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Lithium ion conductivity of polymers containing *N*-phenyl-2,6-dimethoxybenzamide framework in their side chains: possible role of bond rotation in polymer side chain substituents for efficient ion transport

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Abstract:

A new carbon—carbon main chain polymer with *N*-phenyl-2,6-dimethoxybenzamide on its each main chain carbon atom is prepared by Pd-initiated polymerization of diazoacetate containing the benzamide group, and the Li ion conductivity of the polymer doped with lithium bis(trifluoromethylsulfonyl)imide is evaluated along with its vinyl polymer counterparts with the same benzamide substituent. Although the expected high ion conductivity at low temperatures derived from a unique ion transport mechanism based on the bond rotation in the benzamide moiety reported in a literature is not observed, it is revealed that the dense packing of the benzamide group along the polymer main chain results in the enhanced ion conductivity. In addition, investigation of the correlation between ion conductivity and glass transition temperature of these solid polymer electrolytes (SPEs) reveals that other ion transport mechanism would operate in the benzamide containing SPEs than that derived from segmental motion of polymer chains observed in PEO-based SPEs.

Keywords:

Solid polymer electrolyte, Li ion conductive material, *N*-phenyl-2,6-dimethoxybenzamide,

Pd-initiated polymerization of diazoacetate

1. Introduction

Solid polymer electrolytes (SPEs) have attracted much attention as ion conducting materials with some important advantages over electrolyte materials with low molecular weight flammable and volatile liquid [1]. As a polymer for SPEs, poly(ethylene oxide) (PEO) is most representative and frequently employed, where Li cation coordinates oxygen atoms in the polymer backbone and Li cation is transported with segmental motion of the polymer chain [2-6]. Although somewhat high Li conductivity has been achieved with PEOs doped with an appropriate Li salt, the drawback of the materials is that the conductivity significantly drops at lower temperatures, especially below glass transition temperature (T_g) of the Li salt-doped PEOs, where the polymer segmental motion is greatly suppressed. To overcome the defect of the PEO-based SPEs, poly[2,6-dimethoxy-*N*-(4-vinylphenyl)benzamide] **poly1** (Chart 1) was prepared by Nishimura and coworkers in 2005 [7], and was proposed as a new SPE material, where not the segmental motion of a polymer chain but C—C bond [C(carbonyl)—C(Ph)] rotation in the side chain benzamide moiety was supposed to induce an efficient ion transport with much lower activation energy, thus, resulting in the high conductivity even at low temperatures. Actually, it was reported that the conductivity of **poly1**-doped with lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) in the order of 1×10^{-4} - 10^{-5} S cm⁻¹ was retained down to -20 °C, suggesting the effectiveness of the use of the bond rotation with lower activation energy instead of segmental motion of a polymer chain for ion transport [7].

If the above-mentioned ion transport with bond rotation actually operates, because the Li

cation should be exchanged between adjacent substituents along the polymer main chain, more dense packing of the side chain substituents would be favorable for an efficient ion transport. In that context, our originally developed Pd-initiated polymerization of diazoacetates could be quite advantageous, because the resulting polymer, poly(alkoxycarbonylmethylene), has an ester substituent at each main chain carbon atom, leading to dense packing of the substituents around the C-C main chain [8-12], if we can prepare an appropriate diazoacetate monomer containing the *N*-phenyl-2,6-dimethoxybenzamide group and the monomer can be polymerized as expected.

In this paper, we tried to examine the possibility of developing a new SPE material by the polymerization of a diazoacetate bearing the *N*-phenyl-2,6-dimethoxybenzamide group as an ester substituent. The main chain of the resulting polymer **poly2'** (Chart 1) should be densely surrounded with the benzamide group, hopefully realizing a high ion conductivity with the combination of ion transport with the bond rotation and dense packing of the transporting groups. To confirm the effect of dense packing of the substituents, we prepared a vinyl polymer counterpart, **poly3**, with the same benzamide substituent as well, and also **poly1** itself, as following the literature [7] for precise comparison of the ion conductivities.

Chart 1. Structures of **poly1**, **poly2'**, and **poly3**.

