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Improved solubilization of pyromellitic dianhydride and 4,4′-oxydianiline in ionic liquid by the addition of zwitterion and their polycondensation

Masahiro Tamada, Takahiro Hayashi and Hiroyuki Ohno*

Department of Biotechnology, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan

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Abstract—Three different ionic liquids were prepared and examined as solvents for polyimide synthesis. The solubility of 4,4′-oxydianiline and pyromellitic dianhydride as starting materials in ionic liquids was first evaluated, and then their polycondensation was carried out. Although these starting materials were hardly soluble in 1-benzyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (**3**), addition of imidazolium type zwitterion, 1-(1-butyl-3-imidazolio)butane-4-sulfonate (ZI), certainly improved their solubility. When **3** containing 40 mol % ZI was used, nothing was phase separated from this mixed solution containing both starting materials after cooling down to room temperature. After preparing prepolymer in **3** containing 40 mol % of ZI at room temperature, polycondensation was carried out in the same solution at 100, 200, and then 300 °C for every 1 h to obtain polyimide. An inherent viscosity of the obtained polyimide (0.05 g in 10 ml concentrated sulfuric acid) was 1.3 dL g^{-1}, higher than that prepared in only **3** (0.9 dL g^{-1}). The higher average molecular weight of the polyimide was attributed to the improved solubility of the starting materials by the addition of ZI that enabled the preparation of the prepolymer, poly(amide acid), without heating before imidation.

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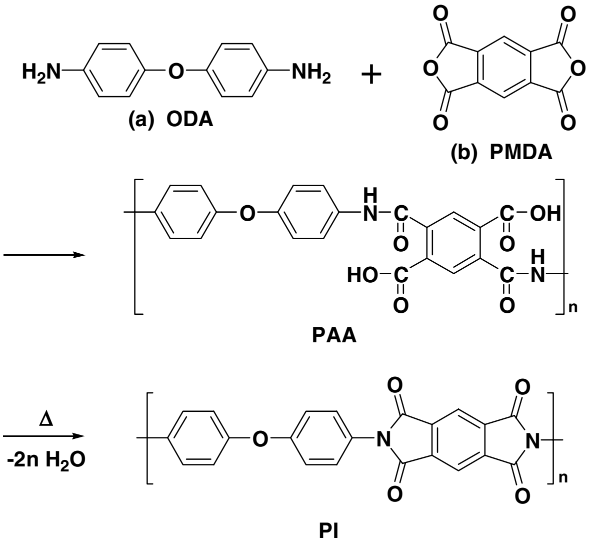
1. Introduction

Ionic liquids (ILs), composed of only ions, have a potential as liquid media with negligible vapor pressure, flame resistance until decomposition temperature, high ionic conductivity, electrochemical stability, and so on.[1] Therefore, ILs have been studied as novel reaction media[2] and ion conductive materials.[3] Polymerization of several monomers is one of the important subjects of IL technology. From the viewpoint of the environmental care and safety, these polar and non-volatile ILs should be required instead of volatile and toxic organic solvents for the synthesis. In these studies, there are several papers on the characterization of some ILs for polymerization.[4] Most of these are based on free-radical polymerization[5] because of its widely applicable possibility with small restriction. Against this, polycondensation, especially the synthesis of aromatic polyimides, is quite difficult in ILs.

Aromatic polyimides have excellent properties such as thermal stability, chemical stability, mechanical strength, and so on. Among these, polyimides prepared from 4,4′-oxydianiline (ODA) and pyromellitic dianhy-



Scheme 1. Synthesis of typical PI.

Keywords: Solubilization; Polycondensation; Polyimides; Ionic liquids; Zwitterions.

