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### COMMUNICATION

# Dissolution of oligo(tetrafluoroethylene) and preparation of poly(tetrafluoroethylene)-based composites by using fluorinated ionic liquids

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Fluorophilic ionic liquids (ILs) showing enhanced compatibility with poly(tetrafluoroethylene) (PTFE) have been newly synthesised. Thus designed ILs contributed both to the dissolution of PTFE oligomer and to the preparation of composites with PTFE with no fear of bleed-out of the ILs.

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Poly(tetrafluoroethylene) (PTFE)<sup>1</sup> is acknowledged as the most resistive polymer against chemical-, thermal-, and electrochemical-stresses. All of these properties are realised by the fact that PTFE is composed of only C-C and C-F bonds with high binding energy. PTFE is a vital material in several industrial fields such as semiconductors, office automation systems, and automobiles which require operation at high temperature and with the use of corrosive fluids. On the other hand, there are only a few reports of functionalised material where PTFE is used as a matrix,<sup>2</sup> although other kinds of fluorinated polymers such as poly(vinylidene fluoride) (PVdF) and its copolymer with hexafluoropropylene (PVdF-HFP) are widely used as a base material for polymer electrolytes.<sup>3</sup> This is because PTFE cannot retain liquid additives within their structure due to their infinite inertness. PTFE composites thus have been prepared mainly through two processes: one is the incorporation of solid  $\operatorname{additives}^{4, 5}$  and the other is the modification of PTFE polymer backbones.<sup>6, 7</sup>

In this study, a series of ionic liquids (ILs) is examined to find a compatible partner with PTFE. ILs are molten salts at ambient temperature which exhibit negligible volatility, excellent thermal stability, and considerable ionic conductivity. In addition to this, ILs exhibit a wide diversity of ion structure because they are composed of organic ions. ILs have been recognised as a unique partner for polymers and developed as additive salts<sup>8</sup> and/or plasticizer<sup>9</sup> for polymers, as well as

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solvents for polymer dissolution<sup>10</sup> and for polymerisation.<sup>11</sup> These have been achieved by designing the ILs, taking the structure and property of polymers into consideration. For example, cellulose was believed to be insoluble in any kind of organic solvent under mild condition because of many interchain hydrogen bonds. In spite of this, some ILs, designed to show a high hydrogen bonding basicity, have succeeded in dissolving cellulose.<sup>12</sup> Subsequently, the utilisation of cellulose such as ionogel, electrolyte, and bio-plastics has been accelerated considerably with the aid of newly designed polar ILs.<sup>13</sup> Polymers, that were believed to be difficult to be used because of their very poor solubility such as PTFE, have the possibility of being utilised widely only by suitably designed ILs as solvent and/or additives. Some composites composed of PTFE and ILs have been reported.<sup>4,14,15</sup> However, these composites have been prepared by using the ILs, which are solid at room temperature. In case of liquid ILs, binders between PTFE and the ILs are required. This is because the compatibility between PTFE and ILs was still low, and bleedout of ILs was still the remained subject to be clarified.

Here, we have attempted first to improve the compatibility between ILs and PTFE by considering the fluorophilicity of the ILs. As of now, some ILs composed of cation or anion with fluorinated-alkyl chains have been reported, and these have been applied as surfactant to stabilise emulsions of perfluorohexane (PFH),<sup>16</sup> as well as solvent for fluorinated gases<sup>17-19</sup> or alcohols.<sup>20,21</sup> However, even in those literatures, it was also reported that no one has yet succeeded in the complete dissolution of perfluoroalkane and of course that of PTFE. With respect to fundamentals of fluorine chemistry, there exist some empirical rules in achieving enhanced fluorophilicity: the fluorophilic molecules are generally known to have higher fluorine content (at least 60 wt%), longer and/or many fluorinated-alkyl chains, etc.<sup>22</sup> Also, the number of functional moieties that induce attractive interactions such as hydrogen bond and induction forces should be small to obtain a higher fluorophilicity. These rules have never been considered in designing ILs even though these should be useful in improving their fluorophilicity. It should be possible to

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32.9

41.1

[P<sub>666,14</sub>]

[P<sub>4446</sub>]