2. Experimental

2.1. Materials.

Tetrahydrofuran (THF: Junsei Chemical, 99%) was dried over Na/K alloy and distilled before use. *t*-Butyldimethylchlorosilane (TCI, >98%), imidazole (TCI, 98%), 4-(2-hydroxyethyl)aniline (Aldrich, 98%), 2,6-dimethoxybenzoic acid Wako, 99%), triethylamine (Et₃N: Wako, 99%), *N*-methylpyrrolidone (NMP: Wako, 99%), tetrabutylammonium fluoride (TBAF: 1.0 M in THF, TCI), bromoacetyl bromide (TCI, >98%), pyridine (Wako, 99.5%), *N,N*-dimethylformamide (DMF: Nacalai Tesque, 99.5%, H₂O < 50ppm), 1,8-diazabicyclo[5.4.0]-7-undecene (DBU: Nacalai Tesque, 97%), acryloyl chloride (TCI, 95%), (□-allylPdCl)₂ (Strem Chem, 99%), NaBPh₄ (Kanto Chemical, >99.5%), 1,1'-azobis(cyclohexane-1-carbonitrile) (VAZO: Wako, 95%), lithium bis(trifluoromethylsulfonyl)imide (LiTFSI: Kishida Chemical, > 99.9%) were used as received. Monomer **1** [7], (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate **8** [13], *N,N'*-Ditosylhydrazine [14], were prepared according to the literatures. **Caution!** Extra care must be taken for preparation and handling of the diazo compounds because of their potential explosiveness.

2.2. Monomer Syntheses.

2.2.1. 4-(2-*t*-butyldimethylsilyloxyethyl)aniline **6**.

Under a N₂ atmosphere, a THF (40 mL) solution of *t*-butyldimethylchlorosilane (24.7 g,

164 mmol) was added to a THF (370 mL) solution of a mixture of imidazole (22.3 g, 328 mmol) and 4-(2-hydroxyethyl)aniline (15.0 g, 109 mmol) at room temperature, and the resulting mixture was stirred for 2.5 h at room temperature. After a minimum amount of water to dissolve the HCl salt of imidazole was added to the mixture, a large part of THF was removed using an evaporator. An organic layer was separated with a separatory funnel after adding ethyl acetate and water, and the organic layer was dried over Na₂SO₄. Volatiles were removed under reduced pressure from the filtrated solution, to give crude **6** quantitatively. ¹H NMR (400 MHz, CDCl₃, δ): 6.95-7.03 (m, 2H, Ar-H), 6.58-6.66 (m, 2H, Ar-H), 3.75 (m, 2H, CH₂-O), 3.4-4.0 (br, 2H, NH₂), 2.72 (m, 2H, CH₂-Ar), 0.88 (s, 8H, *t*Bu), 0.00 (s, 6H, Me₂Si).

2.2.2. *N*-[4-(2-hydroxyethyl)phenyl]-2,6-dimethoxybenzamide **10**.

Under a N₂ atmosphere, 2,6-dimethoxybenzoic acid **7** (19.9 g, 110 mmol), Et₃N (15.2 mL, 110 mmol), and (2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate **8** (46.2 g, 120 mmol) were dissolved in *N*-methylpyrrolidone (60 mL). After a gradual addition of **6** (27.5 g, 110 mmol), the reaction mixture was stirred at room temperature for 26 h. After an aqueous solution of 3% NaHCO₃ (3%, 1500 mL) was added, an organic layer was extracted with ethyl acetate using a separatory funnel. The organic layer was dried over Na₂SO₄, and volatiles were removed under reduced pressure from the filtrated solution, to give crude **9**, which was directly subjected to the following desilylation without purification. Under a N₂ atmosphere, the crude **9** obtained from the above-described procedure was dissolved into THF (550 mL). A THF solution of

tetrabutylammonium fluoride (TBAF, 1.0 M, 95 mL, 95 mmol) was gradually added to the solution, and the reaction mixture was stirred at room temperature for 40 min. An aqueous solution of HCl (1 M, 600 mL) was added, and the mixture was stirred at room temperature overnight. An organic layer was separated with chloroform using a separatory funnel, and the organic layer was dried over Na₂SO₄, and volatiles were removed under reduced pressure from the filtrated solution. By washing the residual solid with a small amount of CH₂Cl₂ afforded pure **10** in 48% total yield from the initially employed **7**.

¹H NMR (400 MHz, CDCl₃, δ): 7.53-7.65 (m, 2H, Ar-H), 7.35-7.46 (br, 1H, NH), 7.30 (m, 1H, Ar-H), 7.13-7.26 (m, 2H, Ar-H), 6.52-6.64 (m, 2H, Ar-H), 3.74-3.90 (m, 8H, MeO and OCH₂), 2.78-2.90 (m, 2H, ArCH₂), 1.38 (br, 1H, OH).

