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Synthesis and properties of heptadecane-functionalized poly(propylene oxide) based single-ion polymer electrolytes

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Lithium methacrylate and heptadecane-functionalized poly(propylene oxide) (PPO) methacrylate based single-ion polymer electrolytes have been synthesized by radical copolymerization and neutralization. The thermal and electrical properties of the polymer electrolyte have been characterized by differential scanning calorimetry (DSC) and AC impedance spectroscopy, respectively. The results showed that the crystalline melting behavior of PPO segment was changed significantly by the presence of lithium ion due to the coordinative interaction and enhanced crystallinity. The ionic conductivity was 1.8×10^{-7} S cm $^{-1}$ at 25 °C in the case of the lithium ion concentration of [PO]:[Li] = 30:1 due to the single-ion nature but its transference number reached roughly 1, indicating no migration of counter anions. Inspection with control sample suggested that the polymer electrolyte with ion conduction channel formed by a self-assembly is favored to realize relatively high ionic conductivity and decoupled lithium ion motion. The contact angle measurement onto the polymer electrolyte surface showed a strong hydrophobic wetting behavior due to the integrated hydrophobic nature of PPO and heptadecane alkyl chains.

1. Introduction

Solid polymer electrolytes have gained a significant attention in the last several decades relating to energy storage systems because of its potential advantages derived from flexibility, formability, enhanced safety, and higher energy density [1,2]. Poly(ethylene oxide) (PEO) [3,4], which can dissolve lithium salt is the most studied polymer electrolyte system among various alternatives such as poly(propylene oxide) (PPO) [5–7], poly(vinylidene fluoride) [8], and poly(methoxy polyethylene glycol monomethacrylate) [9]. Moderate and enhanced ionic conductivities have been reported from the above solid polymer electrolytes within the range of 10^{-7}–10^{-4} S cm^{-1} at 25 °C with various lithium salts, i.e., noted as a salt-doped systems. However, the presence of mobile anions prevents these materials from high lithium ion transference number, which can reduce total energy density especially under high rate discharge. Furthermore the concentration gradients developed in solid polymer electrolyte are expected to decrease battery capacity and cycle performance since once generated polarization is difficult to recover in less movable matrix [10–12]. Therefore it is necessary to design single-ion conducting polymer electrolyte to guarantee the performance gain and the stability of anions [13]. Generally there are two methods to prepare single-ion polymer electrolyte. The one is utilizing lithium salt with high molecular weight counter anion, i.e., polymeric anion, which may lead to less mobile environment [14,15]. The other is to use organic–inorganic hybrid lithium salt materials to suppress the mobility of anion [16]. On the other hand, however, it should be noted that the ionic conductivity of single-ion polymer electrolyte is generally lower than that of salt-doped system because of the lost conductivity contribution from anion transfer by immobilization. In order to improve the ionic conductivity, various methods have been applied in PEO-based single-ion polymer electrolyte system like lowering the ionic interactions between lithium and counter anion, which leads to enhanced mobility of charge carrier [17]. As an alternative we have suggested in a previous work that the structural isolation of counter anion outside of the ion conducting domain enhances the ion dissociation and thereby increases conductivity in PEO-based single-ion polymer electrolyte [18]. Although many efforts have been made to enhance the ionic conductivity in single-ion polymer electrolyte, the subject still remains as a strong challenge. In addition to above, there have been only a few publications on single-ion polymer electrolyte system instead of PEO-based matrix. Therefore PPO-based polymer electrolyte may be regarded as an alternative system to extend possible candidate for lithium rechargeable battery applications.

In the present work, we report the synthesis and electrochemical properties of lithium methacrylate and heptadecane-functionalized poly(propylene oxide) methacrylate (PO5) based single-ion polymer

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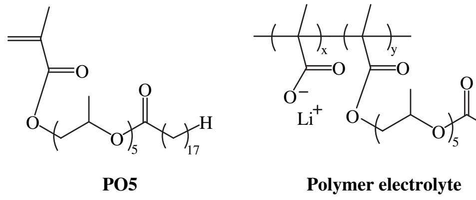


Scheme 1.

