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Attempts at Lithium Single-Ionic Conduction by Anchoring Sulfonate Anions as Terminating Groups of Oligo(oxyethylene) Side Chains in Comb-Type Polyphosphazenes

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Novel comb-type polyphosphazenes with anchored lithium sulfopropyl oligo(oxyethylene) side chains [SEP] were synthesized by a one-step reaction with lithium bisulfite and polyphosphazenes containing oligo(oxyethylene) side chains terminated with allyl groups [AEP]. The dc ionic conductivity (σ) of SEP was measured using lithium electrodes and compared with hybrid (polymer–salt complexes) between $LiSO_3CF_3$ and the corresponding non-sulfonate comb-type polymer [MEP], i.e., poly{bis[ω-methoxyoligo(oxyethylene)]phosphazene}. While the time dependence of σ/σ_0 (σ_0: initial conductivity) of SEP showed a constant value, that of the hybrid system drastically decreased with time due to the self-polarization by mobile anions. The stationary values of σ after prolonged electrolysis were 7.1×10^{-8} S cm^{-1} for SEP and 8.5×10^{-7} S cm^{-1} for the hybrid at 1.0-V dc supply.

Introduction

Lithium rechargeable batteries that can supply 3 V from a single cell are important for driving large-scale integrations (LSI) or related devices such as liquid-crystal displays (LCD) and electrochromic displays (ECD). Solid electrolytes with high ionic conductivities are desirable for such batteries due to much simpler cell construction, easier processing, and packaging that might result in extrathin cells.

Solid electrolytes of alkali metal salt/polymer hybrids have been extensively studied.[1] When used in a battery, two ionic species, i.e., lithium cations and their counter-anions, migrate between two electrodes during the charging or discharging processes. In such "biionic" conductors, the migration of anions toward the electrode causes self-polarization, resulting in a serious current drop during the discharging process. One of the simplest ways to minimize the self-polarization is to prohibit long-distance anion migration by anchoring them to polymer matrices. The resulting polymers are "polyelectrolytes" with low-T_g segments, and are often called "single-ion" conductors. Tsuchida and Shigehara[2] demonstrated single-ion conductors with a copolymer of lithium methacrylate and an ω-methoxyoligo(oxyethylene)methacrylate macromer, but the large ion dissociation energy for Li^+–OOCR units decreased the ionic conductivity to ca. 10^{-8} S cm^{-1}. Sulfonate salts have lower dissociation energies; McIntyre et al.[3] reported anionic polymers containing lithium alkylsulfonate side groups. However, when blended with a low-T_g polymer matrix, poly(ethylene oxide), to produce the free volume required for ion-hopping, serious phase separation resulted. Smid et al.[4] investigated cation-transporting polyelectrolytes with sulfonate groups immobilized on the pendant oligo(oxyethylene) chains of comb-type siloxane polymers. Though the ionic conductivities of these polysulfonates were 10^{-7}–10^{-6} S cm^{-1} at room temperature, these polymers carry terminal –OH groups equimolar to the sulfonate groups. Allcock, Shriver and et al.[5] realized a higher ionic conductivity (10^{-5} S cm^{-1}) by hybridization of alkali metal salts and MEEP, poly[bis((methoxyethoxy)ethoxy)phosphazene]. Shriver et al.[6] later reported the conductivities of MEEP-type

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polymers carrying covalently bonded alkali metal sulfonates. However, cation species of these polymers was sodium rather than the lithium ion used in the lithium battery.

This paper describes studies on the preparation and conductivity of comb-type polyphosphazenes with lithium sulfopropyl oligo(oxyethylene) side chains [SEP]. We provide a method for the direct introduction of lithium sulfonate groups in the side chain. SEPs were synthesized by the reaction of lithium bisulfite with polyphosphazenes containing oligo(oxyethylene) side chains terminated with allyl groups [AEP]. The dc ionic conductivity of the new SEP was measured and compared with hybrids between $LiSO_3CF_3$ and the corresponding non-sulfonated comb-type polymer [MEP], i.e., poly{bis[ω-methoxyoligo(oxyethylene)]phosphazene} with an average number of oxyethylene repeating unit of 7.

Experimental Section

Materials. Hexachlorocyclotriphosphazene $(NPCl_2)_3$ was purified by recrystallization from hexane and dried under reduced pressure. Oligo(ethylene glycol) monomethyl ether [EGME] (Aldrich Chemical Inc.) and oligo(ethylene glycol) monoallyl ether [EGAE] (Nippon Nyukazai Co., AG-7) had average molecular weights of 350 and 367, respectively, corresponding on average to 7 oxyethylene repeating units.

Preparation of AEP 1–4 and SEP 5–8. Typical procedures are described below.[7] In the case of MEP, only the EGME-Li salt was used instead of EGME-/EGAE-Li salts mixture.

