



Antistatic effects of ionic liquids for polyether-based polyurethanes



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ABSTRACT

Mobility of component anions of ionic liquids (ILs) was found to be a most effective factor to enhance antistatic properties of polyether-based polyurethanes (PUs). Then, the antistatic effects were discussed with Kamlet-Taft parameters (hydrogen bond acidity: α and basicity: β) of the added ILs. A strong correlation was found between β value and surface resistivity (R_s) of the PUs containing the ILs. On the contrary, α value was found to have a weak influence on the R_s . Since there was a weaker interaction between polyether chains and anions than cations, antistatic effects of the ILs were weakened by fixing the component anions into the PUs. This strongly suggests that effective antistatic effects are supported by the anion migration of ILs.

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1. Introduction

Polyurethanes have been recognized as important materials whose properties are tunable between rubber-like elasticity and plastic-like toughness. These can be controlled by changing the ratio of polyisocyanate to polyols, their plasticizing conditions, and other factors [1]. Polyether-based polyols are widely used among engineering and electronics fields to prepare elastic and flexible polyurethanes which can be used in a wide range of temperatures [2]. However, these polyether-based polyurethanes (PUs) are insulative and they cause electrostatic discharge (ESD) and damage of electronic devices which have contact with PUs. To apply these PUs in the electronics field, there is a strong requirement to prevent ESD of PUs.

In order to prevent ESD of PUs, their resistivity should be reduced, and antistatic agents have hitherto been added to polymer materials for this purpose. Materials showing surface resistivity (R_s) greater than $10^{12} \Omega \text{sq}^{-1}$ are generally classified as insulators [3], and the R_s of $10^{10} \Omega \text{sq}^{-1}$ is practically recognized as a preferable value to keep the antistatic effects [4]. There are two

main possibilities to reduce R_s of polymers: one is based on the electronic conduction and the other is on the ionic conduction. Carbon black and inorganic fillers have been used as antistatic agents employing electronic conduction [5], while surfactants and intrinsically conductive polymers have been used as ones employing ionic conduction [6]. From the viewpoint of method to keep mechanical properties of polymer matrices, organic additives are used for organic matrices, and their added amount should be as smaller as possible. This should also be preferred to keep their properties such as transparency, morphology, and elasticity. Despite these advantages of organic additives, excellent antistatic effects are not achieved under dry conditions and considerable amount of additives are needed to form successive conduction pathways.

Ionic liquids (ILs) have been recognized as potential organic salts due to their low glass transition temperature (T_g) [7]. Since many ILs are highly dissociable and their T_g are quite low as compared to inorganic salts, ILs are expected to be excellent additives to prepare ion conductive polymers [8]. Based on this expectation, we have previously applied 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C₄mim][Tf₂N]) as antistatic agents for the PUs [9]. The R_s of the PU films has been reduced from 2.1×10^{12} to $5.5 \times 10^9 \Omega \text{sq}^{-1}$ under dry conditions when only 500 ppm of [C₄mim][Tf₂N] was added. These IL-doped PUs have been evaluated to be sufficient to avoid ESD. Smaller volume resistivity was found as compared to R_s suggesting ILs were considered to be dispersed and dissociated

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into ions in the polyether domain of the PUs. The mobility of ions are considered to affect their antistatic effects. However, few studies have been made to discuss the relationship between mobility of ions and their antistatic effect in the PUs, and no strategy has been proposed yet to design novel antistatic agents based on ILs.

2. Experimental section

2.1. Materials

Fig. 1 shows structure of ILs and zwitterion (ZI) used in this study. Abbreviation and preparation for all salts are summarized in the Supplementary Information.

In this study, linear PU was used to evaluate the solubility to ILs and network PUs were used to evaluate the conductivity of the PU films (Fig. 2). Precursors such as diphenylmethane-4,4'-diisocyanate, Millionate® MT (MDI, from Nihon Polyurethane Co., Ltd.), poly(propylene glycol) (PPG, average Mw is 4,000, from Asahi Glass Co., Ltd.), polymeric diphenylmethane diisocyanate, Sumidur 44V20 (PDI, from Sumika Bayer Urethane Chemical Co., Ltd.), trifunctional polyether polyols based on propylene-ethylene oxides 80/20 mol/mol (P(PO/EO), Mw = 7,000, from Asahi Glass Co., Ltd.), and dibutyltin dilaurate (DBTDL, from Kyodo Yakuhin Co., Ltd.) were purchased and used without further purification. DBTDL was diluted tenfold with Exxsol™ D40 Fluid (from Exxon Mobil Chemical).