* Corresponding author. Tel./fax: +81 42 388 7024; e-mail: ohnoh@cc.tuat.ac.jp

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dride (PMDA) (**a** and **b**, respectively, in Scheme 1) have been most commonly studied and widely used.[6] Hereafter, polyimide composed of ODA and PMDA is abbreviated as PI. Synthesis of PI is generally carried out by two step reactions as also shown in Scheme 1. First, both ODA and PMDA reacted generally in the amide type polar solvents such as dimethylformamide to obtain soluble poly(amide acid) (PAA) as a prepolymer. Then, the solution of the prepared PAA was heated in order both to proceed imidation and to remove solvents. In these steps, especially the second step, the solvent was vaporized to the environment and was also at risk of ignition. ILs, which have negligibly small vapor pressure, are expected as solvents for materials synthesis, and some studies on the PI synthesis have already been tried.[7] In a previous study, polycondensation of various starting materials including ODA and PMDA has been carried out in 1,3-diisopropylimidazolium bromide.[7b] The ILs containing halide anions are known as relatively polar ILs and show better solubilizing ability of many kinds of molecules. Also, biological polymers were found to be soluble in some ILs containing halide anions.[8]

However, these halide anion-containing ILs have a few drawbacks as solvents for polycondensation reactions. First, the melting point of halide-containing ILs is relatively high. Almost all of these ILs containing halide anions are solid at room temperature. It is quite important to lower the reaction temperature for PAA synthesis, because the molecular weight of PAA was reported to be lower when the reaction was carried out at higher temperature.[9] Since the average molecular weight of PI clearly reflects the molecular weight of the prepolymer (PAA),[10] the PAA should be prepared at a low temperature. However, halide-containing ILs were solid at room temperature. These halide-containing ILs needed heating when used as solvents. The ILs, having lower viscosity and lower melting point than those ILs having halide anions are quite favorable for the PAA syntheses. Second, halide-containing ILs are hydrophilic and hygroscopic. The reactivity of starting materials, especially anhydrous dicarboxylic acid (e.g., PMDA), decreases considerably in the presence of water.[11] ILs containing halide anions are generally hygroscopic, and thus, contaminated water considerably lowers the reactivity. Therefore polycondensation in halide-containing ILs requires a special care to avoid humidity from the reaction systems. Hydrophobic ILs are much more favorable for this point of view. Even in the case of hydrophobic ILs, there are small amounts of water. However, these water molecules are not free but strongly hydrated. Accordingly, hydrophobicity is another important factor of ILs. Last, halide-containing ILs generally decompose around 200 °C. The thermal imidation of prepolymers should be carried out above 250 °C, otherwise imidation was not completely proceeded. The decomposition temperature of ILs containing halide anion was around 200 °C, suggesting insufficient imidation.

In this study, we prepared ILs to satisfy the sufficient solubility of both ODA and PMDA and the above three requirements namely: (1) a low melting point, at least liquid state at room temperature, (2) hydrophobic ILs, and (3) thermally stable above 300 °C.

2. Results and discussion

Figure 1 shows the structure and abbreviation of ILs used in this study. We focus on the ILs containing imide anion. ILs containing imide anion such as bis(trifluoromethane sulfonyl)imide (Tf_2N) have advantages of low melting point, low viscosity, hydrophobicity, thermal stability, and so on.[12] These characteristics are quite favorable for the polycondensation media of PI. ILs containing Tf_2N (**1**, **2**, and **3**) were synthesized by applying the method as reported previously.[12] Solubility of the starting materials, ODA and PMDA, in **1**, **2**, and **3** was evaluated. These starting materials were insoluble in ILs **1** and **2**. On the other hand, **3** solubilized ODA after heating (as shown in Table 1). However, dissolved ODA in hot **3** was easily recrystallized after cooling the solutions down to an ambient temperature. IL **3** also solubilized PMDA but only slightly. At the initial stage, ILs having Tf_2N anions were concluded to be unsuitable as a solvent for PI synthesis. It was requested to improve the solibilizing ability of **3** by some polar additives.

