

Short communication

Ionic conductance of PDMAEMA/PEO polymeric electrolyte containing lithium salt mixed with plasticizer

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Abstract

Novel plasticized polymer electrolytes were synthesized with poly(*N,N*-dimethylamino-ethyl-methacrylate) (PDMAEMA), polyethylene oxide (PEO), LiTFSI as a salt, tetraethylene glycol dimethyl ether (tetraglyme), EC/PC and DEP as plasticizers. The ionic conductivity of various compositions of polymer electrolytes was investigated as a function of temperature, various concentrations of LiTFSI, plasticizers and various ratio of PDMAEMA/PEO. The ionic conductivity of PDMAEMA/PEO/LiTFSI (1.5 mol kg⁻¹) with DEP as a plasticizer (1.5 × 10⁻⁴ S cm⁻¹) exhibited lower than PDMAEMA/PEO/LiTFSI (1.2 mol kg⁻¹)/tetraglyme (5.24 × 10⁻⁴ S cm⁻¹) and PDMAEMA/PEO/LiTFSI (1.5 mol kg⁻¹)/EC + PC (2.1 × 10⁻⁴ S cm⁻¹). As increasing the PDMAEMA concentration up to 13.3%, the ionic conductivity was decreased rapidly. As increasing the PDMAEMA concentration the ionic conductivity was decreased due to high viscosity and some interactions reducing ion pairing. These plasticized polymer electrolytes were characterized by impedance spectroscopy and DSC.

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1. Introduction

Polymers containing polymethacrylate main chain have good mechanical properties and chemical stability. Characteristics of PDMAEMA are cheap polyelectrolytes, which are mainly used as flocculants, ion exchange resin and water-soluble polymers with very good membrane-forming properties [1]. It can be also used as the active layer material of a composite membrane which was prepared by PDMAEMA aqueous solution coated on its support layer and fixed by means of heat cross linking. PDMAEMA is a polymethacrylate backbone with dimethyl amino groups as pendant groups [2]. The conductivity of the polymer-blended electrolytes has been affected by the natures of plasticizers and lithium salts. Tetraglyme was used as a plasticizer to increase the conductivities of the materials. Tetraglyme should be the preferable model for quantum-mechanical studies, since lithium has

been observed to coordinate five ligands in the first solvation shell in water [4,5]. Recent calculational results for different ether oxygen containing ligands suggest a coordination number of four to five for lithium [6]. Gel electrolytes are also formed by immobilizing liquid electrolytes (lithium salts dissolved in, for example, EC and PC in a rigid polymeric matrix). The ion transport mechanism in these composite materials appears to be dominated by the liquid electrolyte, based on the observation that the conductivity of the gel is not much lower than that of the liquid electrolyte [7]. Diethyl phthalate (DEP), which is used as a plasticizer, detergent base, and binder in incense sticks and after-shave lotions. The conductivity is affected by the T_g value, particularly the polymer solvent ratio, and the nature of the plasticizing solvent. At fixed polymer/solvent/salt composition, in some cases the particular salt can also influence T_g , as is well known for the plasticizing imides anions. Especially, the changing the plasticizer has a far greater effect than changing the salt anion [7].

DEP (diethyl phthalate) is widely used as industrial solvent, plasticizer and important component of many materials. But

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the ionic conductivity of polymer electrolyte blend with DEP as a plasticizer with lithium salt, exhibited very poor. In this paper, we studied to compare the ionic conductivity of polymer blend PDMAEMA/PEO/LiTFSI containing DEP as a plasticizer with the ionic conductivity of PMMA/PVC/LiTFSI/DEP ($2.12 \times 10^{-8} \text{ S cm}^{-1}$) [8]. And also we compared the ionic conductivity of PDMAEMA/PEO/LiTFSI with tetraglyme (EC/PC) as a plasticizer, which already reported the ionic conductivities [1]. Ionic conductivity of PDMAEMA/PEO/tetraglyme/LiTFSI exhibited higher than that of PDMAEMA/PEO/EC/PC/LiTFSI and PDMAEMA/PEO/DEP/LiTFSI. So we investigated the ionic conductivity of PDMAEMA/PEO/tetraglyme/LiTFSI in proportion to changing the PDMAEMA/PEO blend ratio.

