMMAs are not soluble in 1-butyl-3-methylimidazolium tetrafluoroborate ($BMIBF_4$) at room temperature. The slight difference in the counteranion significantly influences not only the solubility of the stereoregular PMMAs but also their stereocomplex formation.

The crystallization rate of the stereocomplex (*it*/*st* = 1/2) in $BMIPF_6$ was then investigated by DSC as a function of the cooling rate from the melt state (Figure 3). The T_m and ΔH_m values were determined during the second heating at 10 °C/min. The T_m values were independent of the cooling rate over the range 10−40 °C/min, while the ΔH_m tended to increase with the decreasing cooling rate from the melt and became a constant value at a cooling rate below 20 °C/min, indicating that the crystallization of the stereocomplex rapidly and quantitatively occurs in $BMIPF_6$ at these rates.

We next investigated the effect of the mixing ratio of the *it*- and *st*-PMMAs on the T_m and ΔH_m during the stereocomplex formation in $BMIPF_6$ at the polymer concentration of 30 wt % (Figure 4). The T_m value remained constant, and a maximum ΔH_m was observed at *it*/*st* = 1/2 in $BMIPF_6$. The broken line in Figure 4b indicates the calculated ΔH_m values on the assumption that the stereocomplexes quantitatively form at the ratio of *it*/*st* = 1/2 regardless of their mixing ratios. The observed ΔH_m values were in good agreement with the calculated ΔH_m (broken line), indicating the quantitative stereocomplex formation at *it*/*st* = 1/2 with remaining PMMA uncomplexed, irrespective of the feed ratios of *it*- and *st*-PMMAs. This composition of the stereocomplex agrees with that reported in many references,[1,7a,8,9,16] indicating the very efficient stereocomplex formation in the IL.

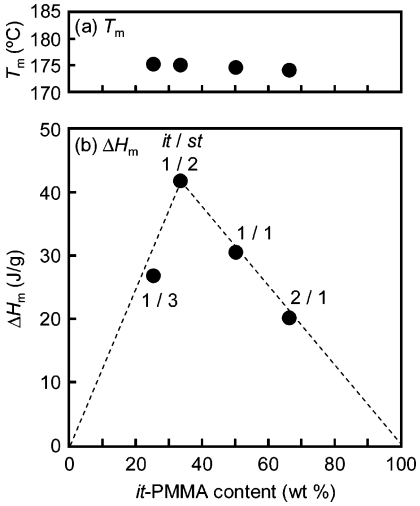


Figure 4. Dependence of the mixing ratio of *it*-PMMA and *st*-PMMA in $BMIPF_6$ on the T_m (a) and ΔH_m (b) of the resultant stereocomplex. The total polymer concentrations were 30 wt %. The DSC measurements were conducted after heating the samples at 200 °C for 1 min followed by cooling to 0 °C and then heating to 200 °C. The cooling and heating rates were 10 °C/min. The broken line represents the expected ΔH_m by assuming that the stereocomplex may form at the ratio of *it*/*st* = 1/2, independent of the mixing ratio.

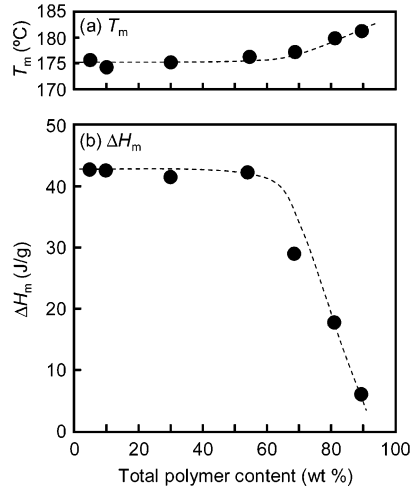


Figure 5. Changes in T_m (a) and ΔH_m (b) of blends of *it*- and *st*-PMMAs (*it*/*st* = 1/2 in unit molar base) in $BMIPF_6$ as a function of total polymer concentrations (5, 10, 30, 54, 69, 81, and 89 wt %). The DSC measurements were conducted after heating the samples at 200 °C for 1 min followed by cooling to 0 °C and then heating to 200 °C. The cooling and heating rates were 10 °C/min.