We have been studying zwitterionic type IL (ZI).[13,14] ZIs show unique characteristics because both cation and anion of the IL were tethered.[13] ZIs have similar characteristics to general ILs except for a high melting point. Although most ZIs are solid at room temperature, the mixture of these solid ZIs with other solid salts or strong acids is obtained as a liquid.[13,14] The properties of solid salts and acids are expected to be improved by adding ZIs in many cases. In spite of the certain limitation of the added salts and acids, ZIs are quite useful to liquidize these salts and acids. These results as mentioned above forced us to examine the properties of ILs after mixing ZIs. The properties such as the solubility of starting materials are expected to be improved by the ZIs. We added ZIs to these ILs to improve the solubility of both ODA and PMDA keeping their hydrophobicity and thermal stability. The synthesis of ZI, 1-(1-butyl-3-imidazolio)-butane-4-sulfonate (Fig. 1), will be mentioned in Section 4.3. The solubility of ODA and PMDA in **3**/ZI has also been evaluated. Table 1 shows the effect of composition of **3** to ZI on the solubility of both ODA and PMDA in the **3**/ZI mixture. Solubility of the start-

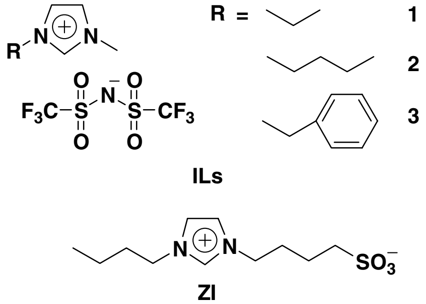

Figure 1. Structure and abbreviations of ionic liquids and zwitterion used in this study.

Table 1. Solubility (wt %) of ODA and PMDA in **3**/ZI mixture

3: ZI/molar ratio	Temperature/°C		
	20	50	80
(a) ODA			
6:4	0	0.5	7.5
7:3	0	0.5	7.0
8:2	0	0.5	7.0
9:1	0.5	1.0	5.5
10:0	0	0.5	5.0
(b) PMDA			
6:4	0	1.5	5.5
7:3	0	2	5.5
8:2	0.5	2.5	5.0
9:1	1.0	2.0	3.5
10:0	1.0	1.5	1.5

ing materials in **3** at 80 °C was improved by adding ZI. Even addition of 10 mol % ZI improved the solubility of the starting materials, especially ODA, as seen in Table 1. Furthermore, in the mixture containing 20 mol % or more amount of ZI, solubility of both ODA and PMDA was significantly improved at 80 °C. Especially, when the mixture containing 40 mol % of ZI was used, no component was recrystallized or phase separated from this mixed solution by cooling down to room temperature. This improved solubility forced us to examine the effect of ZI addition to other ILs (**1** and **2**, containing 40 mol % of ZI). However, the mixture of ZI with **1** or **2** showed a phase separation after a few days by keeping them at room temperature. As described above, we selected **3** containing 40 mol % ZI as a solvent for ODA and PMDA. Hereafter, **3** containing 40 mol % ZI was abbreviated as **3**/ZI.

In order to discuss the effect of ZI on the solubility of ODA and PMDA in **3**, polarity of the ILs was evaluated. Table 2 shows Kamlet–Taft parameters and thermal properties of **1**, **2**, **3**, and **3**/ZI. A β value (hydrogen bond basicity) of **1**, **2**, and **3** (0.22–0.24) was much lower than that of DMF (0.69) in spite of higher α (hydrogen bond acidity) and π^* (polarizability) values. On the other hand, β value of **3**/ZI (0.57) was much higher than that of **3** (0.22) in spite of the same α and π^* values. The β value of **3**/ZI approached closely that of DMF (0.69). BMICl is also compared and mentioned in Table 2 as a typical IL, which is known to solubilize several valuable materials, including biological polymers.[8] These halide-containing ILs are favorable for their high β value. However, these ILs lack a few other properties as mentioned above. Addition of ZI was confirmed to elevate β value, which is required for the solubilization of both ODA and PMDA. The reason for the increased β value by ZI addition will be reported elsewhere.

Table 2. Kamlet–Taft parameters and thermal properties of ILs and **3**/ZI

Entries	Kamlet–Taft parameter			Thermal properties/°C	
	α	β	π	T_m	T_d
1	0.71[a]	0.23[a]	0.98[a]	−4[d]	453[f,i]
2	0.62[b]	0.24[b]	0.98[b]	−5[e]	397[j]
3	0.57	0.22	1.03	−60[h]	381[j]
3/ZI	0.54	0.57	1.04	−48[h]	345[j]
BMICl	0.41[c]	0.95[c]	1.17[c]	73	234[g]
DMF	0	0.69	0.88	−61	153[k]

T_m: melting point, T_d: decomposition temperature.

