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Description	

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Enhancement of Glass Transition Temperature for

Poly(methyl methacrylate) by Salt

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34 **Abstract**

35 We investigated the effects of two metal salts—lithium trifluoromethanesulfonate

36 ($LiCF_3SO_3$) and lithium bromide (LiBr)—on the glass transition temperature of

37 poly(methyl methacrylate) (PMMA). Both $LiCF_3SO_3$ and LiBr greatly enhanced the

38 glass transition temperature (T_g) of PMMA in dry conditions. However, once the sample

39 films were exposed to humidity, PMMA containing $LiCF_3SO_3$ absorbed a large amount

40 of water, which acts as a plasticizer. As a result, the T_g shifted to a lower temperature,

41 which restricts the usefulness of the polymer in industrial applications. In contrast, the

42 T_g of PMMA containing LiBr was barely affected by the absorption of water. This

43 phenomenon can be explained by an ion–dipole interaction with a small number of

44 dissociated lithium cations.

45

46 **Keywords:** PMMA, T_g, segmental motion, dynamic tensile modulus, oscillatory shear

47 modulus, relaxation

48 **Highlights:**

49 T_g of poly(methyl methacrylate) (PMMA) was enhanced by the addition of metal salt.

50 Long-term relaxation of segmental motion in PMMA containing LiBr.

51 High water-resistant property was obtained by the addition of LiBr.

1. Introduction

Amorphous plastics are widely used in various applications, and they inevitably affect people's daily lives. For practical reasons, it is necessary that such plastics have high glass transition temperatures (T_gs). Therefore, various means of increasing the T_g have been proposed, such as decreasing the number of chain ends—i.e., increasing the molecular weight[1–4]—adding miscible polymers with high T_gs,[5,6] and suppressing molecular motion by introducing chemical/physical crosslink points.[7–11] Apart from the chemical crosslinking generally used in rubber processing, other crosslinking structures include hydrogen bonding,[6,10,11] π–π stacking,[12] and electrostatic interactions[13].

We have recently reported that the T_g of poly(methyl methacrylate) (PMMA) is greatly increased by the addition of lithium trifluoromethanesulfonate ($LiCF_3SO_3$).[14] Although the metal salt addition was known to enhance T_g of an ionomer,[15–17] this should be noted because PMMA does not contain any acid/base functions like carboxyl group. The ion–dipole interaction between dissociated lithium cations and oxygen atoms in the carbonyl groups of PMMA causes reduced segmental motion in the glass-to-rubber transition region, leading to an increase in T_g.[14] This phenomenon has a large impact on industry. Therefore, the hygroscopic nature of polymers, and the effect of moisture on their T_gs should be elucidated prior to application, because the water

70   absorption of salts has a marked effect.

71   In the present study, we focused on the effects of the addition of metal salts—i.e.,

72   lithium trifluoromethanesulfonate ($LiCF_3SO_3$) and lithium bromide (LiBr)—on the T_g

73   of PMMA under dry and humid conditions.

74

75   **2. Experimental Section**

76   **2.1. Materials**

77   The polymer used in this study was a commercially available PMMA (ACRYPET V;

78   Mitsubishi Chemical Corp.). The number- and weight- average molecular weights,

79   which were determined by size-exclusion chromatography (HLC-8020; Tosoh Corp.)

80   using chloroform as a solvent, were $M_n = 8,900$ and $M_w = 15,000$, respectively. Two

81   lithium salts—lithium bromide (LiBr > 99.0 %; Tokyo Chemical Industry Co., Ltd.) and

82   lithium trifluoromethanesulfonate ($LiCF_3SO_3 \geq 98.0$ %; Kanto Chemical Co.,

83   Ltd.)—were used without further purification.

84   **2.2. Sample preparation**

85   The PMMA and the metal salt were completely dissolved in a mixture of

86   dichloromethane and methanol in 9-to-1 weight ratio, and stirred for 1 h. The molar

87   ratios of lithium ions to PMMA carbonyl groups were 0, 0.01, 0.03, and 0.07, which

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88 corresponded to 0, 2, 6, and 10 wt.% LiCF$_3$SO$_3$, and 0, 1, 3, and 6 wt.% LiBr in the

89 blends. The solutions were cast in petri dishes and dried at 160°C for 30 h under

90 vacuum. The samples were then compression molded into 350-µm-thick films. After

91 heating at 200°C for 10 min, the samples were quenched at 25°C in a compression

92 molding machine. Some of the sample films were investigated immediately after

93 compression molding. The other films were kept at 25°C and 50% relative humidity

94 (RH) or 50°C and 50% RH in a temperature- and humidity-controlled chamber.