electrolyte, which lithium ion can migrate but counter anion is immobilized in polymer backbone as shown in Scheme 1. The designed polymer electrolyte compromises advantages from both alkyl oxide chain and hydrophobic wetting behavior. The former can dissolve a wide variety of salts up to high concentrations similar to PEO system. The latter makes it possible to be used in energy storage devices designed for operating under much humidified conditions. For that purpose, polymer precursors consisted of methacrylic acid and PO5 were synthesized and neutralized by treatment with lithium methoxide. The phase transition behaviors of the polymer electrolytes were investigated by differential scanning calorimetry (DSC) and the ionic conductivity and lithium ion transference number were studied by AC impedance spectroscopy and polarization test, respectively. The hydrophobic wetting behavior was demonstrated by contact angle measurement and its structural dependence on the conductivity was discussed with control sample in detail.

2. Experimental

2.1. Materials

Poly(propylene glycol)methacrylate (PPGM, M_n: 375 g mol^{-1}), stearoyl chloride (99%), methacrylic acid (99%), triethylamine (99.5%), *N*,*N*-dimethylformamide (DMF, anhydrous), hexane (95%), hydroquinone (99%) and lithium methoxide (98%) were purchased from Aldrich and used without further purification otherwise stated. Inhibitors were removed from the methacrylic acid prior to polymerization by passing through an alumina (activated, Aldrich) column. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich) was purified by recrystallization from its ethanol solution and stored at −10 °C before use. Toluene (anhydrous) was purchased from J.T. Baker and used as a solvent in polymerization. Acetone, tetrahydrofuran (THF) and ethanol (reagent grade, Duksan Chemical) were used without further purification.

2.2. Macromonomer synthesis

PO5 was synthesized as follows: DMF (120 ml) solution of PPGM (14.0 g, 37.0 mmol) and triethylamine (7 g, 69.2 mmol) with trace amount of hydroquinone (usually around 0.01 g) was purged with nitrogen for 30 min to remove dissolved oxygen. Stearoyl chloride (12 g, 39.6 mmol) was then slowly added into the above DMF solution at room temperature. The heterogeneous reaction mixture was allowed to stir overnight and the yellowish liquid was filtered and passed through an alumina column to give a colorless liquid with 19.2 g (643 g mol^{-1}, 29.9 mmol, 81% yield) of PO5. The ^{1}H NMR spectroscopy was used to determine the quantitative coupling reaction by comparing integral ratio between methacrylate double bond protons and heptadecane end-chain protons corresponding to 5.6 (or 6.1) ppm and 0.9 ppm, respectively.

2.3. Polymerization and electrolyte preparation

The precursor polymers were synthesized by radical copolymerization of PO5 and methacrylic acid. A typical reaction procedure of polymerization is as follows: the synthesized macromonomer, PO5 (2.3 g, 3.6 mmol), and methacrylic acid (0.1 g, 1.2 mmol) were dissolved in toluene (30 ml) and purged with nitrogen for 20 min. After heating up to 60 °C, AIBN (0.01 g) was added at once and allowed to stir for 24 h. The viscous reaction mixture was then poured into large amount of methanol to precipitate the polymers. They were re-dissolved in THF solvent and re-precipitated twice to remove remained monomer. Colorless polymer was obtained after vacuum dried at 100 °C overnight to give 2.0 g (83% yield). Analysis by size exclusion chromatography (SEC) showed the number average molecular weight to be around 20 and 40 kg mol^{-1} based on polystyrene standard samples. The composition of the resulting polymer was estimated by titration of methacrylic acid with lithium methoxide. In a typical titration procedure, a dilute THF solution of polymer droplets was taken out after adding lithium methoxide dissolved in methanol at room temperature and mixed with water to measure pH. After a pH of 7 was reached, the solvent was evaporated and the polymer was dried in a vacuum oven at 100 °C for 3 days. Methacrylic acid concentrations were then defined using the [PO]:[Li] ratio, i.e., the number of lithium ions per corresponding PPO oxygen.

2.4. Characterization of polymers

^{1}H NMR spectra were recorded on a BRUKER 300 MHz in $CDCl_3$. SEC was performed on a JASCO LC2000 instrument with refractive index detection at 40 °C. THF was used as carrier solvent at a flow rate of 1.0 mL min^{-1}. Calibration curves were made to determine molecular weight and molecular weight distribution values using standard polystyrene samples.