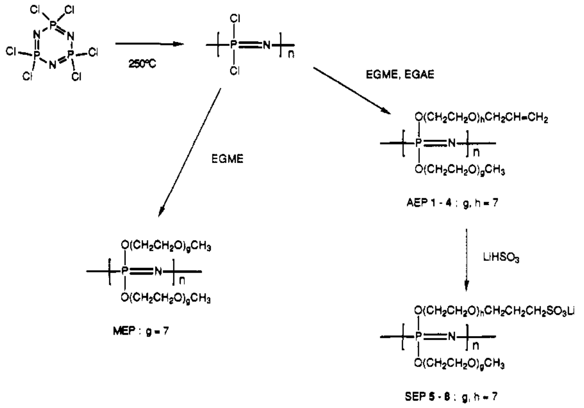
Preparation of AEP 1: Poly(dichlorophosphazene) was prepared by the thermal polymerization of $(NPCl_2)_3$ at 250 °C under reduced pressure. The remaining $(NPCl_2)_3$ was removed by sublimation *in vacuo*. The resulting poly(dichlorophosphazene) (11.6 g, 100 unit mmol) was dissolved in toluene and added at room temperature to the THF/hexane solutions of the EGME- and EGAE-Li salts (289 and 41 mmol, respectively). The mixture was stirred for 5 h at 70 °C and evaporated to remove solvent. Then it was neutralized with dilute HCl solution and was concentrated. The resulting polymer was purified by dialysis against deionized water, and dried *in vacuo*. The results of preparation of AEP 1–4 and MEP are summarized in Table 1.[8]

Preparation of SEP 5: To the aqueous solution of AEP 1 (50 g; 67 mmol, double bond of allyl group; 16.8 mequiv) was added dropwise an aqueous solution of lithium bisulfite (100 mmol) and lithium sulfite (50 mmol) prepared by reacting gaseous SO_2 and 8.4 g (200 mmol) of $LiOH{\cdot}H_2O$ *in situ*. The mixture was stirred at 80–90 °C for 1 h and purified by dialysis against deionized water. The resulting polymer was dried at 60 °C under vacuum for 4–8 weeks over P_2O_5. The results of preparation of SEP 5–8 were summarized in Table 2.[9]

Sample Preparation. All procedures were conducted in a dry argon atmosphere or *in vacuo*. Concentrated THF solutions of SEP polymers or MEP/$LiSO_3CF_3$ mixtures were cast on Teflon plates, then the resulting films were slowly evacuated and then dried *in vacuo* at 100 °C until no THF peaks were found in GLC analyses of extracts. These films were cut into pieces of the suitable size, sandwiched between freshly cut metallic lithium electrodes and used for conductivity measurements.

Measurements. The glass transition temperature (T_g) of polymers or hybrids was measured with a Seiko I&E DSC 200 differential scanning calorimeter. In ^{31}P NMR spectra, 85% H_3PO_4 was used as an external reference. Size exclusion chromatography was carried out using TSK_{gel} $GMPW_{XL}$ columns (TOSOH Co.) and calibrated by using monodisperse poly(ethylene oxide) standards. Direct current (dc) conductivity of the samples was measured at 28 °C under an applied voltage of 1.0 V with lithium electrodes (10-mm diameter) using a Yokogawa-Hewlett-Packard 4192A LF-impedance analyzer. The manipulations for electrical measurements were carried out under dry argon atmosphere. The water content in polymers or solid electrolytes were measured by Karl–Fischer method.

Scheme 1



Results and Discussion

In detailed discussions of the ionic conductivity of comb-type biionic hybrid electrolytes,[10,11] an average of seven repeat units was the best for the oligo(oxyethylene) side chains. In view of these results, AEP 1–4 were synthesized from $(NPCl_2)_n$ using lithium salts of EGME and EGAE with oxyethylenes with an average of 7 repeat units. (Scheme 1) The use of the lithium salts was essential because of their high reactivity and suitable solubility in reaction media.[12] The structure of AEP was determined by IR, ^1H, and ^{31}P NMR spectra and elemental analysis as shown in Table 1.[8] Using the present procedure, the unreacted chlorine in the AEP was extremely low, i.e., less than 0.05% without the ammonium salt catalyst[13] often used in such reactions. However, AEP showed large polydispersities, because EGME and EGAE were the number of oxyethylene repeating unit of 2–13 in GLC analyses. AEP showed IR and ^1H NMR spectra characteristic of the allyl group at 1640 cm^{-1} (ν(C=C)) and δ = 5.1–5.4 (=CH_2), 5.6–6.1 ppm (—CH=), respectively. The ratio of integrated intensities [methyl vs allyl groups] agreed well with the feed ratio of EGME/EGAE. AEP showed only a sharp singlet peak in ^{31}P NMR spectroscopy, and no evidence of P–Cl or P(O)–NH moieties. The elemental analysis of the AEP agreed with calculated value. The AEP polymers containing allyl groups were converted to SEP by a one-step reaction with lithium bisulfite (Scheme 1). The reaction was carried out at pH 6–7 in the presence of lithium sulfite, resulting in the α-addition to allyl group.[14] The structure of SEP was confirmed by IR,

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[7] Lithium bisulfite (6 equiv) and lithium sulfite (3 equiv) were used against 1 equiv of double bond of AEP.