95 **2.3. Measurements**

96 The thermal properties of the polymer were measured by differential scanning

97 calorimetry (DSC) using a DSC 8500 calorimeter (PerkinElmer Co., Ltd.) at a heating

98 rate of 10°C/min from room temperature. The samples (approximately 10 mg each)

99 were encapsulated in an aluminum pan.

100 The temperature dependence of oscillatory tensile moduli, such as storage modulus E'

101 and loss modulus E'', were measured between 30°C and 200°C using a Rheogel-E4000

102 dynamic mechanical analyzer (UBM Co., Ltd.). The frequency and heating rate were 10

103 Hz and 2°C/min, respectively. The frequency dependences on the oscillatory shear

104 moduli were measured using an AR2000ex cone-and-plate rheometer (TA Instruments

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105 Co., Ltd.) under nitrogen flow at 200, 220, and 240°C. The steady-flow properties were

106 also measured using the same plate under nitrogen flow at 240°C.

107   Infrared spectra were evaluated by attenuated total reflection (ATR)

108 measurements using a KRS-5 ATR prism under nitrogen flow. The accumulation count

109 and the resolution were four times and 4 cm^{-1}, respectively.

110

111 **3. Results and Discussion**

112 The DSC heating curves of the dried samples, i.e., immediately after compression

113 molding, are shown in Figure 1. The molar ratio of the salt to the carbonyl groups in the

114 PMMA was 0.07 in both blends. Glass-to-rubber transition was obvious in pure PMMA

115 and PMMA/LiCF$_3$SO$_3$. The glass transition temperature was increased by the addition

116 of LiCF$_3$SO$_3$. In the case of the PMMA/LiBr blend, glass transition occurred over a
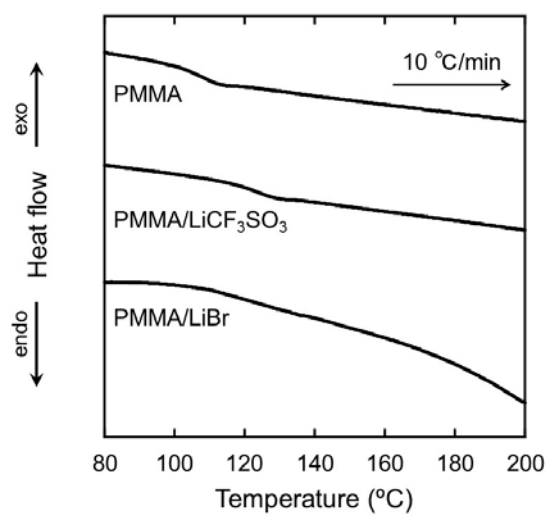
117 broad temperature range.

Figure 1. Differential scanning calorimetry (DSC) heating curves obtained at 10°C/min for pure poly(methyl methacrylate) (PMMA), PMMA/LiCF3SO3 ([Li]/[C=O] ratio of 0.07), and PMMA/LiBr ([Li]/[C=O] ratio of 0.07).

118 Figure 2 shows the temperature dependencies of the dynamic tensile moduli of

119 PMMA/LiCF$_3$SO$_3$ and PMMA/LiBr with the same molar ratios, i.e., [Li]/[C=O] of 0.07.

120 The data for pure PMMA are also represented in the figure as gray symbols for

121 comparison.

122 As demonstrated in the previous study, the addition of LiCF$_3$SO$_3$ extended the glassy

123 region to high temperatures, i.e., increased the T_g. Furthermore, E' was high and

124 insensitive to temperature in the glassy region at high temperatures. Consequently, the

125 peak ascribed to T_g was located at high temperatures. However, after storing for 5 days

126 in a temperature- and humidity-controlled chamber (25°C and 50% RH), the E' in the

127 glassy region decreased. Furthermore, besides the peak at 133°C, there was an

128 ambiguous broad peak in the E'' curve at 94°C, which is indicated by an arrow in the

129 figure. The low-temperature peak represents the T_g in the region containing a large

130 amount of water, as described later. In other words, water molecules act as a

131 plasticizer.[18–20] As a result, following moisture absorption the E' of PMMA/LiCF$_3$SO$_3$

132 was much lower than that of pure PMMA over a wide temperature range. Moreover, it

133 was impossible to define the rheological glassy and transition regions. This

134 demonstrates that, following moisture absorption, the addition of LiCF$_3$SO$_3$ reduces the

135 service temperature of PMMA, especially at high temperatures.