2.5. Thermal properties

DSC (TA Instruments Q100) measurements were carried out over the temperature range of −150 to 150 °C at a heating rate of 20 °C min^{-1} under dry nitrogen atmosphere. The sample was placed in aluminum containers and first heated to 150 °C, cooled down to −150 °C and scanned. Thermal transition temperature was determined relative to Indium reference cell.

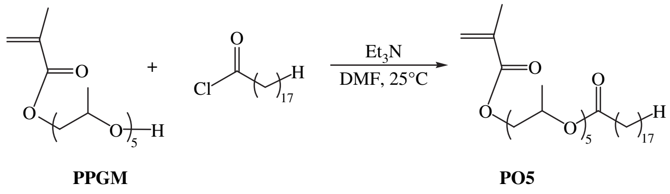
2.6. Electrical properties

AC impedance measurements were carried out using thin film of polymer electrolyte prepared by casting from its benzene solution onto a glass plate and dried in a vacuum oven at 110 °C for 72 h to give thickness of 100–300 μm which is determined by a micrometer. The electrolyte film was then sandwiched between two 15 mm stainless steel blocking electrodes and assembled into a coin-cell type device inside an argon filled glove box. Conductivities of the polymer electrolytes were measured by AC impedance spectroscopy using a Solartron 14552 impedance gain/phase analyzer (Solartron Analytical, England) over a frequency range of 1–10^6 Hz at 10 mV amplitude and 10 points per decade of frequency. The ionic conductivity was calculated from the bulk electrolyte resistance (R_b) found in the impedance diagram using the following relationship:

$$\sigma = l/R_bA$$

where σ is the ionic conductivity and l is the thickness of the polymer electrolyte and A is the surface area of the electrode.

Lithium ion transference number was measured by potentiostatic polarization in which a constant signal of 1 V was applied to a lithium symmetric cell for a long period of time frame. Then the current response under that condition was observed as a function of time using a lithium–lithium symmetric cell sandwiched with the polymer electrolytes (100–300 μm thick, ~1.88 cm^2 area) at 25 °C.



Scheme 2.

2.7. *Contact angle measurements*

The wetting behavior of single-ion polymer electrolytes was investigated using a VCA 2000 video contact angle system (Advanced Surface Technologies, Inc.). In advancing test, dynamic changes in the contact angle of a droplet after sequential addition of 1-μL water were captured from its initial moment of contact with the polymer surface.

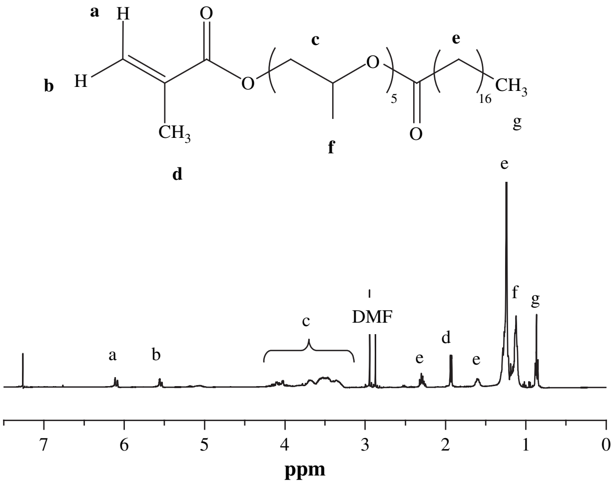


Fig. 2. ^{1}H NMR spectrum of macromonomer in CDCl$_3$.

3. Results and discussion

3.1. *Polymer electrolytes*

The reaction between PPGM and stearoyl chloride is expected to be processed well under a mild condition in the presence of triethylamine as shown in Scheme 2. But it is necessary to control the reaction conditions to obtain high yield of macromonomer from its side polymerized products.

