

Lithium ion conductive polymer electrolyte by side group rotation

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Abstract

Ionic conductive materials are of much interest as an electrolyte for solid-state lithium batteries. Poly(alkylene oxide) and lithium salt complex exhibits high ionic conductivity in terms of its high solubility for lithium salts. However, the temperature dependency of its ionic conductivity is quite large and non-linear, the ionic conductivity drops down at low temperature, especially below glass transition temperature of the polymer. Because its ionic conductive mechanism is derived from its segmental motion of polymer main chain. A novel ionic conductive material, poly[2,6-dimethoxy-*N*-(4-vinylphenyl)benzamide] is synthesized and confirm ionic conductivity even below glass transition temperature. Ionic conductivity of the polymer with lithium ditrifluoromethylsulfonate imide complex shows 10^{-5} S cm⁻¹ from 0 to 60 °C. Its temperature dependency is linear, namely Arrhenius type dependency. Evaluating from these data, activation energy of ionic conductivity for temperature region from 20 to 60 °C is calculated as 31 kJ mol⁻¹ and that for temperature region from -20 to 20 °C is 11 kJ mol⁻¹. Judging from these results, we conclude that the ionic conductivity of the polymer salt complex derived from 2,6-dimethoxyphenyl group rotation, instead of segmental motion of the polymer.

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1. Introduction

Recently, solid polymer electrolyte becomes much important as a key material for several electrochemical devices, such as rechargeable batteries, electrochromic displays, chemical sensors, and so on. Especially, lithium ion conductive materials are much attractive application for solid polymer electrolyte for lithium polymer rechargeable batteries. Since the discovery of ionic conductivity on poly(ethylene oxide) (PEO) alkali metal complexes, poly(alkylene oxide) and lithium salt complexes are paid much attention as a solid polymer electrolyte with high ionic conductivity [1,2]. Poly(alkylene oxide) and lithium salt complex is considered to be applicable to a solid polymer electrolyte for lithium polymer batteries, in terms of its high solubility of lithium salts and high ionic conductivity of lithium ion. Many efforts to increase ionic conductivity of polymer salt complex have focused on improvement of physical properties polymer, such

as glass transition temperature, elastic constant, and so on [3–5]. Some of them are successful to improve ionic conductivity of polymer salt complexes. However, ionic conductivity of polymer salt complex largely decreases in low temperature, especially below glass transition temperature, because its conductivity strongly depends on the segmental motion of polymer main chain above glass transition temperature [6]. In this paper, we show a novel ion conductive polymer of which ionic conductivity is independent of segmental motion of polymer main chain. This material shows lithium ion conductivity in wide range of temperature, even below glass transition temperature.

2. Experimental

2.1. Materials and physical measurements

All of the starting materials were obtained from commercial sources. The solvents were dried over CaH₂ and distilled under Ar atmosphere before use. All manipulations were carried out under inert atmosphere.

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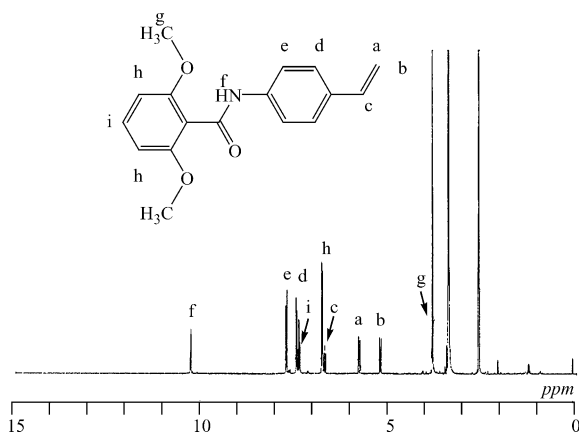


Fig. 1. ^1H NMR spectrum of monomer (3), in dimethylsulfoxide- d_6 .

Mass spectra were measured by Hitachi M-2500 gas chromatography mass spectrometer. ^1H NMR was carried out on a JNM-GSX400 FT-NMR spectrometer, using dimethylsulfoxide- d_6 as a solvent. The molecular weight of obtained polymer was determined by Tosoh HLC-8220GPC gel permeation chromatography equipped with TSK-GEL Super AWM-H column. Differential scanning calorimeter (DSC) was measured by TA instruments DSC2920 differential scanning calorimeter, at heating rate of 5°C min^{-1} . Glass transition temperature (T_g) was determined from the DSC curve of sample.