2. Experimental

N,N-Dimethylamino-ethyl-methacrylate (Aldrich Chemical Co. Inc.) was distilled before use. The monomer was polymerized at room temperature for 2 days in a nitrogen atmosphere and using a potassium peroxydisulfate–copper nitrate solution as catalyst [3]. The polymer was dissolved in ethanol and mixed with PEO (Aldrich, M.W: 6×10^5), various concentrations of $\text{LiN}(\text{CF}_3\text{SO}_3)_2$ and either, tetraethylene glycol dimethyl ether (Aldrich), ethylene carbonate (EC) propylene carbonate (PC) (Merck) (1), or diethyl phthalate (DEP)(Aldrich), to yield the polymer complexes. The nominal sample compositions are listed in Table 1. Sample A was investigated the ionic conductivity of PDMAEMA/PEO/LiTFSI with a different plasticizer. Sample B was investigated the ionic conductivity of tetraglyme/LiTFSI with a different PDMAEMA/PEO ratio. The ethanol was removed together with any remaining water by evaporation under vacuum at room temperature for 3 days. The resultant samples were transparent elastomers.

Conductance measurements were carried out in a locally designed multi-sample conductance cell, which consists of a block of aluminium, into which were machined six sample compartments. The conductance path is formed between the wall of the compartment and a central electrode. The cell constant was designed to be approximately 1 cm^{-1} . The cell constant of each cell was determined by calibration before and after each sample measurement with 0.01 M KCl solution at 25°C . Measurements were carried out in the temperature range

of $25\text{--}75^\circ\text{C}$ at 10°C intervals. The conductance of the samples was obtained by the measurement of the complex admittance of the cell between 20 Hz and 1 MHz using a HP4284A Impedance Meter, and determined from the first real axis touchdown point in the Nyquist plot of the impedance data. The temperature was controlled by a Shimaden digital temperature controller, and a type-T measurement thermocouple was located in the aluminium block close to the sample compartments.

A Perkin-Elmer differential calorimeter (DSC) Model 7 was used for the thermal measurements at a scan rate $20^\circ\text{C min}^{-1}$. A standard sample of cyclohexane, glass transition temperature -87.06°C (m.p.: 6.54°C) was used for the calibration of temperature in the DSC measurements.

3. Results and discussion

DEP is widely used as an industrial solvent, a plasticizer and an important component of many materials. But ionic conductivity of polymer electrolyte blend with DEP as a plasticizer with lithium salt was exhibited very poor ($2.12 \times 10^{-8} \text{ S cm}^{-1}$) [8]. We compared the ionic conductivity of polymer blend PDMAEMA/PEO/LiTFSI containing DEP as a plasticizer with that of different polymer blend [8] and different plasticized polymer electrolytes, that is PDMAEMA/PEO/LiTFSI with tetraglyme (and EC/PC) as a plasticizer. The thermal analysis results for PDMAEMA/PEO/EC/PC/LiTFSI (S1) PDMAEMA/PEO/tetraglyme/LiTFSI (S2) and PDMAEMA/PEO/DEP/LiTFSI (S3) are shown in Fig. 1. The S1 system of the thermal analysis results of S1, S2 and S3 having different plasticizers exhibited one endothermic peaks at 31°C and S2 system exhibited two endothermic peaks ($T_{m1} = 21.48^\circ\text{C}$, $T_{m2} = 41.3^\circ\text{C}$) corresponding to a eutectic point (T_{m1}) and liquidus (T_{m2}) melt, which indicates that the decrease of crystallinity is mild, viz. 70%, on dispersing the plasticizer and lithium salt. But in the case of PDMAEMA/PEO/DEP/LiTFSI (S3), did not exhibit any