In this experiment, a trace amount of hydroquinone (usually around 0.01 g) was used as a polymerization inhibitor and the stearoyl chloride was added slowly so that the reaction was processed slowly and prevents rapid increase of the reaction temperature. The obtained reaction mixtures were characterized by SEC and the result showed that the product had a narrow molecular weight distribution without any trace of polymerization as shown in Fig. 1. The molecular weight of product was measured as 739 g mol^{-1} relative to polystyrene standard and it was similar to that of theoretical value (643 g mol^{-1}). The successful reaction is also supported by ^{1}H NMR analysis. As shown in Fig. 2, the resonance peaks at 0.9 and 5.6 (and/or 6.1) ppm which are corresponding to heptadecane and methacrylate protons, respectively, appear clearly with reasonable integral ratio. The radical polymerization of PO5 and methacrylic acid was carried out by the method described in Section 2. It is easy to notice that the monomers used in this study will have different reactivity ratios toward the radical initiator since PO5 has higher molecular weight and less mobility than that of methacrylic acid although they both have the same methacrylate functions. Especially at high conversions the resulting polymer might be inhomogeneous in composition due to the different reactivity ratios. In the initial stage of the polymerization, however, it can be expected that both the monomers have an almost same reactivity ratios because there is a sufficient chance to meet an active site in less viscous reaction media. Therefore, we can expect a random and a gradient copolymer formation in initial and final stages of the polymerization, respectively. In fact, the more detailed experiment will be necessary to determine the real structure of the polymer chains. Representative SEC chromatogram of polymerization mixture for PO-30 is shown in Fig. 1 and reveals a wide molecular weight distribution as usual in a radical polymerization. The product was then neutralized by lithium methoxide which results in lithium methacrylate contained polymer electrolytes. Table 1 summarizes all the PO5-based polymers prepared and investigated in this study with respect to composition, thermal behavior and molecular weight. It should be noticed that the molecular weights of the resulting polymers are calculated by SEC measurement relative to polystyrene standards. Therefore the value designates a polystyrene-equivalent molecular weight and is somewhat deviated from its true molecular weight as suggested by Netopilík and Kratochvíl [19]. In addition to the above, the present polymer might have a small hydrodynamic volume in solution state because of a relative compact branch-like structure arising from the PO5 macromonomer as reported by Tsukahara et al. [20]. Therefore the real molecular weight of the resulting polymer should be higher than that of the listed value in Table 1 and more experiments are necessary to exploit a correlation factor between structure and molecular weight by an instrumental analysis technique such as a static light scattering (SLS). The polymer sample in a first line

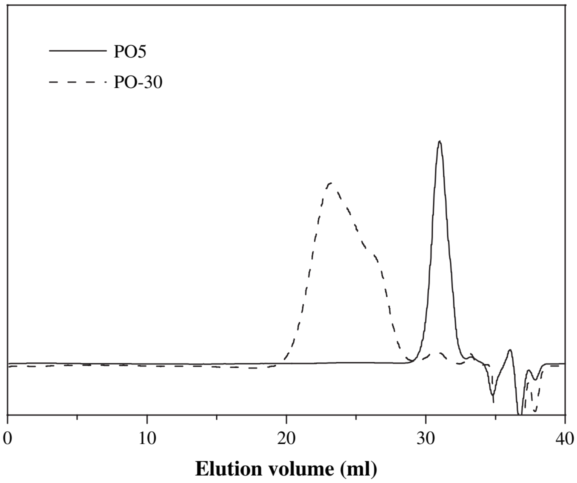


Fig. 1. SEC trace of synthesized macromonomer (PO5) and polymer precursor (PO-30) in THF at 40 °C.

Table 1
Composition and melting behavior of the different PO5-based polymer electrolytes

Sample[a]	Composition[b] (wt%)		[PO]:[Li]	Thermal behavior[c]		Molecular weight[d] (kg mol^{-1})
	MAA	PO5		$T_{m,1}$ (°C)	$T_{m,2}$ (°C)	
PO–H	0	100		13		35
PO-30	2	98	30:1	6	51	20
PO-25	2.6	97.4	25:1	5	73	40
PO-15	4	96	15:1	2	81	40

[a] Yields of polymer: ~80%; molecular weight distribution: 2.5–3.0.

[b] Composition of each polymer was calculated by titration with lithium methoxide.

[c] Crystalline melting temperature from DSC.

[d] Determined relative to polystyrene in THF at 40 °C.