2.2. Synthesis of

2,6-dimethoxy-*N*-(4-vinylphenyl)benzamide

The monomer, 2,6-dimethoxy-*N*-(4-vinylphenyl)benzamide (3) using as a precursor of a polymer electrolyte was prepared as follows. 2,6-Dimethoxy benzoic acid (1) (0.365 g, 2 mmol) was dissolved in *N*-methyl-2-pyrrolidone (NMP, 1 ml), then added triethylamine (2 mmol) and (2,3-dihydro-2-thioxo-3-benzoxazolyl) phosphonate (DBOP). The solution was stirred for half an hour. Then 4-aminostyrene (2) (0.26 ml, 2 mmol) was added slowly to the solution and stirred for 26 h at room temperature. After stirring, the solution was diluted by methanol into 10 times and dropped into 1% sodium hydrogencarbonate aq. (80 ml) to give a suspension. Crude monomer (3) was isolated by filtration and was dried in vacuo at room temperature. The crude product was purified by recrystallization from ethanol/ethyl acetate (1/2) to give colorless crystals (34% yield). The structure and purity of the product (3) was confirmed by mass spectrometry and nuclear magnetic resonance. δ (ppm): 5.17, 5.74 (d, 2H, $\text{CH}_2=\text{C}-$), 6.68 (q, H, $\text{C}=\text{CH}-$), 7.42 (d, 2H, 2(*o*-phenylene)), 7.71 (d, 2H, 2(*m*-phenylene)), 10.27 (d, H, $-\text{NH}-$), 3.75 (d, 6H, 2($-\text{OCH}_3$)), 6.72 (d, 2H, 2(*m*-phenyl)), 7.34 (t, H, *p*-phenyl). MS: $m/z=283$ (M^+). Elemental analysis: Calcd. C: 72.1, H: 6.1, N: 4.9%, Found C: 72.4, H: 6.2, N: 5.0% (Fig. 1).

2.3. Preparation of the polymer electrolyte

The monomer (3) (5.6 g, 20 mmol) and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (2 equiv. for monomer stoichiometry) were dissolved in acetone, then the solution is casted and polymerized on stainless plate and kept at 80°C in vacuo for 2 days, $M_n=3.9 \times 10^5$, $M_w=1.9 \times 10^6$, respectively.

2.4. Ionic conductivity measurement

Ionic conductivity of the sample is measured by AC impedance of electrochemical cell equipped with blocking stainless steel electrodes. AC impedance of the cell was measured in frequency range from 1 Hz to 3 MHz, and temperature range is from 0 to 60°C , using Solartron 1260 frequency response analyzer and 1287 electrochemical interfaces. The cell is kept in certain temperature atmosphere about half an hour before measure. Bulk resistance (R) is determined with Cole–Cole plot, then calculated ionic conductivity σ along with the following equation:

$$\sigma = d/Rs \quad (3)$$

where σ is the ionic conductivity (S cm^{-1}), d and s are thickness (cm) and area (cm^2) of films, respectively.

3. Results and discussion

Armand et al. have reported the mechanism of ionic conductivity of polymer electrolyte based on PEO [1,2]. Ionic conductivity of PEO based polymer electrolyte is derived from the segmental motion of polymer main chain which causes dynamic rearrangement of coordinating oxygen atoms to a cation. It is obvious that the amorphous phase in the polymer play a central role in the ionic conductivity of the polymer electrolytes [6]. Conductivity of the polymer electrolytes has been studied well above their glass transition temperature (T_g). This phenomenon is interpreted in terms of the empirical equation, such as Vogel–Thammann–Fulcher (VTF) equation [7] or “free-volume” theory [8]. The VTF equation for ionic conductivity σ of a polymer electrolyte is expressed as follows:

$$\sigma = AT^{1/2} \exp[-E_a/R(T - T_0)]$$

where A is a weakly temperature-dependent factor, T_0 corresponds to T_g , and E_a is activation energy. As shown in this equation, ionic conductivity strongly depends on temperature and it drops down especially below glass transition temperature. The temperature dependence of ionic conductivity can be described by a model, in which the segmental motion of the polymer main chain is crucial for ion transport. Strong segmental motion of polymer main chain with simultaneous making and braking of cation–oxygen interactions results in a mode of transport which is quite unlike the hopping mechanism observed in inorganic electrolytes. In order

to improve the ionic conductive performance at low temperature, we have designed a polymer electrolyte based on novel ionic conductive mechanism utilizing rotational motion of side chain functional group, of which relatively smaller activation energy than that of segmental motion of polymer main chain.