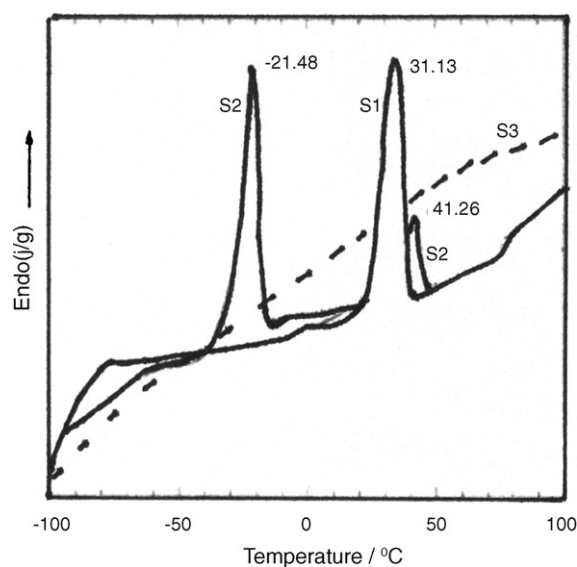


Fig. 1. The thermal analysis results for PDMAEMA/PEO/EC/PC/LiTFSI (S1), PDMAEMA/PEO/tetraglyme/LiTFSI (S2) and PDMAEMA/PEO/DEP/LiTFSI (S3).

Table 1
Compositions of polymer electrolyte

Sample A: PDMAEMA (20%)/PEO (10%)/plasticizer (70%)/LiTFSI
S1: PDMAEMA/PEO/EC + PC/LiTFSI (0, 0.3, 0.6, 0.9, 1.2, 1.5) mol kg ⁻¹
S2: PDMAEMA/PEO/tetraglyme/LiTFSI (0, 0.3, 0.6, 0.9, 1.2, 1.5) mol kg ⁻¹
S3: PDMAEMA/PEO/DEP/LiTFSI (0, 0.3, 0.6, 0.9, 1.2, 1.5) mol kg ⁻¹
Sample B
B1: PDMAEMA (0%)/PEO (30%)/tetraglyme (70%)/LiTFSI (1.2 mol kg ⁻¹)
B2: PDMAEMA (13.3%)/PEO (16.7%)/tetraglyme (70%)/LiTFSI (1.2 mol kg ⁻¹)
B3: PDMAEMA (23.3%)/PEO (6.7%)/tetraglyme (70%)/LiTFSI (1.2 mol kg ⁻¹)
B4: PDMAEMA (30%)/PEO (0%)/tetraglyme (70%)/LiTFSI (1.2 mol kg ⁻¹)

kind of peaks in this temperature range. That is, absence of any peak or change of base line has confirmed the thermal stability of the gels under consideration. It is evident that crystalline nature is predominant in the case of DEP as a plasticizer wherein amorphous nature is predominant in EC/PC and tetraglyme as a plasticizer. Fig. 2 exhibits the ionic conductivities as a function of temperature for the PDMAEMA/PEO/LiTFSI with DEP as a plasticizer (S3). The ionic conductivity of various polymer electrolytes is increased as increasing the temperature and showed the similar trend with S1, S2. Fig. 3 shows the ionic conductivities of PDMAEMA/PEO/LiTFSI/DEP as a function of lithium salt (LiTFSI) concentration. While increasing the amount of the salt in the complex the ionic conductivity increases and reached maximum at 1.5 mol kg^{-1} (LiTFSI) and then decreased gradually. Ionic conductivity of PDMAEMA/PEO/LiTFSI with DEP as a plasticizer ($1.5 \times 10^{-4} \text{ S cm}^{-1}$) exhibited higher than PMMA/PVC/LiTFSI with DEP ($2.12 \times 10^{-8} \text{ S cm}^{-1}$) or PMMA/PEO/LiBF₄/DMP ($6.4 \times 10^{-5} \text{ S cm}^{-1}$) [14]. On the basis of the higher ionic conductivity data, we expect that PDMAEMA should have fairly lower T_g . However we could not observe the glass transition for the PDMAEMA. The persistence of an increasing ionic conductivity with increasing DEP content up to 1.5 mol kg^{-1} in the PDMAEMA samples is also unusual relative to other polymer electrolytes.