We also investigated the effect of the total polymer concentration on the T_m and ΔH_m values during the stereocomplex formation in $BMIPF_6$ from the melt at the cooling rate of 10 °C/min (Figure 5). Interestingly, the *it*- and *st*-PMMAs blends are highly soluble or miscible in $BMIPF_6$ up to 89 wt % and formed stereocomplexes under these conditions. The ΔH_m of the stereocomplex increased with the decreasing polymer concentration and reached an almost constant value (ca. 42 J/g) at around the polymer concentration of less than 50 wt %, while the T_m slightly decreased. We noted that an extremely high concentrated PMMA blend in $BMIPF_6$ at 89 wt % formed a stereocomplex. In sharp contract, the stereocomplex formation in bulk requires an annealing process at high temperatures for a long time and does not take place during this cooling process.

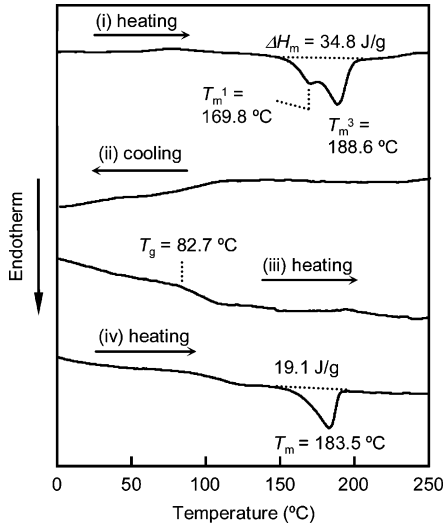


Figure 6. DSC thermograms of a blend of *it*- and *st*-PMMAs (*it*/*st* = 1/2 in unit molar base) obtained from acetonitrile solutions, at the heating or cooling rate of 10 °C/min. The measurements were conducted after cooling the sample at 0 °C, followed by heating to 250 °C (i), cooling to 0 °C (ii), and then heating to 250 °C (iii). The sample was then annealed at 140 °C for 24 h and then heated again (iv).

We then compared the properties of the stereocomplexes formed in $BMIPF_6$ and those obtained from a typically strong complexing solvent, acetonitrile.[9] When the *it*- and *st*-PMMAs solutions in acetonitrile were mixed, a precipitate immediately formed due to the stereocomplex formation, and the thermal property of the resultant stereocomplex was investigated by DSC. The stereocomplex showed two endothermic peaks at 169.8 °C (T_m^1) and 188.6 °C (T_m^3) in the DSC thermogram (i in Figure 6). The total ΔH_m value for the stereocomplex formation was 34.8 J/g, which was smaller than that formed in $BMIPF_6$ (41.6 J/g, see Figure 2c). The two endothermic peaks, denoted here as T_m^1 and T_m^3, in the DSC thermograms have been reported for the stereocomplexes of PMMAs in bulk.[16] Schomaker and Challa investigated the origin of such multiple endothermic peaks of stereocomplexes in detail and proposed that the T_m^1 and T_m^3 could be assigned to the formations of fringed micellar structures (clusters of stereocomplex) and lamellar crystallites, respectively.[16a,b] They also showed that the superheating characteristics of the two types were different since the T_m^1 increased with the increasing heating rate in the DSC measurements, while the T_m^3 was independent of the heating rate. The DSC thermograms of a blend of the *it*- and *st*-PMMAs (*it*/*st* = 1/2) in $BMIPF_6$ as a function of the heating rate showed one sharp endothermic peak, and the T_m values were independent of the heating rate (see Supporting Information), suggesting that the stereocomplex in $BMIPF_6$ consists of rather homogeneous crystallites. The larger ΔH_m value and homogeneous crystallite formation in $BMIPF_6$ indicate that the present $BMIPF_6$ system may be a better system for stereocomplexation than that of acetonitrile. The stereocomplex prepared from acetonitrile did not show any exothermic and endothermic peaks except for a heat capacity change (T_g = 82.7 °C), once melted at temperatures higher than the T_m, as evidenced by the DSC measurements during the cooling and heating processes between 250 and 0 °C (ii and iii in Figure 6). The stereocomplex formation in bulk is a less favorable process and requires a rather long time at high temperatures. In fact, the annealed sample in bulk at 140 °C for 24 h showed a weak endothermic peak due to the melting of the stereocomplex at 183.5 °C; the ΔH_m was only 19.1 J/g (iv in Figure 6). Therefore, a strong complexing solvent such as acetonitrile is essential for the effective and rapid stereocomplex formation. However, common organic solvents vaporize above the T_m of the stereocomplexes. Consequently, $BMIPF_6$ is a novel and powerfully strong complexing solvent with an excellent thermal stability, so that a fully thermoreversible gel due to the rapid stereocomplex formation and deformation in the IL can be obtained, and these processes can be directly visualized by optical microscopy.