A linear PU was prepared with 8.0 g of MDI, 110.5 g of PPG, and 2.0 g of the DBTDL solution as a catalyst. The mixture was stirred at 80 °C for 60 min under N₂ atmosphere, and the linear PU was obtained as a sticky liquid.

The PU films were prepared with 50.0 g of P(PO/EO), 3.59 g of PDI, and 0.9 g of DBTDL solution. This mixture was further mixed homogeneously by MAZERUSTAR KK-102 (from KURABO Industries Ltd.), then cast on a glass plate with a 0.1 mm spacer. The plate was heated to 80 °C for 30 min, and the network PUs were obtained as a

thin film (thickness = 0.1 ± 0.05 mm). ILs having hydroxyl groups, which were reactive with isocyanate, were used for preparation of IL-fixed PU films, and ILs without hydroxyl groups were used for IL-doped PU films. IL-fixed and IL-doped PUs were prepared by the same procedure of the pure PU films by using with P(PO/EO)-dried IL mixtures instead of pure P(PO/EO). The same procedure was applied for the preparation of ZI-doped PUs.

Poly(ethylene oxide) (PEO) based films were prepared by solution casting procedure. Initially, ILs were diluted tenfold with methanol. For 0.30 g of PEO (average Mw = 1,000,000, from Sigma-Aldrich) was added to 5.0 g of methanol, and the solution was mixed at 50 °C for 1 h. To the resulting solution, 3.0 mg of the IL solution was added and mixed for 10 min. The mixture was cast on a 5 cm diameter petri dish at 60 °C. To evaporate methanol, the Petri dish was heated at 60 °C for 30 min, heated at 80 °C for 10 min, and gradually cooled to room temperature.

2.2. Solubility of the linear PU in ILs

The linear PU was freeze dried prior to solubility measurement. Dried ILs and the linear PU were mixed with a ratio of 10.0/1.0 by weight. The mixed solutions were stirred at 25 °C for 24 h, and also 60 °C for 1 h if the PU was not homogeneously dissolved. Their solubility was checked visually by naked eyes at each temperature. All procedures were carried out under N₂ atmosphere.

2.3. Measurement of Kamlet-Taft Parameters

Kamlet-Taft parameters, α : hydrogen bond acidity and β : hydrogen bond basicity (Et(30) and π^* are not discussed in this study), are often used to estimate solubility of polymers in ILs [10]. Three different dyes, *N,N*-diethyl-4-nitroaniline (NN, from Wako Pure Chemical Industries, Ltd.), 4-nitroaniline (4N, from Tokyo Chem. Ind. Co.), and Reichardt' dye 33 (Rei from Fluka) were used. The dry methanol solution, 0.3 mL containing 0.03 g of corresponding dyes were added to ILs. Methanol was then removed by vacuum drying at 60 °C for 6 h. For the solvatochromic measurements, the IL solution containing dyes were placed in quartz cells with light path length of 0.1 mm, and their visible spectra were recorded with Shimadzu UV 2550 (from Shimadzu Corp.). The Kamlet-Taft parameters (π^* , α , and β values) were calculated according to the following equations (Eqs. (1)–(5)):