[a] Ref. 15.

[b] Ref. 16.

[c] Ref. 1 (p 97).

[d] Ref. 17.

[e] Ref. 12.

[f] Ref. 18.

[g] Ref. 19.

[h] Glass-transition temperature.

[i] Onset.

[j] 10 wt % loss.

[k] Boiling point.

Thermal property of **3**/ZI was evaluated as shown in Table 2. Compound **3**/ZI did not show melting point but did a glass transition temperature at −48 °C. The decomposition temperature (10 wt % loss) was found at 330 °C. Compound **3**/ZI was in a liquid-state at room temperature and thermally stable above 250 °C. The temperature range of the liquid state of **3**/ZI was much wider than that of BMICl.

Since we finally got preferable solvents for both ODA and PMDA, we solubilized and polymerized them in both **3** and **3**/ZI. Both systems gave brown powder after polycondensation. Formation of imide bonds was confirmed by FT-IR measurement. For example, two peaks at 1776 and 725 cm^{-1} were characterized to the imide groups according to the literature.[6] The thermal properties of thus obtained PI were measured. DSC measurement (from −130 to 200 °C) and thermogravimetry measurement (from 25 to 500 °C) showed no peak and no weight loss, respectively. These results are the same as those for PI synthesized in DMF.

Since PI was insoluble in organic solvents, average molecular weight cannot be determined by ordinary methods. Thus, the inherent viscosity of these PI was measured in a concentrated sulfuric acid. The inherent viscosity is an indicator of average molecular weight of the polymers. Inherent viscosity is the ratio of the natural logarithm of the relative viscosity (the ratio of the viscosity of the solution to the viscosity of the solvent) to the mass concentration of the polymer. The PI prepared in pure **3** and **3**/ZI showed the inherent viscosity of 0.9 and 1.3 dL g^{-1}, respectively. These values were larger than 0.5 dL g^{-1}, which was previously reported for the PI prepared in IL containing halide anion.[7b] The average molecular weight of the PI prepared in the present study was strongly suggested to be higher. The effect of ZI was obvious, namely the solubility of PMDA was considerably improved, and prepolymer, PAA, was successfully prepared at room temperature.

3. Conclusion

A few ionic liquids were prepared and examined as solvents for polyimide synthesis. The solubility of ODA and PMDA as starting materials in ionic liquids was evaluated, and then the polycondensation of them was carried out in the ionic liquids. Although ionic liquid, 1-benzyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (**3** in Fig. 1), was difficult to dissolve starting materials, their solubility was significantly improved by the addition of imidazolium type zwitterion, 1-(1-butyl-3-imidazolio)butane-4-sulfonate (ZI), because of increasing hydrogen-bond accepting ability. When polycondensation was carried out in **3** containing 40 mol % of ZI, high average molecular weight of the polyimide was obtained because PAA was prepared without heating.

4. Experimental

4.1. Synthesis of ILs

1-Methylimidazole (Wako, distilled, 1.6×10^{-2} mol) was dissolved in acetonitrile (100 ml), and then excess of corresponding alkyl bromide (TCI) was added to the solution. The solution was stirred under dry nitrogen gas at room temperature for 3 days. Then acetonitrile was evaporated. The obtained transparent viscous liquid was washed with ethyl acetate twice and dried at 45 °C under vacuum for 1 day. This prepared 1-alkyl-3-methylimidazolium bromide (9.1×10^{-3} mol) was mixed with equimolar lithium bis(trifluoromethane sulfonyl)imide ($LiTf_2N$, 3 M) in H_2O (200 ml). After decantation, the obtained transparent liquid was washed with H_2O and dried at 45 °C under vacuum for 7 days. No bromide ion was detected by the silver (I) nitrate titration test.