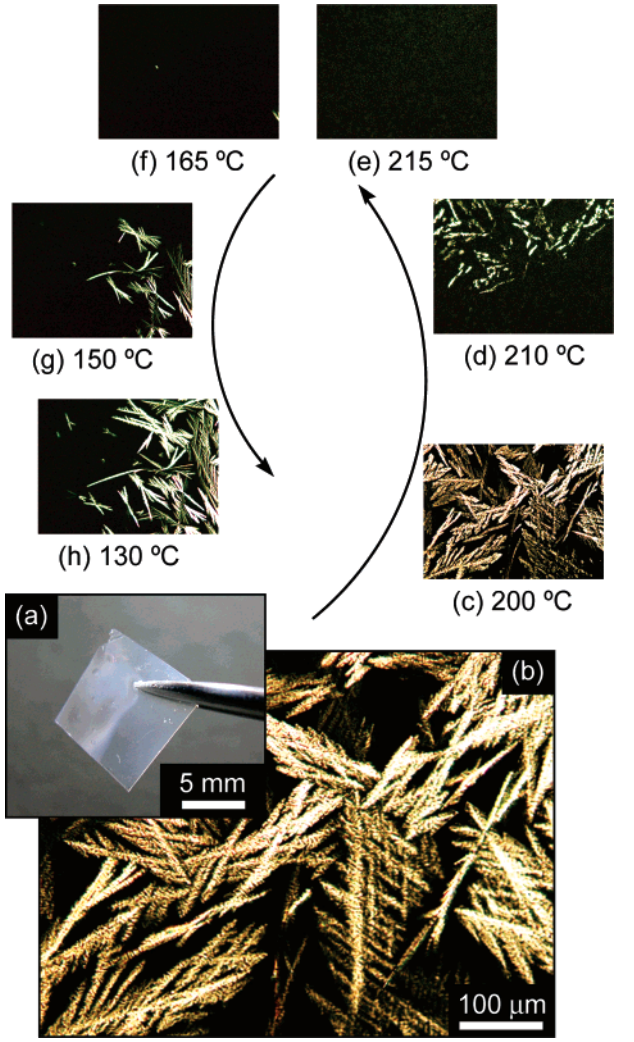
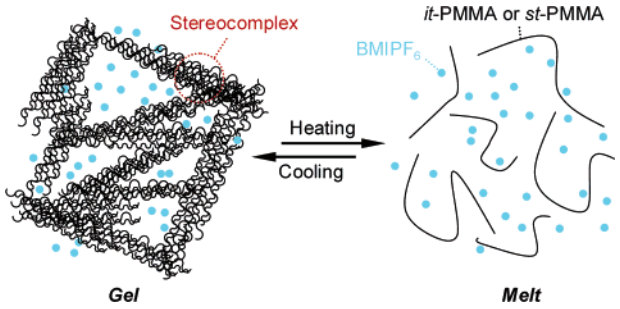