2.2.3. *N*-[4-(2-diazoacetoxyethyl)phenyl]-2,6-dimethoxybenzamide **2**.

This compound was prepared following the general procedure for the synthesis of diazoacetates reported by Fukuyama et al [14]. Under a N₂ atmosphere, bromoacetyl bromide (2.6 mL, 30 mmol) was added dropwise to a stirred solution of **10** (6.0 g, 20 mmol) and pyridine (4.8 mL, 60 mmol) in DMF (135 mL) cooled at 0 °C, and the mixture was stirred for 10 min at 0 °C. After addition of H₂O (150 mL), the mixture was extracted with CH₂Cl₂ three times, and the combined CH₂Cl₂ phase was dried over Na₂SO₄. After filtration and removal of the solvent under reduced pressure, the residual liquid was placed in a round-bottomed flask. *N,N'*-Ditosylhydrazine (13.6 g, 39.8 mmol) and 135 mL of DMF was added to the flask, and the mixture was cooled to 0 °C and

stirred for 10 min. After DBU (14.9 mL, 99.6 mmol) was added dropwise to the mixture, it was stirred for 10 min at 0 °C. Saturated NaHCO₃ aqueous solution was added, and it was extracted with CH₂Cl₂ three times. The combined CH₂Cl₂ phase was washed with saturated NaCl aqueous solution, dried over Na₂SO₄, and filtrated. Volatiles were removed from the resulting solution under reduced pressure, and the residue was purified with silica gel short column (eluent: CHCl₃/MeOH = 9 : 1) and preparative SEC (eluent: CHCl₃) to give **2** in 27 % yield.

¹H NMR (400 MHz, CDCl₃, δ): 7.56-7.66 (m, 2H, Ar-H), 7.50 (br, 1H, NH), 7.32 (m, 1H, Ar-H), 7.14-7.24 (m, 2H, Ar-H), 6.54-6.68 (m, 2H, Ar-H), 4.73 (br, 1H, CH=N₂), 4.36 (t, 2H, OCH₂), 3.86 (s, 6H, MeO), 2.94 (t, 2H, ArCH₂). ¹³C NMR (100 MHz, CDCl₃, δ): 166.8, 163.8, 157.7, 137.1, 133.5, 131.2, 129.5, 119.9, 116.1, 104.2, 65.4, 56.2, 46.3, 34.9. Anal. Calcd. for C₁₉H₁₉N₃O₅: C, 61.78; H, 5.18; N, 11.38. Found: C, 61.72; H, 5.15; N, 10.46.

2.2.4. *N*-[4-(2-acryloyloxyethyl)phenyl]-2,6-dimethoxybenzamide **3.**

Under a N₂ atmosphere, **10** (5.0 g, 17 mmol) and Et₃N (3.5 mL, 25 mmol) were dissolved in THF (200 mL) and cooled to 0 °C. After acryloyl chloride (2.0 mL, 25 mmol) was added, the reaction mixture was stirred at room temperature for 3h. After water and chloroform were added, an organic layer was separated by using a separatory funnel. The organic layer was dried over Na₂SO₄, and after filtration, volatiles were removed under reduced pressure from the filtrate. Purification of the residue with preparative SEC (eluent: chloroform) afforded **3** in 97% yield.

¹H NMR (400 MHz, CDCl₃, δ): 7.56-7.66 (m, 2H, Ar-H), 7.43 (br, 1H, NH), 7.32 (m, 1H,

Ar-H), 7.17-7.24 (m, 2H, Ar-H), 6.55-6.66 (m, 2H, Ar-H), 6.35-6.45 (m, 1H, =CH₂), 6.05-6.18 (m, 1H, -CH=), 5.78-5.87 (m, 1H, =CH₂), 4.36 (t, 2H, OCH₂), 3.84 (s, 6H, MeO), 2.97 (t, 2H, ArCH₂). ¹³C NMR (100 MHz, CDCl₃, δ): 166.2, 163.7, 157.6, 137.1, 133.5, 131.1, 130.8, 129.4, 128.5, 119.8, 116.0, 104.2, 65.1, 56.1, 34.6. Anal. Calcd. for C₂₀H₂₁NO₅: C, 67.59; H, 5.96; N, 3.94. Found: C, 67.84; H, 5.97; N, 3.91.