Fig. 2 shows the molecular structure of the polymer proposed in this work, poly[2,6-dimethoxy-*N*-(4-vinylphenyl)benzamide] (**4**). The polymer has 2,6-dimethoxyphenyl group as a rotating unit, containing two methoxy group as coordination sites for lithium ion. The 2,6-dimethoxyphenyl group, which has lithium ion coordinate to methoxy group, expect to rotate freely at low temperature, even below glass transition temperature. Lithium ions are expected to be transported by rotational motion of side group. Ueyama et al. have reported that pK_a of phenolic proton is influenced by hydrogen bond. Because hydrogen bond acts as electron-withdrawing group to hydroxy group in phenol [9].

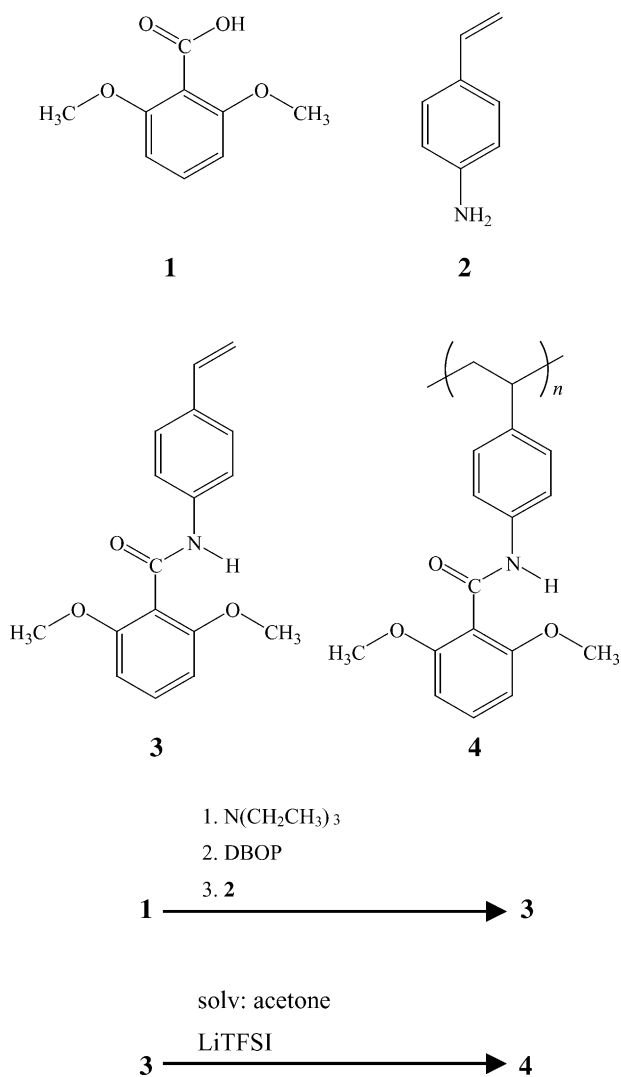


Fig. 2. Structure of synthesized novel polymer electrolyte and its route of synthesis.

In this case, as a result of hydrogen bond between oxygen of 2-methoxy group and proton at amide group, these two methoxy groups shows different coordinating properties each other. Therefore the lithium ion alternates strongly and weakly bonded to methoxy group with rotation of the 2,6-dimethoxyphenyl group. That is to say, lithium ion coordinating to the methoxy group in $-C=O$ side is more stable than that in $-N-H$ side by hydrogen bond. Then coordinated lithium ion to methoxy group in $-N-H$ side is released, and transported to other near methoxy group in $-C=O$ side. As a consequence of rotational motion, lithium ions coordinating to methoxy group, can easily exchange with that of adjacent side group in this polymer, and expected to shows its ionic conductivity. In general rotating energy between single bond is about a few kJ mol^{-1} . Because of its low activation energy, temperature dependence of ionic conductivity is expected to decrease by utilizing rotational motion of side group for ion transport, instead of segmental motion of polymer main chain.