Figure 7. Photograph (a) and polarized optical micrographs (b−h) of a stereocomplex ion gel film. The film was prepared by casting a blend of *it*- and *st*-PMMAs (*it*/*st* = 1/2 in unit molar base) in $BMIPF_6$ (polymer 30 wt %) on a glass substrate followed by heating to 200 °C and then cooling to 25 °C at the heating and cooling rates of 10 °C/min. The observations were carried out at 25 °C (a, b) followed by heating to 230 °C (c−e) and then cooling to 130 °C at the heating and cooling rates of 10 °C/min.

Figure 7 shows a photograph of a stereocomplex gel (a) and polarized optical micrographs (b−h) of a cast film of the gel in $BMIPF_6$ (30 wt %) at different temperatures. The dendritic fractal structure of crystallites of the stereocomplex was observed at room temperature by polarized optical microscopy (b). By heating the sample at 10 °C/min on a slide glass, it began to melt at around 210 °C (d) and was completely molten at 215 °C (e). When the molten sample was

Scheme 1. Schematic Illustration of a Possible Mechanism for the Thermoreversible Gelation of $BMIPF_6$ through the Crystalline Stereocomplex Formation of the *it*- and *st*-PMMAs



cooled at 10 °C/min, the crystallites of the stereocomplex appeared at around 165 °C (f) accompanied by dendritic crystal growth, which could be observed from at around 150 °C (g), and then the solid film was obtained again at 25 °C. These changes are completely reversible.

X-ray measurements were then performed for a stereocomplex obtained from acetonitrile (a) and stereocomplex ion gels in $BMIPF_6$ at 54 (b) and 30 wt % (c), together with that of $BMIPF_6$ (d) (see Supporting Information). The differential diffractogram (e) obtained by subtracting (d) from (b) was similar in their patterns to that of the stereocomplex obtained from acetonitrile, indicating that the stereocomplexes obtained from acetonitrile and formed in $BMIPF_6$ may have almost the same crystalline structure.

On the basis of these results, a possible mechanism for the thermoreversible gelation of the stereocomplex in $BMIPF_6$ can be proposed (Scheme 1). The *it*- and *st*-PMMAs form a stereocomplex at the ratio of *it*/*st* = 1/2 in $BMIPF_6$. Subsequent crystallization results in the gelation of $BMIPF_6$. The gel has a high melting point because the cross-linking regions are constructed from crystallites. At the temperature higher than the T_m, the stereocomplex melts to form a stable and homogeneous solution because $BMIPF_6$ is nonvolatile and thermally stable. The gelation rapidly occurs at temperatures lower than the T_m through the stereocomplex formation.

In conclusion, we have found that a stereocomplex formation between *it*- and *st*-PMMAs efficiently took place in ILs such as $BMIPF_6$. The stereocomplex formation brought about gelation of $BMIPF_6$ and was fully thermoreversible as evidenced by the DSC and optical microscopy measurements. Recently, we successfully prepared a fullerene-end-capped isotactic PMMA (*it*-PMMA-C_{60}).[17] The present results imply that a similar stereocomplex ion gel may be formed using the *it*-PMMA-C_{60} as the component which will produce two- and three-dimensional arrangements of the C_{60} molecules in the ILs. Such well-arranged C_{60}-containing stereocomplex ion gels may be applicable to advanced electrochemical devices. This work is now in progress.