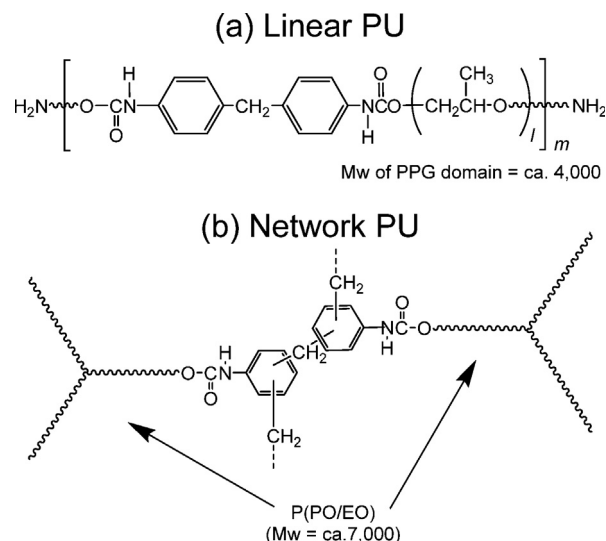
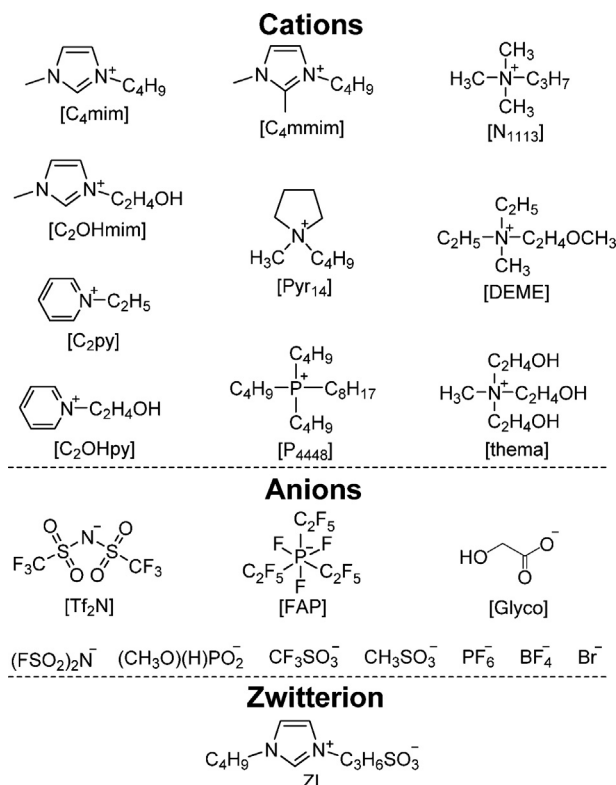


Fig. 1. Structure of ions for ILs and ZI used in this study.

Fig. 2. Structure of (a) a linear and (b) a network PUs used in this study.

$$\nu_{(\text{dye})} = 1/(\lambda_{\text{max}(\text{dye})} \times 10^{-4}) \quad (1)$$

$$E_T(30) = 0.9986(28592/\lambda_{\text{max}(\text{Rei})}) - 8.6878 \quad (2)$$

$$\pi^* = 0.314(27.52 - \nu_{\text{NN}}) \quad (3)$$

$$\alpha = 0.0649 E_T(30) - 2.03 - 0.72\pi^* \quad (4)$$

$$\beta = (1.035\nu_{\text{NN}} + 2.64 - \nu_{4\text{N}})/2.80 \quad (5)$$

where, $\lambda_{\text{max}(\text{dye})}$ is the maximum absorption wavelength of the dye.

2.4. Electrochemical properties

Surface resistivity (R_s) was measured with a Modulab system (Solartron Inc.) at room temperature. Cells with comb-shaped gold electrodes with a four-pair-toothed formation were used. Suitably cut PU films were dried in a vacuum at 60 °C for at least 3 h. These films were layered to a cell and tightly packed with glass cover under N_2 -filled glove box, and measurements were carried out under an ambient atmosphere. Prior to the measurements, +5 and -5 V were alternatively applied for 60 s to generate the same static environment on the film surfaces, then direct currents were measured by applying +5 V to the cell. The R_s was calculated with modified Ohm's law (Eq. (6)), where V is applied potential, l is the total length of electrodes ($l = 3.5$ cm), I_s and d are the measured current intensity and distance between the electrodes ($d = 0.03$ cm).