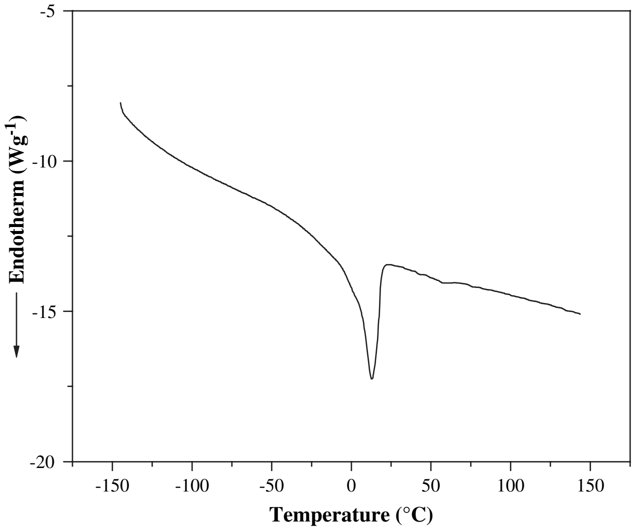


Fig. 3. DSC heating trace of PO5 homopolymer (PO–H). The polymer electrolyte was cooled to −150 °C prior to heating scan. Scan rate: 20 °C min^{-1}.

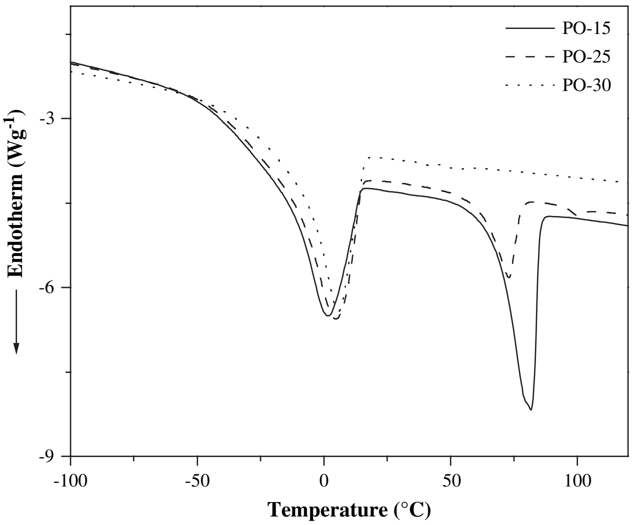


Fig. 4. DSC heating trace of PO5-based polymer electrolytes. Scan rate: 20 °C min^{-1}.

means homopolymer of PO5, in which no lithium salt was added and marked as PO–H. The calculated amount of lithium methacrylate was added in another series of polymer samples and marked as PO-30, PO-25 and PO-15 based on the number of lithium ion per coordinating PPO oxygen. As a representative the PO-30 means 30:1 of [PO]:[Li] ratio and having only 2 wt% of lithium methacrylate in a whole polymer matrix.

3.2. Thermal behaviors

Thermal properties of PO5-based single-ion polymer electrolytes were investigated by DSC. Fig. 3 shows the heating trace of homopolymer in the range of −150 to 150 °C. Clearly there is a sharp melting transition peak of the heptadecane chain at around 13 °C. Comparing with the literature value of heptadecane crystalline, which has a general melting point at 28 °C [21], it can be noticed that the deficiency of mobility due to the formation of polymer structure and corresponding decrease in crystallinity might be the reason of lowering the melting temperature. Interestingly, there is a trace amount of secondary endothermic peak at around 60 °C and it can be interpreted as a melting temperature of PPO crystalline segment [22]. In the next step, synthesized single-ion polymer electrolytes having lithium methacrylate are investigated and their thermal transition patterns are plotted in Fig. 4. There is almost same tendency in heptadecane melting temperature at around 2–6 °C although the value was slightly decreased with increasing of lithium ion concentration. This is a strong indication that the crystalline melting of heptadecane chain has not been changed by the presence of lithium ion at least in this experimental range and is agreed with the result reported by Jannasch [7]. He has studied the influence of crystalline melting temperature of hexadecanoyl functionalized PPO-based polymer electrolytes as change in lithium bis(trifluoromethylsulfonyl)imid, LiTFSi concentration. Although there were multiple endothermic peaks between −45 and 15 °C depending on a distribution of crystalline domain size, no change in the crystalline melting temperature was observed by the lithium salt concentration. On the other hand, it seems clear that the melting temperature of PPO crystalline phase is significantly affected by the presence of lithium ion. A similar phase transition of PPO crystalline was observed in the case of PO-30, which is designated [PO]:[Li] to be 30:1, except decrease in melting temperature of heptadecane group to 6 °C. However, it is obvious that the enthalpy of melting was increased with increasing lithium ion concentration as shown in PO-25 and PO-15 samples. Hence, the crystalline melting temperature of PPO segment is strongly influenced by the presence of lithium ion especially at the higher concentration level. The most probable reason for this is a coordinative interaction with lithium ion which results in enhanced crystallinity of PPO domain and detectable endothermic transition in DSC measurement. Therefore a flow of heat during the melting process is expected to increase with lithium ion concentration and that is consistent with the experimental result from DSC as shown in Fig. 4.