Experimental Section

Materials. The *it*- and *st*-PMMAs were synthesized according to the reported methods by the living anionic polymerization of MMA in toluene at −78 °C with *t*-C_4H_9MgBr[12] and *t*-C_4H_9Li/(*n*-$C_4H_9)_3Al$,[13] respectively, as initiators. The number-average molecular weights (M_n), molecular weight distributions (M_w/M_n), and tacticities (*mm*:*mr*:*rr*) were as follows: *it*-PMMA: M_n = 21 800, M_w/M_n = 1.12, and *mm*:*mr*:*rr* = 97:3:0; *st*-PMMA: M_n = 21 400, M_w/M_n = 1.14, and *mm*:*mr*:*rr* = 1:9:90. The M_n and M_w/M_n values were measured by size exclusion chromatography in chloroform using PMMA standards for the calibration. The tacticities were determined from the ^1H NMR signals due to the α-methyl protons.

Dichloromethane, acetonitrile, and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were obtained from Wako (Osaka, Japan). $BMIPF_6$, $BMICF_3SO_3$, $BMIBF_4$, and 1-butyl-3-methylimidazolium bromide (BMIBr) were purchased from Tokyo Kasei (TCI, Tokyo, Japan) and used without further purification. BMITFSI was prepared by the anion-exchange reaction of BMIBr with LiTFSI in water, followed by repeatedly washing with water and drying under vacuum.[11c,18]

Instruments. DSC measurements were performed using a Seiko (Chiba, Japan) EXSTAR 6000 under a nitrogen atmosphere. The samples were sealed in aluminum pans. The melting temperature (T_m) and crystallization temperature (T_c) were determined from the minimum of the melting endothermic peak and the maximum of the exothermic peak, respectively. The heat of melting (ΔH_m) and the heat of crystallization (ΔH_c) were determined by the peak area of the melting endothermic peak and crystallization exothermic peak, respectively.

X-ray measurements were carried out using a UltraX 18 rotating-anode generator with graphite monochromated Cu Kα radiation (0.154 18 nm) focused through a 0.3 mm pinhole collimator, which was supplied at 45 kV and 60 mA current, equipped with an imaging plate having a specimen-to-plate distance of 120.0 mm.

Polarizing optical microscopic observations were carried out with a Nikon (Tokyo, Japan) E600POL polarizing optical microscope equipped with a DS-5M CCD camera (Nikon) connected to a DS-L1 control unit (Nikon).

Preparation of Stereocomplex in Ionic Liquids at 2 wt %. The appropriate amount of *it*-PMMA was dissolved in dichloromethane, and the solution was diluted with the ILs at room temperature. The homogeneous solution was obtained by evaporating the dichloromethane under vacuum at room temperature. A solution of *st*-PMMA in the ILs was also obtained in the same way. The stereocomplex in the ILs at 2 wt % was prepared by mixing the ILs solutions of the *it*- and *st*-PMMAs.

Preparation of Stereocomplex in Ionic Liquids at 5−89 wt %. The appropriate amounts of the *it*- and *st*-PMMAs were dissolved in dichloromethane, in which stereocomplex formation does not take place,[9] and the solution was diluted with the ILs at room temperature. The stereocomplex gel was obtained by evaporating the dichloromethane under vacuum at room temperature.

Preparation of Stereocomplex from Acetonitrile. Solutions of the *it*- and *st*-PMMAs in acetonitrile (4 mg/mL), which belongs to the strongly complexing solvent,[9] were separately prepared, and they were mixed at the ratio of *it*-PMMA/*st*-PMMA = 1/2 in unit molar base; precipitates immediately formed due to the stereocomplex formation. After the mixed solution was kept at room temperature for 24 h, the solid stereocomplex was separated by centrifugation at 15 000*g* followed by drying under vacuum at room temperature.

Supporting Information Available: DSC thermograms of a blend of *it*- and *st*-PMMAs in $BMIPF_6$ as a function of the heating rate and X-ray diffractograms of a stereocomplex obtained from acetonitrile and a stereocomplex ion gel in $BMIPF_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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