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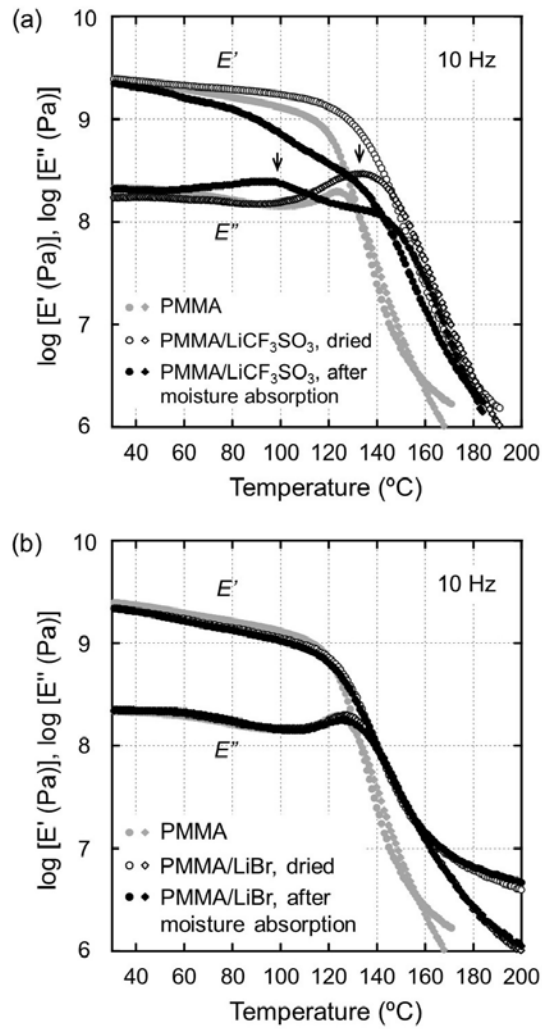
Figure 2. Temperature dependence at 10 Hz of the dynamic tensile moduli of (a) poly(methyl methacrylate) (PMMA)/LiCF$_3$SO$_3$ ([Li]/[C=O] ratio of 0.07) and (b) PMMA/LiBr ([Li]/[C=O] ratio of 0.07) films; gray symbols, pure PMMA; open symbols, dried blends; closed symbols, moisture-absorbed blends.

136   In the case of PMMA/LiBr (Figure 2(b)), the dynamic mechanical properties were

137   different from those of PMMA/LiCF$_3$SO$_3$, although PMMA/LiBr also had a higher T_g

138   than pure PMMA. In the glassy region, E' decreased slightly with temperature in a trend

139   similar to that of pure PMMA. However, beyond the glass-to-rubber transition the E'

140   was significantly higher than that of pure PMMA. Furthermore, the E'' peak became

141   broad, especially in the high-temperature region, suggesting a relaxation mode. These

142   results correspond to the DSC heating curves, and indicate that ion–dipole interactions

143   in the PMMA/LiBr system were significant and provided a prolonged relaxation

144   mechanism. Finally, it should be noted that the dynamic mechanical properties of

145   PMMA/LiBr were barely affected by moisture absorption. This is a very important

146   phenomenon because it implies that LiBr can be used to increase the T_g of PMMA in

147   industrial applications.

148   The growth curves of the sample weight measured using a chemical balance at 25°C or
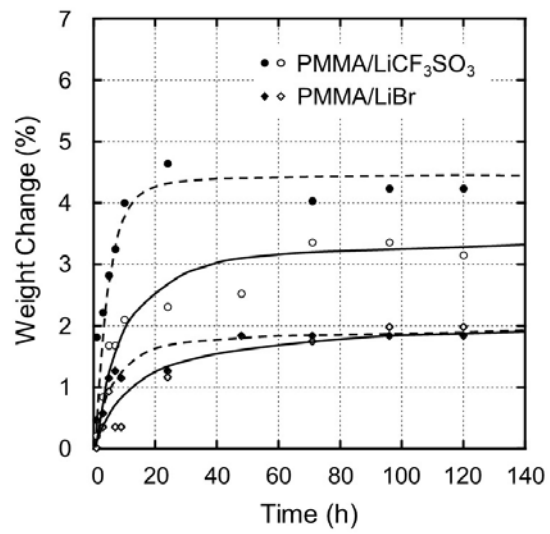
149   50°C and 50% RH are shown in Figure 3.