3.3. Electrical properties

The ionic conductivities of the single-ion polymer electrolytes were measured by AC impedance spectroscopy using stainless steel blocking electrodes cell in the temperature range between 25 and 110 °C [23]. It should be noticed that the AC impedance of the polymer electrolyte generally indicates somewhat complex information about a resistance from bulk, grain boundary and electrode interface. Thus the overall resistance is believed not to be altered by the compositional inhomogeneity described in previous section. As shown in Fig. 5, the ionic conductivity of PO-15 was as low as 2.5×10^{-8} S cm^{-1} at 25 °C, indicating typical result of the single-ion polymer electrolyte [18]. In comparison, the enhanced ionic conductivity was observed when the ion concentration became low. For example, in the case of [PO]:[Li] – 30:1, the ionic conductivity of 1.8×10^{-7} S cm^{-1} was achieved at 25 °C. This

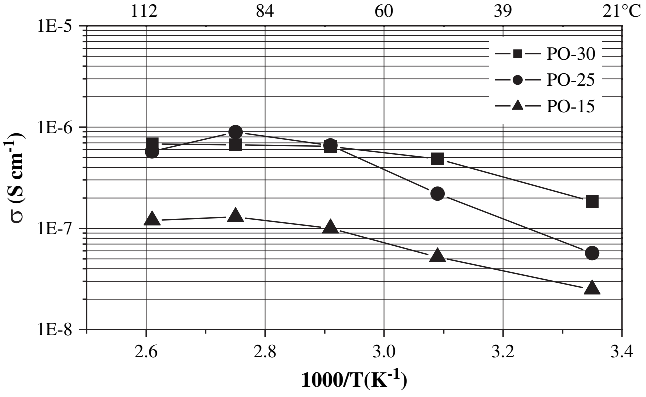
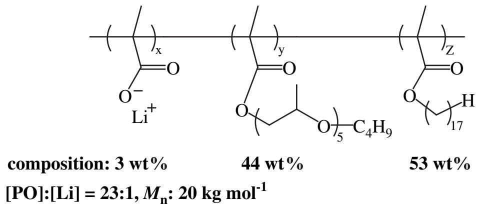


Fig. 5. Temperature dependence of ionic conductivities of the single-ion polymer electrolytes.



Scheme 3.

behavior may be explained by the Vogel–Tamman–Fulcher (VTF) equation as follows [24],