2.3 Polymerization procedures.

2.3.1. Pd-initiated Polymerization of 2.

Under a N₂ atmosphere, a THF (10 mL) solution of (□-allylPdCl)₂ (17.8 mg, 0.0483 mmol) was placed in a Schlenk tube and cooled to -78 °C. NaBPh₄ (50.1 mg, 0.146 mmol) was added to the solution at -78 °C and the mixture was stirred for 10 min. A THF (20 mL) solution of **2** (0.900 g, 2.44 mmol) was added to the mixture at -78 °C, and it was warmed to room temperature and stirred for 13 h. After 1 N HCl/MeOH, 1 N HCl aqueous solution, and CHCl₃ were added to the mixture, the CHCl₃ phase was separated using a separatory funnel, and the aqueous phase was extracted with CHCl₃. The combined CHCl₃ phase was washed with 1N HCl aqueous solution and water, dried over Na₂SO₄, filtered, and concentrated under reduced pressure to afford a crude product. Purification with preparative recycling SEC gave **poly2'** in 24% yield.

2.3.2. Radical Polymerization of 3 and 1.

Under a N₂ atmosphere, a DMF (5 mL) solution of **3** (0.500 g, 1.41 mmol) and

1,1'-azobis(cyclohexane-1-carbonitrile) (VAZO, 13.8 mg, 0.0563 mmol) were placed in a Schlenk tube and degassed by freeze-pump-thaw procedure three times. The mixture was heated to 100 °C and stirred at that temperature for 20 h. After the volatiles were removed under reduced pressure, the residue was purified by using preparative SEC (eluent: CHCl₃) to afford **poly3** in 77% yield,

Radical polymerization of **1** was carried out in a similar procedure, to afford **poly1** in 31% yield.

2.3.3. Anionic Polymerization of **1 with LiTSFI.**

Anionic polymerization of **1** initiated with LiTSFI was carried out according to the literature [7], and the sample was used for conductivity measurement without purification.

2.4. Measurements.

The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were measured by means of size exclusion chromatography (SEC) on a Jasco-ChromNAV system equipped with a differential refractometer detector using THF as eluent at a flow rate of 1.0 mL min⁻¹ at 40 °C, calibrated with poly(methyl methacrylate). The column used for the GPC analyses was a combination of Styragel HR4 (Waters; 300 mm × 7.8 mm² i.d., 5 μm average particle size, exclusion molecular weight of 600K for polystyrene) and Styragel HR2 (Waters; 300 mm × 7.8 mm² i.d., 5 μm average particle size, exclusion molecular weight of 20K for polystyrene), and poly(methyl methacrylate) standards

(Shodex M-75, $M_p = 212000$, $M_w/M_n = 1.05$, $M_p = 50000$, $M_w/M_n = 1.02$, $M_p = 22600$, $M_w/M_n = 1.02$, $M_p = 5720$, $M_w/M_n = 1.06$, $M_p = 2400$, $M_w/M_n = 1.08$) and dibutyl sebacate were used for the calibration. Purification by preparative recycling SEC was performed on a JAI LC-918R equipped with a combination of columns of a JAIGEL-3H (600 mm $\times$ 20 mm² i.d., exclusion molecular weight of 70K for polystyrene) and a JAIGEL-2H (600 mm $\times$ 20 mm² i.d., exclusion molecular weight of 5K for polystyrene) for polymers and a combination of columns of a JAIGEL-2H and a JAIGEL-1H (600 mm $\times$ 20 mm² i.d., exclusion molecular weight of 1K for polystyrene) for monomers, using CHCl₃ as eluent at a flow rate of 3.8 mL min⁻¹ at 25 °C. The sample solution (3 mL containing ca. 0.3 g of the crude product) was injected and recycled before fractionation. ¹H (400 MHz) and ¹³C (100 MHz) NMR spectra were recorded on a Bruker Avance 400 spectrometer in chloroform-*d* (CDCl₃) or dimethyl sulfoxide (DMSO)-*d*₆ at room temperature for monomers or at 50 °C for polymers. ¹H NMR spectra were referenced with internal standard tetramethylsilane ($\delta = 0$ ppm) and ¹³C NMR spectra were referenced by solvent shifts (77.16 ppm). The glass transition temperature (T_g) of the polymer was determined by differential scanning calorimetry (DSC; TA Instruments; Q1000). The heating and cooling rates were 20 °C min⁻¹. The glass transition temperature (T_g) of the polymers was defined as the temperature of the midpoint of a heat capacity change on the second heating scan. Elemental analyses were performed on a YANAKO CHN Corder MT-5.