The addition of a plasticizer, DEP can increase ionic conductivity of the polymer–salt system. The effect of lithium salt (include of LiTFSI) content on T_g in plasticized polymeric electrolyte and free volume were already showed previous paper in our lab [1,2,13]. The ionic conductivity of S3 (S1, S2) increased with increasing salt content up to 1.5 mol kg^{-1} . First, it seems that when the concentration of LiTFSI is increased from 0.3 to 1.5 mol kg^{-1} , T_g (as you can see in Fig. 1) and activation energy were decreased. Second, it seems that the dependence of the conductivity on the polymer chain mobility can be generally associated with the free volume of the polymer. When the concentration of LiTFSI is increased from 0.3 to 1.5 mol kg^{-1} ,

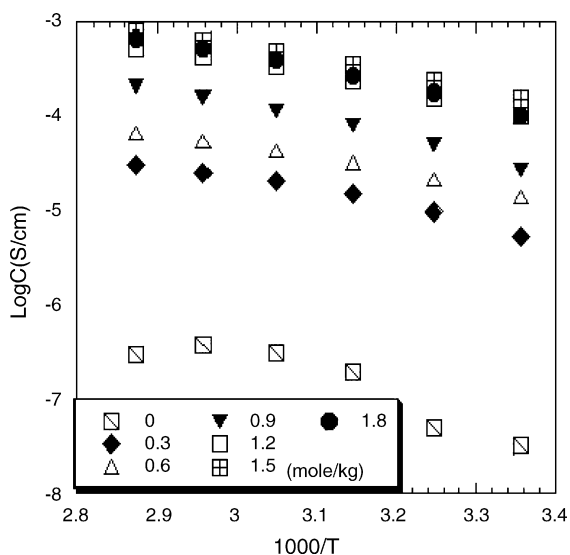


Fig. 2. Ionic conductivities as a function of temperature for the PDMAEMA/PEO/LiTFSI with DEP.

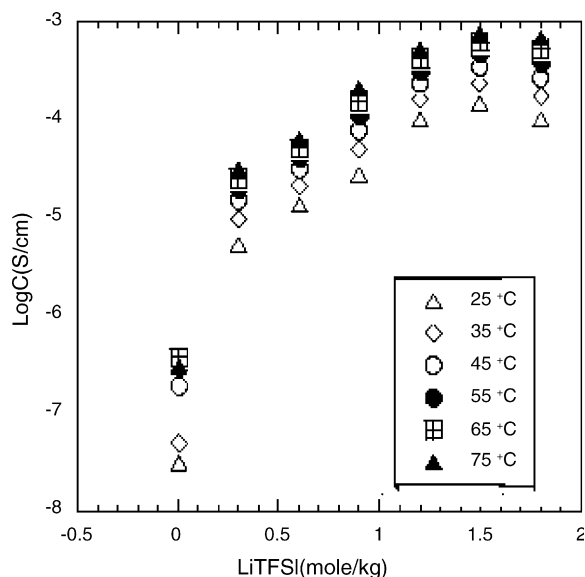


Fig. 3. Ionic conductivities of PDMAEMA/PEO/LiTFSI/DEP as a function of lithium salt concentration.