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

where the term A is proportional to the number of charge carriers, kT is the thermal energy, and T_0 is a glass transition temperature (T_g) of polymer matrix. At the lower temperature, the activation energy, E_a, is the main parameter to determine the ionic conductivity because the polymer system has insufficient energy to activate molecules for ion conduction. For that reason, soft polymer matrix is preferred to reduce required activation energy at low temperature environment. As the concentration of lithium ion is increased counter anion also is increased which can form a brittle domain and lead to the formation of relatively hard polymer matrix. Besides, the ionic conductivity of the polymer electrolyte at high temperature region is more related to the number of charge carrier since there is a sufficient thermal energy. As a result, it is clearly observed that the ionic conductivity of PO-25 and PO-30 was overlapped above 70 °C of cell temperature, indicating change of main parameter from the activation energy to the number of charge carrier. Interestingly, the temperature dependence of the conductivity was not as high as that of a usual polymer electrolyte [1]. Wright and coworkers have studied poly(tetrahydrofuran) (PTHF) based amphiphilic comb copolymer electrolyte, which is blended with homopolymer of PTHF [25]. In that system they found a significant increase of conductivity by thermal treatment and almost decoupled lithium ion motion was observed in the whole investigated temperature range. They explained that the decoupled motion was caused by a fast ion conduction channel formed through self-assembly of PTHF in alkyl polymer matrix. In our polymer electrolyte system, lithium ion conducting PPO chain was surrounded by the heptadecane alkyl side chain due to the macromonomer structure, which lead to the formation of PPO channel by self-assembly. Consequently, low temperature dependence of the conductivity can be attributed to the formation of ion conduction channel which is consistent with Wright's works as described before. In order to verify this, we have synthesized a control sample as shown in Scheme 3 and measured the ionic conductivity as a function of temperature. Control sample has a similar composition with PO-25 but propylene oxide and heptadecane group were separated by using different monomer units. Therefore, it seems difficult to form an inner channel of PPO domain by the similar method already explained in our previous sample.

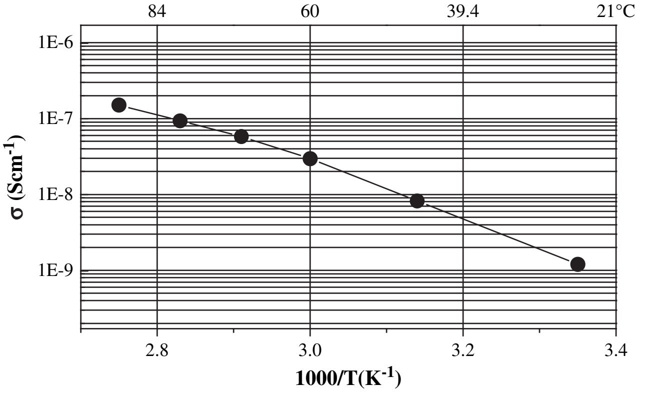


Fig. 6. Ionic conductivities of control sample as a function of temperature.

Fig. 6 shows the temperature dependence of the conductivity. Although the lithium ion concentration, [PO]:[Li], of the control sample is 23:1 and similar with PO-25, the ionic conductivity was found to be 1.2×10^{-9} S cm^{-1} at 25 °C, which is one and half orders of magnitude lower than that of the PO-25. However, significant increase of conductivity was observed in the control sample and 1.5×10^{-7} S cm^{-1} was obtained at 90 °C. Inspection of the control sample suggests that it is better to design polymer electrolyte to have a self-assembled structure and have ion conduction channel to reach high room temperature conductivity and relatively decoupled lithium ion motion. At this point, however, it should be noted that the relative ionic conductivity of single-ion conductor is quite lower than that of binary salt system due to the compensation for the immobilized counter anion's conductivity [26]. Nevertheless, polymer electrolytes have to possess single-ion or at least single-ion like conduction behavior in order to increase energy density, electrochemical stability, and long cycle performance as well as to prevent undesired polarization as mentioned in Section 1. Although it is not a direct technique to determine the single-ion conduction behavior [27], DC-polarization test can be used to elucidate the lithium ion transference number of polymer electrolyte. Simply, 1 V of constant bias is applied to the polymer electrolyte placed in a lithium–lithium symmetric cell at 25 °C. In this experimental condition anions accumulate at the positive electrode with the passage of time and are depleted at the other electrode if a lithium salt is incorporated as a charge carrier, i.e. binary salt-doped system. As a result, a salt concentration gradient is generated inside an electrolyte matrix and the current response dropped substantially [27]. In contrast to the binary salt-doped system, the current and voltage in our experiment were completely in phase, indicating no migration of counter anion and no possible polarization over the time frame of the experiment as shown in Fig. 7. Consequently, the lithium ion transference number can be calculated to be roughly 1 by comparing the initial and final current values obtained by the instrument.