Ionic conductivity was determined from impedance values measured in a following

manner. In a glove box under a N₂ atmosphere, a polymer sample and LiTFSI was mixed in a ratio of [LiTFSI]/[O] = 1.0 ([LiTFSI] = 2 x [repeating unit]) by using acetonitrile as a solvent. After the solvent was removed under reduced pressure, the residual polymer-Li salt complex was dried under vacuum at 60 °C overnight, and was introduced into a cell for the impedance measurement, which was conducted with an impedance meter (Solartron analytical; 1400 cell test or 1470E cell test) under dry nitrogen from -10 to 80°C.

3. Results and Discussion

3.1. Preparation of polymers containing *N*-phenyl-2,6-dimethoxybenzamide group for Li ion conductivity measurement

At first, as a straightforward application of the reported polymer structure of poly[2,6-dimethoxy-*N*-(4-vinylphenyl)benzamide] **poly1**, we tried to prepare and polymerize diazoacetate monomer **4**, with the *N*-phenylbenzamide group directly attached to the ester group in the diazocarbonyl moiety in place of the styrenic C=C in **1** (Scheme 1). However, preliminary attempts for the polymerization of **4** revealed the low polymerizability of **4**, resulting in no polymer formation from **4** using standard conditions for our Pd-initiated polymerization of diazoacetates. We attributed the results to the low reactivity and low solubility of both the monomer and propagating polymeric species, owing to the direct connection between the *N*-phenylbenzamide and ester groups. Accordingly, in order to improve the reactivity and solubility, we incorporated an ethylene (-CH₂CH₂-) spacer between the *N*-phenylbenzamide and ester groups; the synthetic scheme for the modified monomer **2** is shown in Scheme 2, where the silyl-protected 4-(2-hydroxyethyl)aniline **6** was acylated with 2,6-dimethoxybenzoic acid, followed by diazoacetylation of the deprotected alcohol **10** affording **2**. Likewise, acrylate type monomer **3** for the synthesis of a vinyl polymer counterpart **poly3** was prepared by the reaction of acryloyl chloride with the deprotected alcohol **10**.

Scheme 1. Benzamide-containing monomers and polymers.

Scheme 2. Preparation of benzamide-containing monomers and polymers.

The polymerization of **2** was conducted under the standard conditions for other alkyl diazoacetates such as ethyl diazoacetate (EDA), with $\pi\text{-allylPdCl/NaBPh}_4$ in THF at room temperature (Scheme 2). With a rather low [monomer]/[Pd] ratio of 20, we can obtain a polymeric product **poly2'** in 24% yield, whose ^1H NMR spectrum is shown in Fig. 1 along with that of monomer **2**. In the spectrum of **poly2'** in Fig. 1(b), there is no signal at the 4.7 ppm, where a signal for $\text{N}_2=\text{CH}$ appears in the spectrum of **2**. On the other hand, in the spectrum of **poly2'**, all the signals assignable to the repeating unit structure appear as broad signals, including the signal for the

main chain CH appearing at 3.0-3.6 ppm. From the ^1H NMR spectra, we can conclude that the polymerization of **2** proceeded to afford **poly2'** as shown in Scheme 2. As for molecular weight of the **poly2'** sample, the low solubility of the polymer in THF hampered the SEC measurement. However, the measurement of a THF-soluble part of the **poly2'** showed $M_n = 2500$, suggesting that M_n of the whole sample should be much higher than the M_n value. In addition, the broad signal for the **poly2'** sample also indicated that the product is polymeric compound with rather high M_n .

As reported in our previous publications in detail [8-12], the conditions employed here afford polymers with $M_n >$ a few tens of thousands when applied for polymerization of common monomers such as ethyl and benzyl diazoacetates. Even though polymeric products were obtained from **2** by the introduction of the ethylene spacer, the unsatisfactory polymerization results indicate difficulty of obtaining high molecular weight polymers from the *N*-phenylbenzamide-containing monomers. Further, a similar difficulty was observed in radical polymerization of both acrylic and styrenic monomers containing the *N*-phenylbenzamide as described below.

Fig. 1. ^1H NMR spectra of **2** (a) and **poly2'** (b).