$$R_s = VI/I_s d \quad (6)$$

3. Results and Discussion

3.1. Affinity between ILs and the linear PUs

First, the affinity between ILs and PUs is discussed based on the Kamlet-Taft parameters of the ILs (Table 1). ILs and 10 wt% of the linear PU were mixed, then their solubility was checked visually by naked eyes both at room temperature and at 80 °C, and the results were found to be the same under both conditions. The ILs formed by coupling $[\text{TF}_2\text{N}]$ anion with $[\text{C}_4\text{mmim}]$, $[\text{P}_{4448}]$, $[\text{Pyr}_{14}]$, $[\text{DEME}]$, $[\text{N}_{1113}]$, or $[\text{C}_2\text{py}]$ cation showed poor compatibility with the PU. On the contrary, $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$ completely dissolved the PUs. The different solubility of $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$ and $[\text{C}_4\text{mmim}][\text{TF}_2\text{N}]$ was considered to be due to the interaction with ether oxygens of the PU via hydrogen bonds. Then, the α value of Kamlet-Taft parameter was measured to estimate hydrogen bond acidity of the ILs, and it was found to be 0.62 for $[\text{C}_4\text{mim}][\text{TF}_2\text{N}]$, while it was less than 0.60 for other $[\text{TF}_2\text{N}]$ salts which showed poor solubility of the PU. To confirm the effect of hydrogen bond acidity to dissolve the PUs, we prepared $[\text{C}_2\text{OHmim}][\text{TF}_2\text{N}]$, $[\text{C}_2\text{OHpy}][\text{TF}_2\text{N}]$, and $[\text{thema}][\text{TF}_2\text{N}]$ which all contain OH group(s) on the cations. High hydrogen bond acidity of these ILs was confirmed by α value greater than 1.00 (Table 1 (a), lower three). These $[\text{TF}_2\text{N}]$ salts easily dissolved 10 wt% of the PU at room temperature. From these results, we may conclude that strong hydrogen bond acidity of ILs is important factor to dissolve the PU.

Then, we have analyzed the effect of β value on the solubility of the PU. The ILs, which are designed to possess strong hydrogen bond acidity, have the ability to enhance ion-dipole interaction with polyether and/or to break hydrogen bonds among urethane

Table 1

Solubility of linear PU in a series of (a) $[\text{TF}_2\text{N}]$ and (b) $[\text{C}_4\text{mim}]$ salts.

(a) $[\text{TF}_2\text{N}]$ salts			
Cation species	α value	β value	Solubility
$[\text{C}_4\text{mmim}]^+$	0.38	0.24	×
$[\text{P}_{4448}]$	0.40	0.44	×
$[\text{Pyr}_{14}]$	0.49	0.23	×
$[\text{DEME}]$	0.53	0.23	×
$[\text{N}_{1113}]$	0.55	0.21	×
$[\text{C}_2\text{py}]$	0.60	0.23	×
$[\text{C}_4\text{mim}]^+$	0.62	0.24	○
$[\text{C}_2\text{OHpy}]$	1.00	0.20	○
$[\text{thema}]^+$	1.12	0.16	○
$[\text{C}_2\text{OHmim}]^+$	1.14	0.28	○
(b) $[\text{C}_4\text{mim}]$ salts			
Anion species	α value	β value	Solubility
$[\text{FAP}]$	0.67	0.10	○
$[\text{TF}_2\text{N}]^+$	0.62	0.24	○
$(\text{FSO}_2)_2\text{N}$	0.65	0.21	○
PF_6^-	0.63	0.21	×
BF_4^-	0.63	0.38	×
CF_3SO_3^-	0.63	0.46	×
$(\text{CH}_3\text{O})(\text{H})\text{PO}_2^-$	0.52	1.02	×

○: soluble, ×: insoluble.

* Kamlet-Taft parameters of these ILs were cited from reference [11].

groups. If the dissolution of the PU in the ILs is affected by the break of hydrogen bonds among urethane groups, the ILs with high β value may also enable PU dissolution because such ILs are expected to interact with proton donors of urethane groups. To check our hypothesis, we have prepared $[\text{C}_4\text{mim}](\text{CH}_3\text{O})(\text{H})\text{PO}_2$ and checked solubility of linear PU in the IL. Despite the strong hydrogen bond basicity of $[\text{C}_4\text{mim}](\text{CH}_3\text{O})(\text{H})\text{PO}_2$, this IL showed poor solubility of the PU. This suggests that the high hydrogen bond basicity is not a major factor to solubilize the PUs in the ILs. Since the fraction of the urethane units is not dominant in the PU used here, the dissolution of the PU in ILs cannot be explained only by the breakdown of hydrogen bonds. In spite that the urethane units have minor volume fraction, polyether domain is the dominant fraction for the PU. The dissolution of linear polyethers in the ILs has been understood as the results of interaction of cation-ether oxygen atoms substituting for cation-anion interaction [12]. Strong basic anions interrupt the hydrogen bond between imidazolium cation and ether oxygen atoms which results in lowering the miscibility due to their strong interaction with imidazolium cations. The solubility of the PUs has been examined using $[\text{C}_4\text{mim}]$ salts containing 7 different anions, since the β value of ILs is generally affected by the anion species. The PUs were insoluble in $[\text{C}_4\text{mim}]$ salts having high β value suggesting the interaction between cations and anions prevailed over the interaction between cations and polyethers. On the other hand, the PUs were dissolved in $[\text{C}_4\text{mim}]$ salts having low β value except for $[\text{C}_4\text{mim}]\text{PF}_6$ which may be due to the spherical structure of anion. From these results, Kamlet-Taft parameters are found to be useful to estimate affinity between the PUs and ILs.