[8] The IR spectra of all AEP showed the following absorption bands. IR (KBr): 2860 (s, CH), 1640 (C=C), 1350 (POC), 1240 (s, P=N), 1100 cm^{-1} (vs, POC). The ^1H NMR spectra of all AEP showed the following peaks. ^1H NMR ($CDCl_3$): δ = 5.6–6.1, 5.1–5.4 (m, allyl), 4.0 (b, H^{POCH}), 3.5–3.7 (m, H^{OCH}), 3.35 (s, methyl).

[9] The IR spectra of all SEP showed the following absorption bands. IR (KBr): 2860 (s, CH), 1640 (C=C), 1350 (POC), 1240 (s, P=N), 1100 (vs, POC), 1040 cm^{-1} (s, S=O). The ^1H NMR spectra of all SEP showed the following peaks. ^1H NMR (D_2O): δ = 4.15 (b, H^{POCH}), 3.6–3.8 (m, H^{OCH}), 3.4 (s, methyl), 2.8–3.1 (m, H^{SCH}), 1.9–2.3 (m, H^{CHCH_2CH}).

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Table 1. Characterization Data for AEP 1–4 and MEP

		EGAE:EGME	yield (%)	^{31}P NMR (ppm)	$\bar{M}_w/10^4$	$\bar{M}_w/\bar{M}_n$		C (%)	H (%)	N (%)	P (%)
AEP	**1**	0.25:1.75	72	−7.2	148	36	calcd	50.29	8.58	1.87	4.14
							found	50.14	8.96	2.18	4.32
AEP	**2**	0.21:1.79	75	−7.2	157	26	calcd	50.24	8.58	1.87	4.15
							found	49.98	9.34	2.22	4.28
AEP	**3**	0.18:1.82	74	−7.3	156	41	calcd	50.19	8.59	1.88	4.15
							found	49.00	9.11	2.34	4.39
AEP	**4**	0.15:1.85	69	−7.3	142	40	calcd	50.15	8.59	1.88	4.16
							found	49.78	8.94	2.15	4.29
MEP		0:2.00	72	−7.2	195	19	calcd	49.91	8.65	1.89	4.17
							found	49.43	8.58	2.17	4.23

Table 2. Characterization Data for SEP 5–8

SEP	^{31}P NMR (ppm)	$\bar{M}_w/10^4$	$\bar{M}_w/\bar{M}_n$	T_c (°C)		C (%)	H (%)	N (%)	P (%)	S (%)	Li (%)
5	−7.2	30.0	5.6	−69.3	calcd	48.86	8.37	1.82	4.02	1.04	0.23
					found	48.44	8.92	2.00	4.33	1.31	0.22
6	−7.1	27.6	5.1	−68.5	calcd	49.02	8.40	1.83	4.05	0.88	0.19
					found	48.11	8.97	1.90	4.35	1.04	0.25
7	−7.1	44.6	7.8	−71.3	calcd	49.15	8.43	1.84	4.06	0.76	0.16
					found	48.17	9.10	2.17	4.54	0.99	0.28
8	−7.2	69.1	8.2	−70.8	calcd	49.28	8.46	1.84	4.08	0.63	0.14
					found	48.80	9.56	1.87	4.00	0.93	0.22

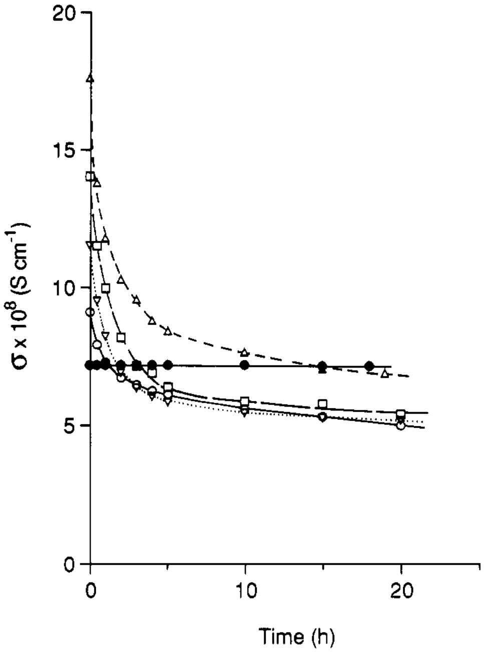

Figure 1. Time dependence of apparent dc conductivity at 28 °C estimated from the change in current under an applied voltage of 1.0 V with lithium electrodes. SEP **5**–**8** dried for 4 weeks at 60 °C under vacuum: open symbols ▽, □, △, and ○, respectively. SEP **8** dried for 8 weeks in the same conditions: closed symbols ●.