Figure 3. Growth curves of the weight change for (circles) poly(methyl methacrylate) (PMMA)/LiCF3SO3 ([Li]/[C=O] ratio of 0.07) and (diamonds) PMMA/LiBr films ([Li]/[C=O] ratio of 0.07); open symbols, 25°C and 50% relative humidity (RH); closed symbols, 50°C and 50% RH.

150   The figure reveals that water adsorption occurred immediately over a short period, and

151   the moisture content became constant, i.e., reached equilibrium. The moisture content of

152   PMMA with $LiCF_3SO_3$ was approximately 4%. In contrast, the PMMA containing LiBr

153   had a moisture content of only 2%. Although the values were both larger than that of

154   pure PMMA (approximately 1%), the result demonstrates that the species of salt

155   strongly affects the hygroscopic property of the polymer.

156   The difference in the moisture content of the polymer compositions containing the two

157   types of salt, which greatly affects the T_g, presents a fundamental question about the

158   interaction between the salt and the PMMA. The dissociation and ionization of the salts

159   in the PMMA are described using the binding energy based on coulombic interaction, as

160   defined by the following equation:[21]

161    $$U(r) = \frac{Q_1 Q_2}{4\pi\varepsilon_0\varepsilon r} \tag{1}$$

162   where Q_1 and Q_2 are charges, $\varepsilon = 3.6$ and ε_0 are the dielectric constants of the

163   medium and vacuum, respectively,[22,23] and r is the distance between the cation and the

164   anion. Here, we can assume that r is equal to the sum of the radii of the cation and

165   anion (where a_+ is the radius of the cation[24] and a_- is the radius of the anion,[25] which are

166   shown in Table 1). Based on this equation, dissociation occurs readily when the sum of

167   the ionic radii is large, as shown in Table 1.

Table 1. Ionic radii of lithium cation, triflate anion, and bromide anion from references. U is the calculated binding energy considering the coulombic interaction between the cation and anion in the case of ionic crystals in PMMA as a medium.

	a_+ (nm)	a_- (nm)	U (J)
$LiCF_3SO_3$	0.073	0.230	-2.1×10^{-19}
LiBr	0.073	0.196	-2.4×10^{-19}

168   The coulombic interaction energies of the ionic crystals in the PMMA are estimated as

169   shown in the table. Because the sum of the ionic radii of $LiCF_3SO_3$ is relatively large

170   owing to the large ionic radius of the triflate anion, the dissociation of $LiCF_3SO_3$ occurs

171   more readily than that of LiBr in the same solvent. Furthermore, smaller ions tend to be

172   more easily solvated by the surrounding molecules because of their higher charge

173   density. Therefore, lithium cations are strongly solvated, whereas marked solvation is

174   not expected for triflate ions. Considering both dissociation and solvation states, LiBr is

175   expected to associate more closely with PMMA because of the difficulty of dissociation

176   due to the stronger coulombic interaction between the lithium cations and the bromide

177   anions. This explains the wide glass-to-rubber transition region of the dynamic tensile

178   moduli of PMMA/LiBr, as shown in Figure 2(b).

179   Moreover, water adsorption by the lithium cation and bromide anion was prevented by

180   the strong dipole interaction between them. However, the triflate anion was "naked",

181   which increased its solvation by water molecules. This is reasonable because metal

182   trifluoromethanesulfonates act as Lewis acids in water,[26] and are therefore stable in

183   aqueous media.

184   The ATR spectra of each film suggest that the lithium ions and the PMMA carbonyl

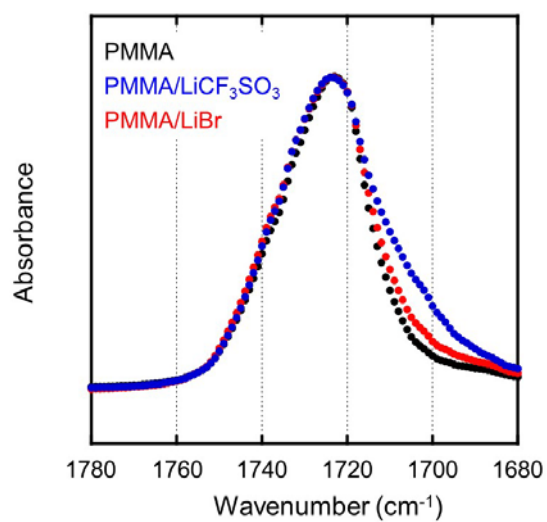185   groups interacted with each other, as shown in Figure 4.