3.2. Factors to affect R_s of the PU films containing ILs

To discuss factors to lower R_s of the PUs containing ILs, R_s is plotted as a function of some properties of ILs. Reduction of R_s was found by adding ILs to the PUs. By considering that the cells for R_s measurement was packed in N_2 -filled glove box, these ILs were confirmed to enhance antistatic effects even under dry condition. We have found that there is a strong correlation between ionic conductivity and R_s of the PU films; however, intrinsic conductivity of pure ILs have concerned weakly to the R_s [13]. Here, we discuss also the effect of glass transition temperature: T_g and viscosity: η of

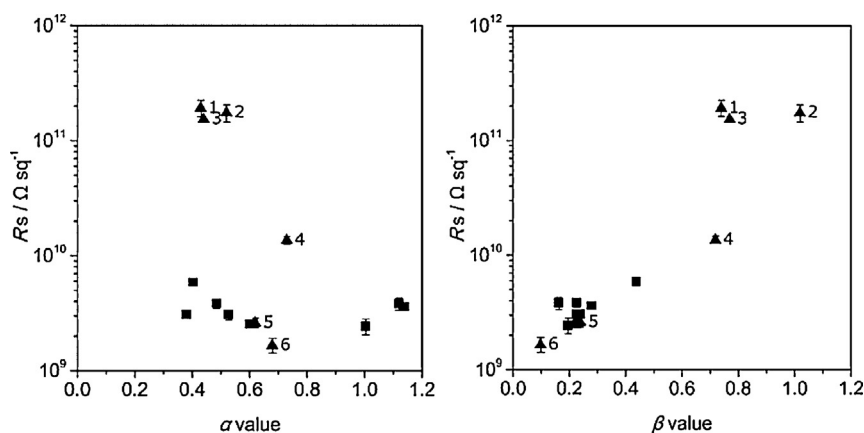


Fig. 3. Effect of Kamlet-Taft parameters (α and β) of ILs on R_s of the PUs containing the ILs. Square points represent data for $[\text{Tf}_2\text{N}]$ salts and triangular points represent that for $[\text{C}_4\text{mim}]$ salts. The anions combined with $[\text{C}_4\text{mim}]$ cation correspond to 1: Br, 2: $(\text{CH}_3\text{O})(\text{H})\text{PO}_2$, 3: CH_3SO_3 , 4: BF_4 , 5: $[\text{Tf}_2\text{N}]$, and 6: [FAP]. Kamlet-Taft parameters for some ILs were cited from references as mentioned in Table 1.