T_g was seemed to decrease. So the ionic conductivity of S3 increased with increasing salt content up to 1.5 mol kg^{-1} . And also the larger the free volume, the greater the ability of the chain rotate, hence the ions transport more rapidly. Ionic conductivities of S1, S2 and S3 are shown in Table 2 in detail. The ionic conductivities of S3 exhibits lower than that of S1 and S2 systems. Generally the nature of plasticizer and lithium salts has been found to increase the ionic conduction of the polymer electrolyte. However, in the case of a polymer electrolyte with DEP as a plasticizer the conductivity is poor. This trend was evident from X-ray studies, that is the amorphous nature of the polymer electrolyte formed with EC/PC and tetraglyme as a plasticizer reflects higher conductivity compared with crystalline nature of a polymer electrolyte formed with DEP as plasticizer [8]. Especially in polymer electrolyte containing the plasticizer rich phase interconnected with each other acts as a tunnel for ionic transport. In the case of DEP, the tunnel for ionic transport as in the case of other plasticizers may be absent in DEP, which accounts for the poor conductivity in this system [10]. The ionic conductivities of S1, S2 and S3 as a function of temperature were compared in Fig. 4. The polyelectrolyte complex containing the tetraglyme (S2) exhibited the highest ionic conductivity ($5.24 \times 10^{-4} \text{ S cm}^{-1}$ at rt, $3.41 \times 10^{-3} \text{ S cm}^{-1}$ at 65°C) of all (S1, S2, S3), while S3 exhibited the lowest ionic conductivity of all (S1, S2, S3) ($1.5 \times 10^{-5} \text{ S cm}^{-1}$ at rt). This enhancement in ionic conductivity (S2) was likely to preserve the amorphous phase of the gel by the dispersion of lithium salt and tetraglyme [2]. It seems that the dependence of the conductivity on the polymer chain mobility can be generally associated with the free volume of the polymer. The larger the free volume, the greater the ability of the chain rotate, hence the ions transport more rapidly [2,9]. Adding the plasticizer increases the dynamic free volume of the system, hence increasing conductivity seems to explain that $(\text{CH}_2\text{CH}_2\text{O})$ -ether structures in which the plasticizer, oxygen atoms may be able to solvate the cation [1]. So

Table 2
Ionic conductivities ($S\text{ cm}^{-1}$) of S1, S2, S3 with various LiTFSI contents (mol kg^{-1}) and temperatures

	LiTFSI						
	0 mol kg^{-1}	0.3 mol kg^{-1}	0.6 mol kg^{-1}	0.9 mol kg^{-1}	1.2 mol kg^{-1}	1.5 mol kg^{-1}	1.8 mol kg^{-1}
25 °C							
S1 ($\times 10^{-5}$)	0.006	0.11	0.11	0.34	0.21	0.16	
S2	0.06	0.2	0.23	0.35	0.52	0.47	0.10
S3	0.00003	0.005	0.01		0.10	0.15	
35 °C							
S1	0.010	0.18	0.18	0.48	0.40	0.30	
S2	0.097	0.26	0.31	0.55	0.84	0.78	0.18
S3	0.00005	0.01	0.02		0.16	0.24	
45 °C							
S1	0.14	0.27	0.28	0.82	0.46	0.51	
S2	0.39	0.36	0.54	1.01	1.61	2.81	0.27
S3	0.0002	0.02	0.03		0.24	0.35	
55 °C							
S1	0.19	0.38	0.41	1.10	0.90	0.73	
S2	0.39	0.50	0.74	1.24	2.34	3.00	0.39
S3	0.0003	0.02	0.04		0.34	0.49	
65 °C							
S1	0.23	0.48	0.585	1.33	1.15	0.94	
S2	0.58	0.65	0.85	1.45	2.91	3.41	0.53
S3	0.0004	0.03	0.05		0.43	0.63	
75 °C							
S1		0.54	0.68	1.37	0.30	1.06	
S2		0.75	0.92		3.27		0.68
S3		0.03	0.07		0.53	0.78	

the Li–polymer interaction was made weaker. The conductivity of gel electrolytes with EC/PC (S2) exhibits fairly high conductivity. Similar behavior is also observed in this case of polymer blends with EC/PC as a plasticizer [11] with LiBF_4 as salt [8]. In binary solvents EC + PC as a plasticizer EC has a high dielectric constant (89°C at 25°C) and lower viscosity (1.9 cP at 40°C). The lower viscosity of EC may also be contributed to the

