Thermally Stable Polymer Gel Electrolytes Composed of Branched Polyimide and Ionic Liquid/Zwitterion Mixture Prepared by In Situ Polycondensation

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Branched polyimide was synthesized by in situ polycondensation of 4,4′-oxydianiline, pyromellitic dianhydride, and 1,3,5-tri(4-aminophenyl)benzene in ionic liquid/zwitterion mixture. Compatibility between network and ionic liquids is important to keep gel shape and ionic conductivity. Only 6.0 wt % of polyimide was enough to keep gel state without phase separation or leakage. The obtained polyimide gel showed excellent thermal stability with decomposition temperature of above 300 °C, low glass-transition temperature, and stable ion conduction in a wide temperature range.

As rapid expansion of application of energy devices, improvement in operating temperature range of the batteries has been required. To improve safety of the energy devices, further thermal stability of the compounds is required. Ionic liquids (ILs), which show melting point below 100 °C, have a potential as a liquid with negligible vapor pressure, flame resistance until decomposition temperature, high ionic conductivity, electrochemical stability, and so on.[1] Even when ILs are utilized as ion conductive materials, it is strongly requested to convert there ILs into solid films. Gelation of ILs is one of convenient methods, and various systems have been reported.[2] However, decomposition temperature of general host polymers is generally low (Figure 1, left). Their decomposition temperature was far lower than that of ILs. The use of thermally stable ILs was not reflected to the properties of polymer electrolyte gels. It is therefore strongly required to prepare thermally stable host matrix.

As thermally stable polymers, polyimide is one of strong candidates[3] (Figure 1, right). However, general ILs are incompatible with the starting materials for polyimides. In 2004, Vygodskii, et al. tried to synthesize several polyimides in 1,3-diisopropylimidazolium bromide.[4] However, these halide anion-containing ILs have a few drawbacks such as high melting point, high viscosity, and low ionic conductivity.

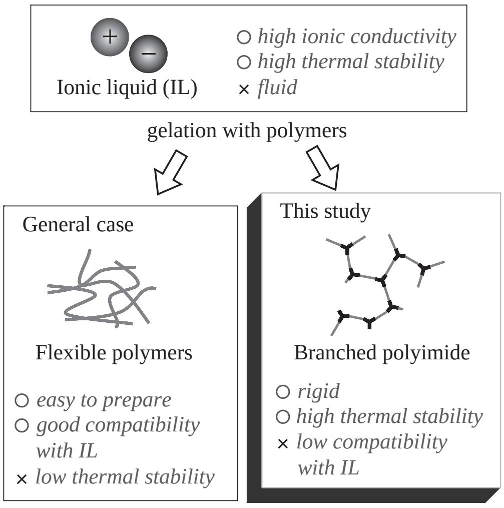

Figure 1. Strategy to prepare polymer gel electrolytes containing ionic liquids.

Then, we first focused ILs composed of bis(trifluoromethane sulfonyl)imide (Tf_2N) anion because of their advantages such as high decomposition temperature, low viscosity, and high ionic conductivity. However, known ILs composed of Tf_2N anion did not dissolve starting materials of polyimides, i.e., 4,4′-oxydianiline (ODA), pyromellitic dianhydride (PMDA). We designed 1-benzyl-3-methylimidazolium Tf_2N (**a** in Figure 2) in which the starting materials were found to be slightly soluble. Addition of imidazolium-type zwitterion, 1-(1-butyl-3-imidazolio)butane-4-sulfonate (**b** in Figure 2) in **a**, was confirmed to improve their solubility.[5] The mixture of **a** and **b** was abbreviated as **c**, hereafter. The objective of this study is to prepare thermally stable polyimide gels by in situ polycondensation in **c**.

Both **a** and **b** were synthesized as reported previously,[5] and **c** was prepared by mixing **a** and **b** in the molar ratio of 6 to 4. As a cross-linker, we used a tri-functional amine, 1,3,5-tri(4-aminophenyl)benzene (TAPB).[6] PMDA, ODA, and TAPB as starting materials were individually dissolved in the **c**. The solutions of PMDA and ODA were mixed with the molar ratio of x:($x - 1$) ($x = 1$–5) and stirred for 1 day at room temperature. The **c** solution of the cross-linker TAPB was added to thus prepared oligo(amide acid) with terminal acid anhydride groups with a stoichiometric ratio of the amino group to the terminal acid anhydride group. Components were added to reach 6.0 wt % as a final polyimide concentration in the **c**. The mixture was further stirred for 4 h at room temperature and then for 5 h at 180 °C. After the products were dried at 60 °C under vacuum to expel generated water molecules, thermogravimetric measurement (TG/DTA 220, Seiko Instruments Inc., from 25 to 500 °C, 5 °C min^{-1}), DSC measurement (DSC-6200, Seiko Instruments Inc., from −120 to 200 °C, 5 °C min^{-1}) and ionic conductivity measurement (Solartron gain phase analyzer, Model 1260, Schlumberger, from 15 to 200 °C) were carried out.