Acrylate monomer **3** with the benzamide group was polymerized via radical polymerization using 1,1'-azobis(cyclohexane-1-carbonitrile) (VAZO) as an initiator in DMF as a solvent at 100 °C, resulting in the formation of **poly3**, whose THF soluble part possessed $M_n = 1800$ and ^1H NMR spectrum is shown in Fig. 2 along with that of monomer **3** (Scheme 2). In a similar manner as described for polymerization of **2**, $\text{CH}_2=\text{CH}$ -signals in **3** completely disappear in the spectrum of **poly3**, and all the signals became broad and CH_2 and CH signals in the main chain appears as expected for the progress of the polymerization.

Fig. 2. ^1H NMR spectra of **3** (a) and **poly3** (b).

In addition, to confirm the reported results of the effect of bond rotation for high ion conductivity, we prepared by ourselves 2,6-dimethoxy-*N*-(4-vinylphenyl)benzamide **1** and conducted radical polymerization of **1** using VAZO in DMF (Scheme 1), although in the literature the polymerization of **1** for the sample preparation for ion conductivity measurement was performed via anionic initiator LiTFSI, which also acts as a Li cation doping agent [7]. Again, the progress of the polymerization was confirmed by comparison of ^1H NMR spectra of the monomer and the product (See Fig. S1 in supplementary data for the spectra). The SEC measurement of the THF soluble part of the **poly1** sample revealed that M_n of the soluble part was 1800.

3.2. Li conductivity measurement of polymers containing *N*-phenyl-2,6-dimethoxybenzamide group

All the polymer samples were subjected to Li ion conductivity measurement, including a commercial PEO sample ($M_n = 2000$) for comparison. As for **poly1**, in addition to the isolated sample, an *in situ* generated **poly1** with the anionic initiation with LiTFSI was also prepared following the literature procedure [7], and its ion conductivity was evaluated. For comparison, the [LiTFSI]/[O] ratio was adjusted to 1.0 for all the measurements, following the literature [7]. No sample degradation was observed during the measurement, indicating that the polymers possesses enough electrochemical stability as SPE materials at least under the conditions we employed.

The results of the measurement are shown in Fig. 3. First of all, at lower temperatures, we could not reproduce the reported preservation of the same order conductivity as those at higher temperatures. As shown in Fig. 3, for the measurement of the isolated **poly1**-doped with LiTFSI, the conductivity value at 60 °C ($1.69 \times 10^{-5} \text{ S cm}^{-1}$, which is about 1/30 of the reported value of the *in situ* prepared sample) drops to $1.18 \times 10^{-8} \text{ S cm}^{-1}$ at 10 °C. When the sample was prepared *in situ* following the reported procedure [7], the conductivity value increased to $1.35 \times 10^{-5} \text{ S cm}^{-1}$ at 60 °C, which is still about 1/4 of the reported value, and again decreased with the decreasing temperature to $5.83 \times 10^{-8} \text{ S cm}^{-1}$ at 10 °C. By ^1H NMR analysis of the *in situ* prepared sample

(Fig. S2 in supplementary data), we observed the presence of unreacted monomer in 14 mol% of the original amount, which could be the reason for the conductivity increase compared to the isolated polymer-derived sample. At the moment, the reason for the discrepancy from the reported data is not clear, but technical details for the sample preparation and conductivity measurement could impart strong influence for the conductivity results.

Fig. 3. The temperature dependence of ionic conductivity of different SPEs.

On the other hand, the comparison of the conductivity of doped samples of **poly2'**, **poly3**, and PEO reveals interesting trend. As shown in Fig. 3, in a temperature range of 80 to 25 °C, these three samples exhibit the same level of conductivity with slight difference of an order of **poly2'** >

PEO > **poly3**. At 10 °C, the difference became more apparent with the actual values of 8.76×10^{-7} (**poly2'**), 4.63×10^{-7} (PEO), and 1.91×10^{-7} (**poly3**) (1.89 : 1 : 0.41); at -10 °C, the difference between **poly2'** and PEO became even larger: 3.39×10^{-8} (**poly2'**), 1.02×10^{-8} (PEO), and 4.89×10^{-9} (**poly3**) (3.32 : 1 : 0.48). Interesting to note is that, even though the conductivity at higher temperatures was not retained at lower temperatures, the benzamide-containing **poly2'** is actually effective as a medium for Li ion transport like PEO. Considering the T_g of the polymers doped with LiTFSI as described in the following section, it seems reasonable to assume that other mechanism such as bond rotation than segmental motion as in PEO actually operate in the benzamide-containing polymers. In addition, we can clearly demonstrate that the dense packing of the benzamide-framework in **poly2'** is quite effective for high Li conductivity as most clearly shown in the about 7 times higher conductivity of **poly2'** compared to that of its vinyl polymer counterpart **poly3** at -10 °C. It should also be noted that the conductivity of **poly2'** is higher than that of PEO in the whole range of the temperature.