NN*R			Table 1. %F and $\chi_{\text{PFH}}$ of salts examined in this study.				
	Ř2 R==C4H2, R==C4H43; [P4440]		(a) [Tf <sub>2</sub> N] salts			(b) [C <sub>2</sub> mim] salts	
$R_1 = C_4 H_9; [C_4 mim]$	R <sub>2</sub> =C <sub>5</sub> H <sub>13</sub> , R <sub>3</sub> =C <sub>1</sub> ,	2 <sub>6</sub> H <sub>13</sub> , R <sub>3</sub> =C <sub>14</sub> H <sub>29</sub> ; [P <sub>B66,14</sub> ]		%F	$\chi_{ m PFH}$	Anions	
	R2=C8H13, R3=(CH2/3(CH2/7CH3; [M888F]		[C <sub>2</sub> OHmim]	28.0	5.2	BF4*	
	$\square$		[C₄py]	27.4	5.4	PF <sub>6</sub> *	4
∽Ń <sub>、∕∕</sub> Ň <sup>‡</sup> ~ <sub>C/Ho</sub> Ň	N <sup>t</sup> C₄H <sub>9</sub> −I	h <sup>+</sup> −CH₃ └ +┘	[C <sub>2</sub> mim]	29.1	6.1	[FAP]	6
Ϋ́́ς, '', '' Ċ <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub>	C <sub>4</sub> H <sub>9</sub> C <sub>4</sub> H <sub>9</sub>	[C₄mmim]	26.3	7.8	[FSI]	1
[C <sub>4</sub> mmim] [C <sub>4</sub> py]	[Pyt <sub>14</sub> ] [N <sub>4</sub>	<sub>441</sub> ] [Pip <sub>14</sub> ]	[Pip <sub>14</sub> ]	26.1	7.9	[Tf <sub>2</sub> N]	1
Anione			[Pyr <sub>14</sub> ]	27.0	10.9	[Pf <sub>2</sub> N]	3
0, - 0 5, N, 5 F <sub>2n+1</sub> C <sub>n</sub> S, S C <sub>n</sub> F <sub>2n+1</sub>	0.5	CE-SO-	[N <sub>4441</sub> ]	23.7	12.4	[Nf <sub>2</sub> N]	4
	G2F5 F⊾I−∠F F	- 01 3003 IF4	[P <sub>666,14</sub> ]	14.9	25.3	CF <sub>3</sub> SO <sub>3</sub> *	:
	$C_2F_5 \stackrel{P_{-}}{=} C_2F_5$	C <sub>4</sub> F <sub>9</sub> SO <sub>3</sub>				$C_4F_9SO_3$	4
n=0; [FSI]	[FAP] F	PF <sub>6</sub> C <sub>6</sub> F <sub>17</sub> SO <sub>3</sub>				*[C₄mim] salt	ts
Fig. 1. Structure of ILs used in this study.			(c) C <sub>8</sub> F <sub>17</sub> SO <sub>3</sub> salts			(d) [P <sub>666F</sub> ] salts	
			Cations	%F	$\chi_{ m PFH}$	Anions	
obtain ILs that have a	[C <sub>2</sub> mim]	52.9	solid	[Tf <sub>2</sub> N]	4		

R<sub>2</sub>

obtain ILs that have a higher compatibility with PTFE while taking these rules into account.

Structure and abbreviation of ILs used in this study are summarised in Fig. 1, and their synthesis methods are reported in the ESI. In an effort to seek ILs having better compatibility with PTFE, we have evaluated the solubility of perfluorohexane (PFH) in the IL, which was chosen as a model compound of PTFE. Equivolume ILs and PFH were mixed with a vortex mixer, and the mole fraction of perfluorohexane dissolved in the IL phase ( $\chi_{PFH}$ ) was determined thermogravimetrically after the IL-rich phase containing a trace of PFH was separated from the PFH-rich phase. Taking into account the fact that the dissolution of fluoro-alkane, such as PTFE and PFH, is known to be governed by the "like dissolves like" principle,  $^{23}$  a higher  $\chi_{\rm PFH}$  indicates higher fluorophilicity. The change in  $\chi_{\rm PFH}$  in relation to the polarity and fluorine content (%F) of ILs was discussed.

Table 1 (a) summarises  $\chi_{PFH}$  and %F in a series of [Tf<sub>2</sub>N] salts. In contrast to the fact that the fluorophilicity of organic molecules increases with an increase of their %F, a clear correlation between  $\chi_{PFH}$  and %F was not observed in the case of [Tf<sub>2</sub>N] salts. On the contrary, the IL having the smallest %F,  $[P_{666.14}]$ [Tf<sub>2</sub>N], exhibited the highest  $\chi_{PFH}$  among a series of [Tf<sub>2</sub>N] salts. When we focused on the cation structure of the ILs, PFH was found to be dissolved into the ILs having less polar cations. For example, [C<sub>2</sub>mim][Tf<sub>2</sub>N] dissolved 6.1 mmol mol<sup>-1</sup> of PFH, and the  $\chi_{\rm PFH}$  decreased when we used the IL [C<sub>2</sub>OHmim][Tf<sub>2</sub>N] that had polar hydroxide group on its cation structure. On the other hand, the  $\chi_{\rm PFH}$  increased when the polarity of the cation was decreased by replacing the proton on the C(2)-position of the imidazolium-ring with a methyl group (i.e., [C<sub>4</sub>mmim][Tf<sub>2</sub>N]). These two results are well comprehended by the fact that PFH is apolar and exhibits better compatibility with relatively apolar ILs. The presence of orientation forces, hydrogen bonds, and induction forces in ILs reduced the compatibility between PFH and ILs.<sup>22</sup> The effect of polarity on  $\chi_{\text{PFH}}$  was also found when the  $\alpha$  value of Kamlet-Taft parameters, which denotes the hydrogen-bonding acidity of ILs, was compared with  $\chi_{\rm PFH}$  (Fig. S1). The ILs with an  $\alpha$ value less than 0.5 dissolved a higher amount of PFH