In the case of $x = 1$–4, final products were obtained as brown opaque solids with no phase separation. These gels were prepared with 6.0 wt % polyimides that were enough to keep the gel shape. This is the first report that branched polyimide was synthesized by in situ polycondensation in IL. These polyimide

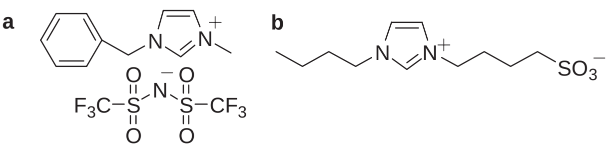

Figure 2. Structure of **a** and **b**.

Table 1. Thermal properties and ionic conductivity of polyimide gels containing **c**

x value	Polyimide content/wt %	$T_d{}^a$/°C	T_g/°C	$\sigma_i{}^b$ /10^{-4} S·cm^{-1}
only **c**	0	326	−48	3.6
1	6	308	−48	1.0
2	6	319	−43	1.4
3	6	320	−49	3.5
4	6	310	−48	1.1

[a] 10 wt % loss. [b] At 50 °C.

gels became soft by increasing x value. In case of $x = 5$, no solid-state product was obtained within the fixed reaction time. This is attributable to the increased viscosity of reaction mixture and steric hindrance between oligo(ODA-PMDA).

Table 1 shows decomposition temperature (T_d), glass-transition temperature (T_g), and ionic conductivity (σ_i) at 50 °C of polyimide gels containing **c**. In every polyimide gel, T_d and T_g are detected above 300 °C and around −50 °C, respectively. These gels showed almost the same thermal properties as that of only **c** as shown in Table 1. It has been reported that polyimide shows no melting point, and its decomposition temperature is above 600 °C.[3] The similarity of T_d clearly indicated that the polyimide matrix is thermally more stable than the **c**. Since the T_d of **b** has measured to be 326 °C by thermogravimetric measurement, the T_d in Table 1 was attributed to the decomposition of **b**. In addition, since T_g of these polyimide gels was similar to that of **c**, it was expected that ionic conductivity of polyimide gels should be the same as that of only **c**. Table 1 also shows σ_i at 50 °C for polyimide gel containing **c**. In comparison with that of only **c**, σ_i of polyimide gel showed no significant difference. Especially, in the case of $x = 3$, these values as shown in Table 1 are almost the same as those for only **c**.

Since polyimide gels were thermally stable, it was expected to be used as ion conductive matrices in a wide temperature range. Figure 3 showed temperature dependence of σ_i for the polyimide gel containing **c** ($x = 3$). In this study, ionic conductivity measurement was carried out from 200 to 15 °C. In our laboratory, ionic conductivity has generally been measured with Peltier devices from 65 to 15 °C. However, the Peltier devices are incapable of heating upper around 70 °C. Thus, ionic conductivity measurement from 200 to 65 °C has carried out with heating apparatus. Measurement at higher temperature cannot be conducted due to properties of heat-conduction sheets around the heater. To collect data at higher temperature range, sample was heated from 65 to 200 °C and then cooled by air during impedance measurement. There was no hysteresis in the ionic conductivity at higher temperature range from 65 to 200 °C under heating and cooling. These two independent data are depicted in the same Arrhenius plots (Figure 3), and a small crack is seen in this at around 65 °C. It is clear that the gel we prepare in this study shows smooth conductivity change by heating and cooling suggesting thermally stable electrolyte gels. Therefore, the present polyimide gel is expected to be novel ion conductive material which was maintained high σ_i even at high temperature.

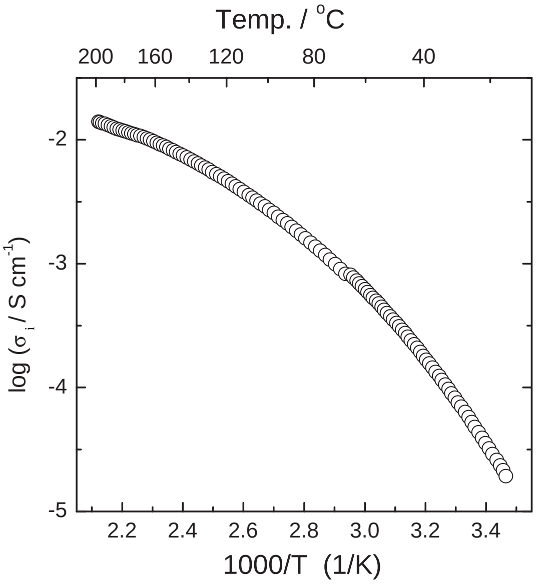

Figure 3. Temperature dependence of ionic conductivity for polyimide gels containing **c** ($x = 3$).

In conclusion, we made polyimide gels in the mixture of ionic liquids and zwitterions. The polyimide gels containing **c** showed excellent thermal stability with decomposition temperature above 300 °C, low T_g, and stable ion conduction in a wide temperature range.

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