3.4. Wetting behavior

Practically, PPO related polymer electrolyte can dissolve lithium salt like PEO system but it is known to have a hydrophobic wetting behavior because of the presence of methyl group in ethylene oxide unit [28]. Besides, the presence of heptadecane alkyl chain is expected to drive whole polymer electrolytes to more hydrophobic nature and can be realized in our system if the amount of lithium methacrylate is controlled as a small quantity. As summarized in Table 1, the incorporated amount of lithium methacrylate was controlled to place between 2 and 4 wt% thus almost no effect on

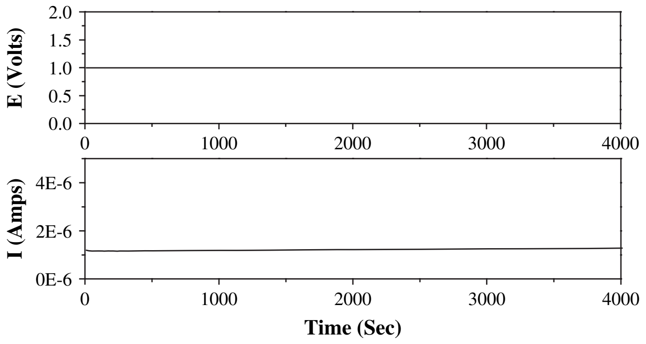


Fig. 7. DC-polarization test for PO-25 at 25 °C in a lithium–lithium symmetric cell.

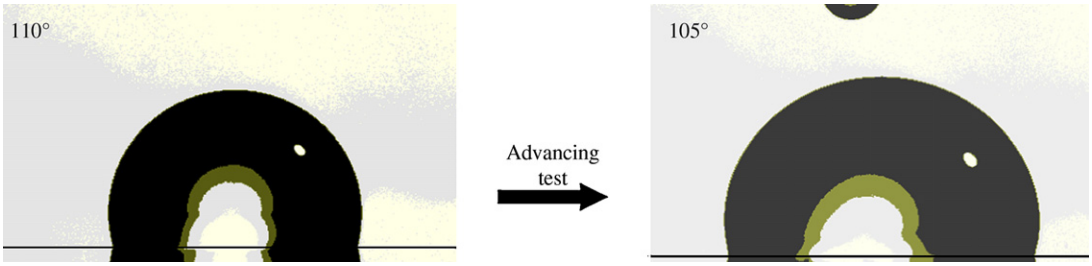


Fig. 8. Contact angle measurements onto PO-15 coated glass (left: after one droplet, right: after five more droplets).

wetting behavior is expected. The polymer electrolyte was coated on a glass plate and the smooth film was confirmed by the instrumental resolution prior to measurement. Fig. 8 shows the result of contact angle measurement on the surface of PO-15 sample. As clearly seen, the PO-15 film displayed hydrophobic wetting behavior with a contact angle of 110° from one deionized water droplet and persisted for 3 min without any spread onto the surface. The water droplet was then allowed to evaporate for several minutes and 5 more water droplets were added into the same region on the surface and the regenerated contact angle was determined to be 105°. This result is indeed a strong evidence to support the hydrophobic wetting behavior of PPO related single-ion polymer electrolytes, which is difficult to realize in PEO-based polymer electrolyte system.

4. Conclusions

In this work, the thermal transition and ionic conductivity of PO5-based single-ion polymer electrolytes were investigated by DSC and impedance spectroscopy. On the basis of the DSC results, the crystalline melting temperature of the heptadecane group was almost constant regardless of whether the lithium ion is present or not. In contrast to this, the existence of lithium ion was found to have effect on PPO segment significantly since this group has to reorient to coordinate lithium ion, which leads to generation of crystalline phase. The ionic conductivities of single-ion polymer electrolytes followed the VTF equation with activation energy and number of charge carrier as a main parameter at the lower and higher temperature regions, respectively. It was interesting to note that, the formation of ion conduction channel was found to be favored to achieve a relatively high ionic conductivity and decoupled lithium ion motion. Polarization test reveals that the lithium ion transference number was roughly 1 in the investigated PO5-based polymer electrolytes, indicating no migration of the counter anion thoughout the system. The hydrophobic wetting behavior of the PO5-based polymer electrolyte was observed due to the presence of heptadecane alkyl chain and PPO itself.

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