ILs on the R_s , since both properties are known to be effective to the ionic conductivity of the ILs. The ILs having both low T_g and low viscosity are found to be favorable to reduce R_s ; however, a strong correlation is not observed between these properties and the R_s (Fig. S1 in the Supplementary Information). Physico-chemical properties of pure ILs are considered not directly to affect the R_s . The declinations are considered to be enhanced by different affinity and morphology of ILs in the PUs. As mentioned above, Kamlet-Taft parameters are useful to describe affinity between ILs and the PUs. Then, we analyzed the relation between Kamlet-Taft parameters (α and β) of ILs and the R_s . There are two ion species which may contribute to antistatic effects: i.e. cations and anions. If the cation mobility of ILs dominated to realize the antistatic effects, ILs having high α value are expected to show poor antistatic effects because they are considered to be trapped into polyether domain in the PUs. However, the strong correlation between α value and the R_s was not observed in this case. The data suggest that the nature of cation is less powerful to induce antistatic effects of the polyether-based PUs. On the other hand, strong relation was observed between β value of ILs and the R_s of the composite. As shown in Table 1, ILs such as $[\text{C}_4\text{mim}][\text{Tf}_2\text{N}]$ and $[\text{C}_4\text{mim}][\text{FAP}]$ show high affinity with the PUs, and they effectively reduce the R_s (see $\blacktriangle 5$ and $\blacktriangle 6$ in Fig. 3). On the contrary of this, $[\text{C}_4\text{mim}]$ salts containing anions such as Br ($\blacktriangle 1$), $(\text{CH}_3\text{O})(\text{H})\text{PO}_2$ ($\blacktriangle 2$), CH_3SO_3 ($\blacktriangle 3$), and BF_4 ($\blacktriangle 4$) which show poor affinity with the PUs have less impact to lower the R_s . Considering that the poor solubility of the PUs in ILs is derived from interruption of hydrogen bond between cation and polyethers triggered by strong basic anions, the antistatic effects of these ILs is weakened by the strong interaction between ion pairs. These data suggest that the properties of anions are important factors to control the R_s . Consequently, the mobility of anion is a key factor to enhance antistatic effects of ILs in the PU matrices.

3.3. Active ion species for antistatic effects

In order to confirm the previously posed hypothesis, we have designed two kinds of PUs: one containing ZI and the others are ion-fixed PUs, and their R_s were compared with R_s of IL-doped PUs. First, ZI, in which both cation and anion are tethered, was used to check the contribution of ion conduction to realize the antistatic effects. The R_s of the PU films containing 1000 ppm of the ZI was $6.2 \times 10^{11} \Omega \text{sq}^{-1}$, which is almost similar to that of the pure PUs ($2.1 \times 10^{12} \Omega \text{sq}^{-1}$). This suggests that ions can migrate along with the potential gradient if ILs are added to the PUs. However, they cannot migrate under the same condition when cations and anions

are tethered. Then, we prepared ion-fixed PU films to check the contribution of each ion mobility to the antistatic effects. In a previous report, we have found that ILs consisting cations having hydroxyl groups were fixed into the PU films during plasticization via urethane bonds, and that fixation of 1000 ppm of the ILs reduced R_s to a value comparable with that of IL-doped PU films [13]. In this study, $[\text{DEME}][\text{Glyco}]$ which has a terminal hydroxyl group on the anion was used to prepare anion-fixed PUs that showed R_s value of $8.3 \times 10^{11} \Omega \text{sq}^{-1}$ when 1000 ppm of $[\text{DEME}][\text{Glyco}]$ was fixed. Because there is a possibility that $[\text{DEME}][\text{Glyco}]$ intrinsically possesses poor antistatic effect, the R_s value of the composite before anion fixation was also evaluated. To prepare $[\text{DEME}][\text{Glyco}]$ -doped polymer films, PEO matrices were used instead of the PUs, because PEO is inert to hydroxyl groups.