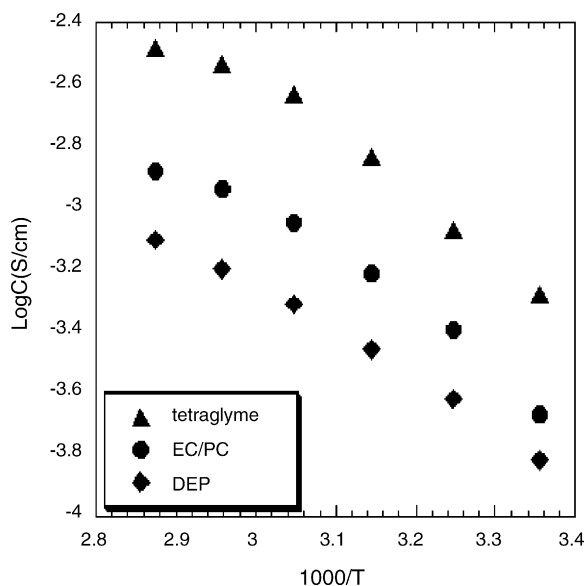


Fig. 4. Ionic conductivities of S1, S2 and S3 as a function of temperature.

enhancement in conductivity. The anionic part of Li salt plays an important role in contributing towards the conductivity and stability of the resultant electrolyte [12]. As you can see in Fig. 4, the polymer electrolyte containing DEP (S3) exhibits the lower conductivity than that of S1 and S2. It is evident that crystalline nature is predominant in the case of PDMAEMA/PEO/LiTFSI containing DEP as plasticizer wherein the amorphous nature is predominant in polymer electrolytes containing tetraglyme and the EC + PC system. These composite of polymer electrolyte (S3) seem to appear barrier to localized lithium motion than S1 and S2 system. This result means that PDMAEMA/PEO/LiTFSI containing DEP as a plasticizer exhibits the higher ionic conductivity (1.5×10^{-4}) than that of PMMA/PVC/LiTFSI/DEP ($2.12 \times 10^{-8}\text{ S cm}^{-1}$). High ionic conductivity of PDMAEMA/PEO/LiTFSI/tetraglyme seemed to be caused by PDMAEMA and PEO ratio. So we investigated the ionic conductivity of PDMAEMA/PEO/tetraglyme/LiTFSI in proportion as changing the PDMAEMA/PEO blend ratio. Fig. 5 represents the Arrhenius plot of the ionic conductivity with the fixed plasticizer (tetraglyme) and LiTFSI with the various PDMAEMA/PEO ratios. It is also observed that as temperature increases, the ionic conductivity also increases. At higher temperatures, thermal movement of polymer chain segments and the dissociation of salts would be improved, which increased ionic conductivity. At a lower temperature, the presence of lithium salt lead to salt–polymer interaction, which increases the cohesive energy of polymer networks. The overall trends of the Arrhenius plot are quite similar with the