4.1.1. 1 (1-Ethyl-3-methylimidazolium Tf_2N). Methylimidazole was reacted with ethyl bromide (TCI); yield 76%; ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 1.42$ (t, $J = 8$ Hz, 3H), 3.86 (s, 3H), 4.21 (m, $J = 7$ Hz, 2H), 7.76 (s, 1H), 7.82 (s, 1H), 9.16 (s, 1H).

4.1.2. 2 (1-Butyl-3-methylimidazolium Tf_2N). The same procedure as for the case of **1** was used with *n*-butyl bromide (TCI) instead of ethyl bromide; yield 84%; ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 0.90$ (t, $J = 8$ Hz, 3H), 1.27 (m, $J = 8$ Hz, 2H), 1.77 (m, $J = 6$ Hz, 2H), 3.86 (s, 3H), 4.17 (m, $J = 7$ Hz, 2H), 7.72 (s, 1H), 7.79 (s, 1H), 9.17 (s, 1H).

4.1.3. 3 (1-Benzyl-3-methylimidazolium Tf_2N). The same procedure as above was applied with benzyl bromide (TCI); yield 81%; ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 3.87$ (s, 3H), 5.42 (s, 2H), 7.43 (m, $J = 5$ Hz, 5H), 7.72 (s, 1H), 7.78 (s, 1H), 9.20 (s, 1H).

4.2. Solubility of ODA and PMDA in IL or IL/ZI mixtures

ODA or PMDA (10 mg) was added in 2.0 g of IL or IL/ZI mixture, and then the mixtures were stirred for 1 h. After that, solubility of them was evaluated by the visual observation. When the mixed solution turned clear, further PMDA or ODA (10 mg) was added again to the transparent solutions and repeated the addition until the solubility limit. The suspensions, which contain insoluble fraction were heated stepwise on a hot plate and the solubility was measured similarly. The highest concentration thus observed at every temperature was recorded as the solubility.

4.3. Synthesis of ZI (1-(1-butyl-3-imidazolio)butane-4-sulfonate)

ZI was synthesized according to the previous reports.[13] 1-Butylimidazole (Aldrich) (6.2 g, 0.05 mol) was dissolved in acetonitrile (100 ml), and then 1,4-butanesultone (TCI) (6.8 g, 0.05 mol) was added to the solution. The solution was stirred under dry nitrogen at 80 °C for 7 days, and then acetonitrile was evaporated. The obtained yellow powder was washed with acetone. It was further purified by recrystallization from acetonitrile to give 10.5 g (82%) white solid. ^1H NMR (DMSO-d_6, 500 MHz): $\delta = 0.90$ (t, $J = 7$ Hz, 3H), 1.26 (m, $J = 7$ Hz, 2H), 1.54 (m, $J = 8$ Hz, 2H), 1.77 (m, $J = 7$ Hz, 2H), 1.89 (m, $J = 7$ Hz, 2H), 2.45 (t, $J = 8$ Hz, 2H), 4.18 (m, $J = 8$ Hz, 4H), 7.81 (d, $J = 2$ Hz, 2H), 9.24 (s, 1H).

4.4. Synthesis of PI

Synthesis of PI was carried out by the following procedure. ODA (TCI) (0.048 g, 2.4×10^{-4} mol) was added to **3** or **3**/ZI mixture (2.0 g) and then the solution was heated to 70 °C to dissolve it completely. After cooling down the solution to room temperature, PMDA (Aldrich) (0.052 g, 2.4×10^{-4} mol) was added to the solution. The mixture was stirred for 1 h at room temperature, and then heated at 100, 200, and 300 °C for every 1 h. The prepared PI was washed with methanol and the precipitate was separated by filtration. The solid fraction was then dried under vacuum at 45 °C for 1 day. Yield: 73 mg, 73% (in **3**) and 75 mg, 75% (in **3**/ZI).

4.5. Evaluation of inherent viscosity in PI

The inherent viscosity was determined by the following measurement. PI (0.05 g) was dissolved in concentrated sulfuric acid (10 ml) and the solution viscosity was measured with Ubbelohde-type viscometer (KRK, No. U-3195) at 25.0 °C.

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