3.3. Evaluation of the relationship between Li conductivity and glass transition temperature of SPEs containing N-phenyl-2,6-dimethoxybenzamide group

It has been recognized that there is a close relationship between SPE materials conductivity

and their T_g s. For example, in the case of PEO, because the conductivity arises from the segmental motion of the polymer chain, their conductivity has been reported to markedly drop below T_g of the polymer-salt complexes. We have measured T_g s of the benzamide-containing polymers, **poly2'**, **poly3**, and **poly1** (isolated polymer sample) and their LiTFSI complexes, including the Li salt complex of PEO employed in our measurements (Table 1). In the case of SPE such as PEO utilizing the segmental motion of polymer chain for the ion transport, the addition of a Li salt is expected to raise the T_g because the Li cation would coordinate some oxygen atoms intermolecularly, resulting in the pseudo-crosslinking and thus, higher T_g value than that of the parent polymer alone. Indeed, the T_g of PEO-LiTFSI complex in our measurement is $-16\text{ }^{\circ}\text{C}$, about $40\text{ }^{\circ}\text{C}$ higher than the reported T_g of PEO alone. On the contrary, it is quite interesting to find that T_g s of the benzamide-containing polymers became lower by the complexation with LiTFSI. In particular, for **poly2'** and **poly1**, huge decrease of T_g s in a degree of about $150\text{ }^{\circ}\text{C}$ was observed, while the T_g decrease was much moderate for **poly3** (about $60\text{ }^{\circ}\text{C}$). The decrease of T_g of the benzamide-containing polymers can be reasonably explained based on the assumption that the Li cation does not coordinate the benzamide moiety intermolecularly, but only within the side chain framework intramolecularly, as described in the ion transport mechanism originally proposed in the literature [7], resulting in enhanced segmental motion of the whole polymer chain with the ion exchange. We can also assume that the complexation of the side chains with Li cation would interfere conceivable intermolecular H-bonding interaction between the benzamide groups, resulting

in the higher molecular motion of the polymer chain leading to lowering of T_g .

In addition, by comparing the T_g data in Table 1, we can realize that the commonly observed correlation between T_g and conductivity for PEO-based SPEs (lower T_g leads to higher conductivity) does not prevail here; apparently conductivity of **poly1** with lower T_g showed lower conductivity than **poly2'** and **poly3** with higher T_g s. These results strongly suggest that the ion conduction mechanism in these benzamide-containing polymers is totally different from that in polymers with segmental motion-derived conductivity. Likewise, it is worthwhile to mention that the conductivity of **poly2'** is higher than that of PEO with much lower T_g .

Table 1. Glass transition temperature of polymers and their LiTFSI complexes^a

Polymer	polymer alone °C	polymer-LiTFSI complex °C
Poly2'	187	40
Poly3	103	43
Poly1	117	−37
PEO	−63 ^b	−16

^a See Fig. S3 in supplementary data for DSC charts.

^b Reported in a literature [15].

4. Conclusions

Three types of polymers [styrenics (**poly1**), poly(alkoxycarbonylmethylene) (**poly2'**), and

acrylics (**poly3**) containing *N*-phenylbenzamide group were prepared and their Li conductivities were evaluated. Although the characteristic conduction behavior at lower temperature reported in the literature [7] was not reproduced in our experiments, we succeeded in revealing some unique characters of these polymers with respect to their application as SPE materials: (1) **poly2'** shows the highest conductivity among them, clearly indicating the effect of dense packing of the benzamide groups around the polymer backbone, (2) the conductivity of **poly2'** exceeds that of PEO, which is the most representative SPE materials, and (3) based on the relationship between the conductivity and T_g , the ion conductive mechanism for these benzamide-containing polymers could be totally different from that derived from segmental motion of polymer chain observed in PEO-based SPEs. These unique characteristics present the promising potential of strategy using densely packed conducting groups and the *N*-phenylbenzamide group for SPE material development. Further investigation along this line is now underway in this laboratory.

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