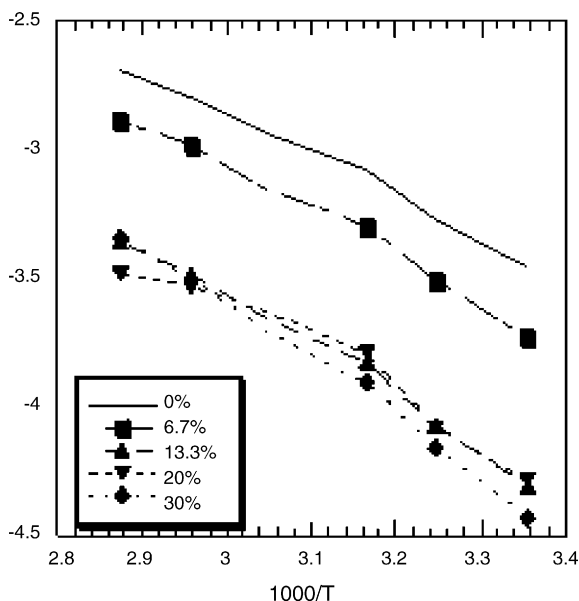


Fig. 5. Ionic conductivities as a function of temperature for the fixed plasticizer (tetraglyme) and LiTFSI with the various PDMAEMA/PEO ratios.

various PDMAEMA/PEO ratios. The curvatures exhibited in this plot explain the ionic conduction obey the VTH relation. It supported that the ion move through the plasticizer-rich phase, which involve plasticizer, the salt and the PDMAEMA, the characteristics of the viscous matrix are seemed to bring out. Fig. 6 shows the ionic conductivities as a function of the ratio of PDMAEMA/PEO for the fixed plasticizer (tetraglyme) and LiTFSI. As the concentration of PDMAEMA to these polymer electrolytes increasing, their ionic conductivity decreased up to 13.3% rapidly. The decreasing of conductivity made progress slow over 13.3%. T_g of the PDMAEMA blends increases strongly with increasing PEO concentration and increased the

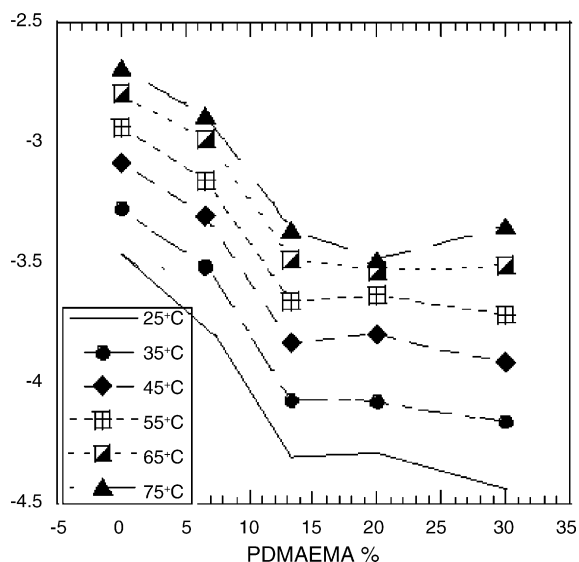


Fig. 6. Ionic conductivities as a function of the ratio of PDMAEMA/PEO for the fixed plasticizer (tetraglyme) and LiTFSI.

viscosity. An increasing viscosity competing with an increasing number of charge carriers normally explains the maximum observed in conductivity as a function of the increasing PEO concentration. It seems that as increasing the PDMAEMA with LiTFSI mixed with plasticizer at such high concentrations have some interactions reducing ion-pairing [12]. So PDMAEMA content over 13.3% seems to be the mixture more like a rubbery transparent solid.

4. Conclusion

This work exhibited the polymer electrolyte containing LiTFSI with tetraglyme, exhibits the highest conductivity ($5.24 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C) of three samples (S1, S2, S3). The polymer electrolyte containing DEP (S3) exhibited the lower conductivity value than that of the other samples. It seemed that it has a substantially higher barrier to localized lithium motion than the other samples. Thus we confirmed again the use of DEP as plasticizer is not preferred for secondary lithium battery. As the concentration of PDMAEMA to these polymer electrolytes increasing, their ionic conductivity decreased up to 13.3% rapidly. As increasing the PDMAEMA concentration the ionic conductivity was decreased due to high viscosity and some interactions reducing ion pairing.

Acknowledgements

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