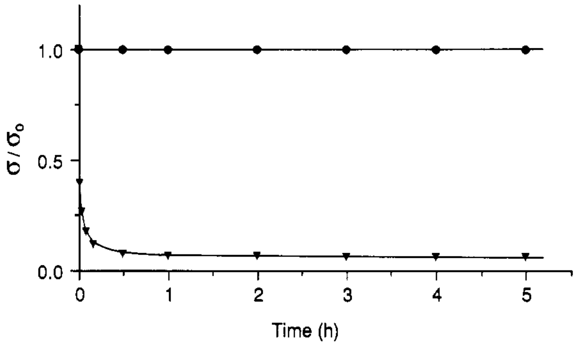

Figure 2. Time dependence of apparent dc conductivity at 28 °C estimated from the change in current under an applied voltage of 1.0 V with lithium electrodes. SEP **8** (Li content: 0.22 wt %): ●, 8 wt % CF_3SO_3Li/MEP hybrid (Li content: 0.36 wt %): ▼.

^1H, and ^{31}P NMR spectra and elemental analysis as shown in Table 2.[9] The decreased molecular weight of SEPs derived from AEPs seems to be dissociation of the main chain. In our previous experiment,[15] the molecular weight of SEPs slowly decreased owing to the dialysis to water for many days. The polydispersities of SEPs decreased along with the decreasing of molecular weight. In the IR spectrum of the SEP, the absorption bands of allyl groups characteristic to AEP disappeared completely, while the new absorption bonds attributed to S=O bond of sulfonate groups appeared at 1040 cm^{-1}. In the ^1H NMR spectrum of the AEP, peaks assigned to the methylene of the sulfopropyl group were recognized at 1.9–2.3 and 2.8–3.1 ppm. The SEP showed only a sharp singlet peak in ^{31}P NMR spectroscopy, and its elemental analysis agreed well with the calculated value.

To exploit these polymers as solid electrolytes in rechargeable lithium batteries, it is important to evaluate their long-term performance during dc electrolysis. Figure 1 shows the time dependence of apparent dc conductivity (σ) for SEP **5**–**8** estimated from the chronopotentiometric response at 28 °C under the constant voltage supply of 1.0 V. The σ value of SEP **5**–**8** dried for 4 weeks (open symbols) gradually declined, but the σ of SEP **8** dried for 8 weeks (closed symbols) was unchanged even after prolonged dc electrolysis. From the water-content measurements, the samples dried for 4 weeks (SEP **5**–**8**) and 8 weeks (SEP **8**) were found to be contaminated with 50 ppm and less than 0.5 ppm, respectively. This result implies the importance of water exclusion, as the contaminating water may yield injurious ionic species, which interfere with the interfacial charge transfer by reaction with lithium electrode.

To determine the difference between the biionic and single-ionic solid electrolytes, the CF_3SO_3Li/MEP hybrid with a water content as low as SEP **8** was prepared. The time dependence of σ/σ_0 (σ_0: initial conductivity) in SEP **8** and CF_3SO_3Li/MEP hybrids were compared in Figure 2. While σ/σ_0 of SEP **8** showed a constant value, that of the hybrid system drastically decreased with time due to self-polarization by mobile anions. At 1.0-V dc supply, the stationary values of σ after prolonged electrolysis were 7.1×10^{-8} S cm^{-1} for SEP **8** and 8.5×10^{-7} S cm^{-1} for the hybrid; the steady-state value of SEP **8** was smaller by 1 order of magnitude than that of the hybrid and the superiority of single-ionic conductor was not obvious. However, when the dc supply increased to 3 V, the conductivity of hybrid system reached only one-tenth of

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(15) Unpublished data.

the stationary value of SEP 8 due to the greater polarization.

Though the anchored alkyl sulfonate groups were chosen in anticipation of a smaller salt dissociation energy than Tsuchida et al.'s carboxylate groups,[2] it was not good enough to obtain the highly conductive single-ionic solid electrolytes. One of the better candidates will be the similar polyelectrolytes carrying fluorinated alkylsulfonate side chains. It is currently being investigated and will be described elsewhere.[16]

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