compared to those having an  $\alpha$  value higher than 0.5. In conclusion, the ILs having apolar cations such as phosphonium cation showed enhanced  $\chi_{PFH}$  among the [Tf<sub>2</sub>N]-salts investigated here.

C<sub>8</sub>F<sub>17</sub>SO3

147.6

232.5

The  $\chi_{PFH}$  value for a series of [C<sub>2</sub>mim] salts was then analysed (Table 1 (b)). When the spherical anions were coupled with imidazolium cation, the  $\chi_{\text{PFH}}$  value decreased in the following order:  $[C_4 mim]PF_6 < [C_4 mim]BF_4 < [C_2 mim][FAP].$ Even though [C<sub>4</sub>mim]PF<sub>6</sub> had a higher %F than [C<sub>4</sub>mim]BF<sub>4</sub>, this IL exhibited a lower  $\chi_{\rm PFH}$ . Compared to the ILs containing BF<sub>4</sub> and PF<sub>6</sub>, the ILs having imide- and sulfonate-anions showed higher  $\chi_{PEH}$  except for [C<sub>2</sub>mim][FSI]. Due to this effect of anion structure, these ILs are considered not to form a fluorine-rich domain apart from charged domain. From the viewpoint of the formation of the fluorine-rich domain, we have compared the effect of fluorinated-alkyl chains in the anions. The ILs dissolved higher amount of PFH when the anion contained longer fluorinated-alkyl chain(s). We also found a positive correlation between %F and  $\chi_{PEH}$  value in the case of [C<sub>2</sub>mim] salts as shown in Fig. S2. The most noticeable improvement in  $\chi_{\text{PFH}}$  was found when imide-anions were coupled with [C<sub>2</sub>mim]. The  $\chi_{\text{PFH}}$  value was improved from 2.3 to 97.2 by replacing [FSI] with [Nf<sub>2</sub>N] anions, in which the carbon number (n) of fluorinated-alkyl chain was 0 and 4, respectively. The  $\chi_{PFH}$  of [C<sub>2</sub>mim][Nf<sub>2</sub>N] was found to be higher than that of [C<sub>2</sub>mim][FAP], in spite of the fact that the %F of the former was lower than the latter. This suggests the modification of ions with longer fluorinated-alkyl chains is important more than the improvement in the %F of ILs with short fluorinatedalkyl chains. In fluorine chemistry, it is known that the fluorophilicity of organic molecules is predominantly governed by the overall %F.<sup>22, 24</sup> However, in the case of ILs, not only the %F but also the position of fluorine atoms was found to be important in improving the fluorophilicity.

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%F

33.6 40.1

61.5

13.0 29.1

38.7

49.5

19.8 41.7

%F

42 5

51.8

exhibited a lower critical soln. temp.