To confirm this ion transport mechanism, the polymer (**4**) has synthesized. After adding lithium ditrifluoromethylsulfonate imide (LiTFSI) as lithium salt for 2 equiv. versus monomeric unit, temperature dependence of its ionic conductivity of the polymer salt complex. Fig. 3 shows temperature dependence of ionic conductivity of the polymer in temperature range from -20 to 60°C . Ionic conductivity of the polymer (**4**) salt complex shows $10^{-5} \text{ S cm}^{-1}$ in this temperature range, while that of PEO salt complex drops down to $10^{-8} \text{ S cm}^{-1}$ at low temperature. Thus it shows VTF type temperature dependency of ionic conductivity. Comparing with PEO salt complex, the polymer (**4**) salt complex shows large ionic conductivity, especially in low temperature. As shown in Fig. 3, ionic conductivity of the polymer (**4**) salt complex indicates linear temperature dependency and the temperature dependency becomes smaller, namely Arrhenius type dependency, rather than VTF. Temperature dependency

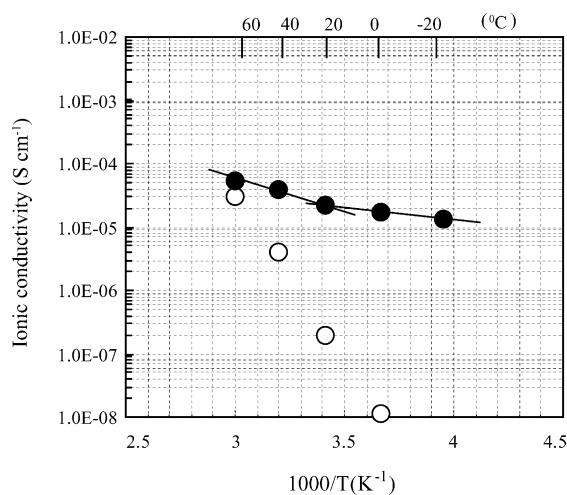


Fig. 3. Arrhenius plot of ionic conductivity of polymer (**4**) salt complex (black circle), in comparison with PEO polymer complex (white circle).

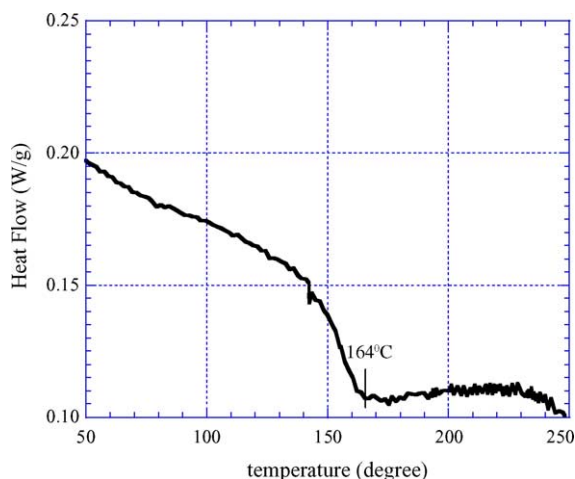


Fig. 4. DSC curve of the polymer (4) at heating rate of $5^{\circ}\text{C min}^{-1}$.

of ionic conductivity for lower temperature, namely below 20°C , is different from that for higher temperature. The activation energy is calculated for higher temperature region and lower temperature region, respectively. Evaluating from Fig. 3, activation energy of ionic conductivity for temperature region from 20 to 60°C is calculated as 31 kJ mol^{-1} and that for temperature region from -20 to 20°C is 11 kJ mol^{-1} . On the other hand, the glass transition temperature of the polymer is 164°C evaluated from DSC curve of the sample, as shown in Fig. 4. In the case of polymer salt complex, its glass transition temperature is lower than polymer itself, because an excess salt acts as plasticizer. Judging from these results, ionic conductivity of this material shows even below its glass transition temperature, especially below 20°C , it means that segmental motion of the polymer main chain should be freeze, lithium ion can be transported in polymer matrix. Above 20°C , its ionic conductivity is influenced by the segmental motion of polymer main chain.

4. Conclusions

In conclusion, we synthesize a novel ionic conductive material, poly[2,6-dimethoxy-*N*-(4-vinylphenyl)benzamide] (4) and confirm ionic conductivity even below glass transition temperature. Ionic conductivity of the polymer (4) with lithium ditrifluoromethylsulfonate imide complex shows 10^{-5} S cm^{-1} from -20 to 60°C . Its temperature dependency is linear, namely Arrhenius type dependency. Evaluating from these data, activation energy of ionic conductivity for temperature region from 20 to 60°C is calculated as 31 kJ mol^{-1} and that for temperature region from -20 to 20°C is 11 kJ mol^{-1} . Judging from these results, we conclude that the ionic conductivity of the polymer (4) salt complex derived from 2,6-dimethoxyphenyl group rotation, instead of segmental motion of the polymer.

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