The open circles in Fig. 4 show R_s of $[\text{DEME}][\text{Glyco}]$ (anion-) fixed PU film and $[\text{DEME}][\text{Glyco}]$ -doped PEO film. For comparison, R_s for both PEO and the PU films containing 1000 ppm of 6 kinds of $[\text{C}_4\text{mim}]$ salts and 7 kinds of $[\text{Tf}_2\text{N}]$ salts are also shown. Two of the $[\text{Tf}_2\text{N}]$ salts are having hydroxyl groups on the cation structure and these cations are fixed into the PUs during polymerization. The diagonal line in Fig. 4 identifies the situation when the ratio of R_s for the PUs and PEO is unity. If the plots are located below this line, R_s values of the PU films are smaller than PEO films, and vice versa if the plots are located above this line, R_s values of PEO films are smaller than the PU films. For the case of IL-free films, 10 times smaller R_s was found for the PU films. This was caused by the difference of T_g reflecting different molecular weight of PEO (M_w : 1,000,000) and polyether domain in the PUs (M_w : 7,000). For the case of the films containing normal $[\text{Tf}_2\text{N}]$ salts (filled triangular points in Fig. 4), smaller R_s was found when the PUs were applied as polymer matrices. Same trend is retained if the cations of $[\text{Tf}_2\text{N}]$ salts were fixed into the PUs (open triangular points). This suggests that cation fixation does not deteriorate the intrinsic antistatic properties of $[\text{Tf}_2\text{N}]$ salts. The points for $[\text{C}_4\text{mim}]\text{BF}_4$ and $[\text{C}_4\text{mim}][\text{FAP}]$ ($\blacksquare 4$ and $\blacksquare 6$ in Fig. 4) are also located below the line. Also for the case of the PU films containing $[\text{C}_4\text{mim}]\text{Br}$ ($\blacksquare 1$), $[\text{C}_4\text{mim}](\text{CH}_3\text{O})(\text{H})\text{PO}_2$ ($\blacksquare 2$), and $[\text{C}_4\text{mim}]\text{CH}_3\text{SO}_3$ ($\blacksquare 3$), the points are located below, however close to the line. This may be due to the difference in dissociation properties of the ILs which are caused by different dipolar moment, as well as that with or without terminal hydroxyl groups of the matrix polymers. On the other hand, the point for $[\text{DEME}][\text{Glyco}]$ locates above the line. This suggests that $[\text{DEME}][\text{Glyco}]$ intrinsically has considerable antistatic effect as observed with PEO films; however, this property is inactivated after fixing anions into the PUs. When we compare the films containing $[\text{DEME}][\text{Glyco}]$ with $[\text{DEME}]$

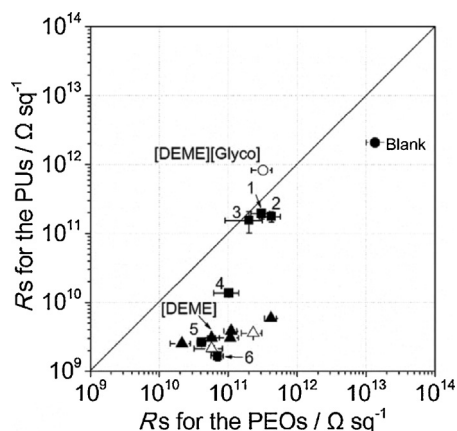


Fig. 4. Comparison of R_s of the PU films with that of PEO films containing 1000 ppm of various ILs. The triangular points represent data for films containing $[\text{Tf}_2\text{N}]$ salts with (open plot) and without (closed plot) hydroxyl groups on cation structure. The square points represent data for films containing $[\text{C}_4\text{mim}]$ salts and the number correspond to 1: Br, 2: $(\text{CH}_3\text{O})(\text{H})\text{PO}_2$, 3: CH_3SO_3 , 4: BF_4 , 5: $[\text{Tf}_2\text{N}]$, and 6: [FAP]. The circles represent films with [DEME][Glyco] (open) and IL-free films (closed).

$[\text{Tf}_2\text{N}]$, we see that R_s is thousand times larger with the PU films, however only ten times larger with PEO films. These results strongly agree with our hypothesis that high anion mobility is indeed a key factor to enhance antistatic effects of ILs in the polyether-based PUs. From these results, we have concluded that design of ILs having dissociative anion is important to improve antistatic effects of ILs in the PUs.

4. Conclusion

Strong contribution of anion migration to antistatic effects of ILs in the PUs was found. Kamlet-Taft parameters (hydrogen bond acidity: α and basicity: β) were used to discuss both affinity between ILs and the PUs and R_s of their composite films. A linear PU was dissolved in ILs having cations with high α value such as $[\text{C}_4\text{mim}]$, as long as they are coupled with anions having low β value. On the contrary, relation was found between the R_s and the β value. This suggests that anion mobility dominantly concerns to the antistatic effects of ILs in the PUs. Comparable R_s was found for cation-fixed and IL-doped PUs. These values were smaller than that for IL-doped PEOs; however, larger R_s value was observed for the [DEME][Glyco]-fixed PU compared to [DEME][Glyco]-doped PEO. Taking inactivation of antistatic effects after anion fixation into account, we have concluded that anion nature considerably contributes to antistatic effects of ILs in the PUs.

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Department of Biotechnology and Life Science at Tokyo University of Agriculture and Technology.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2014.12.128>.

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