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 $\chi_{\rm PFI}$ 3.5

1.5

18.5 2.3

6.1

16.0

97.2 6.7

29.6

**Х**РЕН

296.0

626.5<sup>a</sup>

### Journal Name

Based on the above-mentioned results, we have synthesised  $[C_2mim]C_8F_{17}SO_3$  expecting the formation of fluorine-rich domain. However, this IL was solid at room temperature due to strong aggregation force of fluorinatedalkyl chains.<sup>25,26</sup> To cancel the self-aggregation of anions and to induce amorphous domain, C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub> anion was combined with a cation having longer alkyl chains and larger ion size. The ILs composed of  $C_8F_{17}SO_3$  anion and phosphonium cations  $([P_{666,14}] \text{ and } [P_{4446}])$  were liquid at room temperature. As shown in Table 1 (c), these ILs showed considerably high  $\chi_{\rm PFH}$ compared to the other ILs discussed above. The higher  $\chi_{\rm PFH}$  of [P4446]C8F17SO3 is based on higher %F of the ILs. Also, a fluorinated-alkyl chain was inserted into the cation structure to further improve the fluorophilicity of ILs (see ESI for the synthesis of  $[P_{666F}][Tf_2N]$  and  $[P_{666F}]C_8F_{17}SO_3$ ). When  $[P_{666F}]C_8F_{17}SO_3$  and PFH were mixed at room temperature,  $\chi_{PFH}$ was found to be 626.5 mmol  $mol^{-1}$  (Table 1 (d)). Interestingly, when these were mixed at 0°C, the mixture resulted in a transparent homogeneous phase but gradually separated as it reached room temperature. [P<sub>666F</sub>]C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub> exhibited lower critical solution temperature (LCST)-type phase behaviour when PFH was added. The LCST was found to be around 14°C. Taking the fact that PFH is not compatible with charges nor non-fluorinated-alkyl chains into account, the dissolution of PFH in the IL is considered to be achieved through the formation of micelle-like environment of fluorophilic domain. The micelle formation motivated by the aggregation of fluorinated-alkyl chains is characterised by the triphilic property that is found only in the ILs. Some ILs having a long fluorinated-alkyl chain are known to form three domains containing polar (ionic), non-polar (alkyl chain), and fluorophilic (fluorinated-alkyl chain) moieties.<sup>27, 28</sup> Similarly,  $[P_{666F}]C_8F_{17}SO_3$  may form the domain concentrated with fluorinated-alkyl chains. With increasing temperature above the LCST, PFH and the perfluorinated-octyl chains in  $[P_{666E}]C_8F_{17}SO_3$  are considered to be exposed to the ionic and non-fluorinated-alkyl domain. Hence PFH molecules were aggregated to exclude polar groups so as to keep the entropy high. For this reason, the dissolution of PFH in the IL was achieved only at temperatures below the LCST.

Selected ILs were then applied to prepare composites with PTFE. Equivalent weight of ILs and PTFE was mixed for this experiment. Fig. 2 shows the pictures of thus prepared PTFEbased composites. These were taken at room temperature after sandwiching 5.0 mg of the samples and a 0.1 mm spacer with a pair of glass plates. When  $[C_2mim][Tf_2N]$  was added to PTFE, a homogeneous composite was not obtained (Fig. S3). The aggregated IL bled-out from PTFE when the composite was sandwiched with glass plates. This poor compatibility between PTFE and  $[C_2mim][Tf_2N]$  was also characterised by a large contact angle between them as reported in the ESI. Homogenous composites were obtained when [P<sub>666,14</sub>] cation was used instead of  $[C_2mim]$  cation. However,  $[P_{666,14}][Tf_2N]$ bled-out from PTFE matrix when the composite was pressed. By using  $C_8F_{17}SO_3$  anion, *i.e.*, in the case of  $[C_2mim]C_8F_{17}SO_3$ and  $[P_{666,14}]C_8F_{17}SO_3$ , the amount of bled-out ILs was reduced. Finally, homogeneous composites that can keep the ILs in PTFE

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Fig. 2. Composites based on PTFE and ILs in a ratio of 1:1 (w/w). The picture of PTFE/[ $C_2mim$ ] $C_3F_{17}SO_3$  composite was taken at 60°C because the IL was solid at room temperature.

film even after pressing were successfully obtained by using [P<sub>4446</sub>]C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub>. Also fluoro-functionalised ILs, *i.e.*, [P<sub>666F</sub>][Tf<sub>2</sub>N] and  $[P_{666F}]C_8F_{17}SO_3$ , enabled the preparation of homogeneous composites without bleed-out of ILs. The bleed-out of the ILs from these three composites was not observed during the course of the observation for at least one month. The bleedout is considered to be controlled by the improved wettability between these ILs and PTFE. Indeed,  $[\mathsf{P}_{666F}]\mathsf{C}_8\mathsf{F}_{17}\mathsf{SO}_3$  exhibited the smallest contact angle with PTFE among those ever reported (Table S1).<sup>29, 30</sup> Also, differential scanning calorimetry of PTFE and  $PTFE/[P_{666F}]C_8F_{17}SO_3$  composite was then measured (Figure S4). Though the melting point of PTFE was found to be at similar temperatures, the endothermic drift started at a lower temperature in the case of  $PTFE/[P_{666F}]C_8F_{17}SO_3$  compared to that of the pure PTFE. This suggests that in the case of 1:1 (weight) mixed systems, some PTFE chains are remained but other part of PTFE interact with the ILs. This also shows high compatibility between PTFE and [P<sub>666F</sub>]C<sub>8</sub>F<sub>17</sub>SO<sub>3</sub>

Consequently, the ILs, functionalised with perfluorinatedoctyl chains, were found to possess a high compatibility both with the PTFE oligomer and PTFE polymer. The homogeneous composites based on PTFE, which showed no bleed-out of ILs, were prepared by mixing PTFE with newly designed ILs.

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