Figure 4. Attenuated total reflection (ATR) spectra of (black) poly(methyl methacrylate) (PMMA), (blue) PMMA/LiCF$_3$SO$_3$, and (red) PMMA/LiBr with a [Li]/[C=O] ratio of 0.07.

186   The samples were measured immediately after compression molding at 200°C to

187   eliminate the effect of water absorption on the surfaces of the samples. The spectra were

188   normalized using the peak height at 1724 cm^{-1}, which is attributed to the stretching

189   vibration of the C=O bonds. In the case of PMMA/LiCF$_3$SO$_3$, the peak was broadened

190   to the lower wavenumber region, i.e., the higher energy region. In contrast, the

191   PMMA/LiBr peak was located at the same wavenumber as that of PMMA. This

192   suggests that the ion–dipole interaction between the lithium cation and the carbonyl

193   groups in PMMA/LiCF$_3$SO$_3$ was stronger than that in PMMA/LiBr on average. This

194   may be attributed to the greater number of lithium cations due to the larger degree of

195   dissociation of LiCF$_3$SO$_3$.

196   The dynamic tensile moduli of PMMA/LiCF$_3$SO$_3$ and PMMA/LiBr with different salt

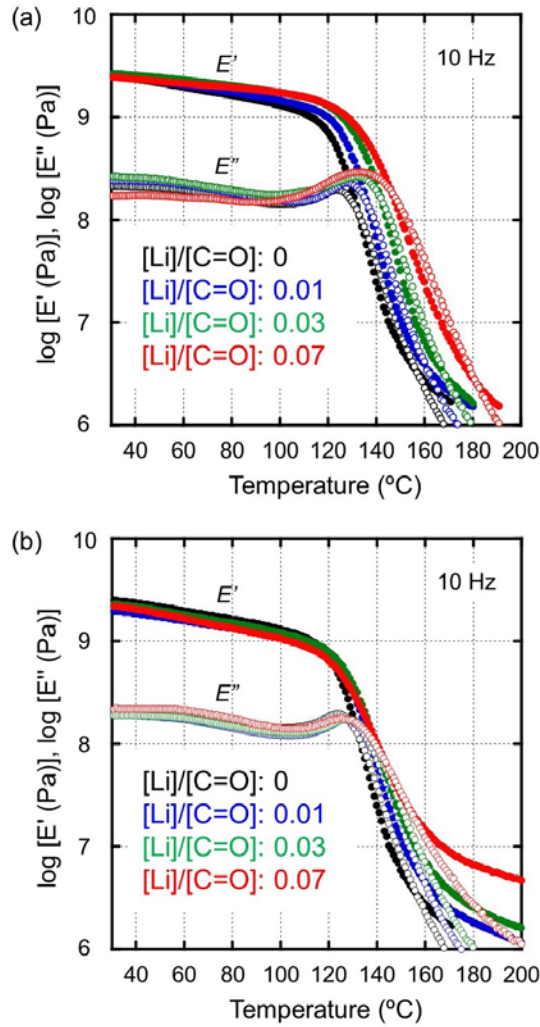197   concentrations are shown in Figures 5(a) and (b), respectively.

Figure 5. Temperature dependence of the dynamic tensile modulus at 10 Hz of (a) poly(methyl methacrylate) (PMMA)/LiCF$_3$SO$_3$ and (b) PMMA/LiBr films with different salt concentrations. The salt concentrations were 0–0.07 mol/mol of molecular weight of PMMA monomer; (black) 0 molar fraction, (blue) 0.01 molar fraction, (green) 0.03 molar fraction, and (red) 0.07 molar fraction of each salt to PMMA monomers.

198   The peak temperature of the E'' curve of PMMA/LiCF$_3$SO$_3$, ascribed to the

199   glass-to-rubber transition, increased dramatically with the salt content. The E'' peak of

200   PMMA/LiBr is located at a lower temperature than that of PMMA/LiCF$_3$SO$_3$ at the

201   same molar ratio of the salt content in PMMA. Furthermore, it is highly significant that

202   the E'' peak position did not change as the LiBr content increased at a [Li]/[C=O] ratio

203   of greater than 0.01, i.e., only 1 wt.% in PMMA. Moreover, the E'' peak became broad,

204   especially in the high temperature region.

205   To investigate the rheological properties in the molten state, the frequency dependence

206   of the oscillatory shear moduli was evaluated for pure PMMA and both blends at a

207   [Li]/[C=O] ratio of 0.01 at various temperatures.

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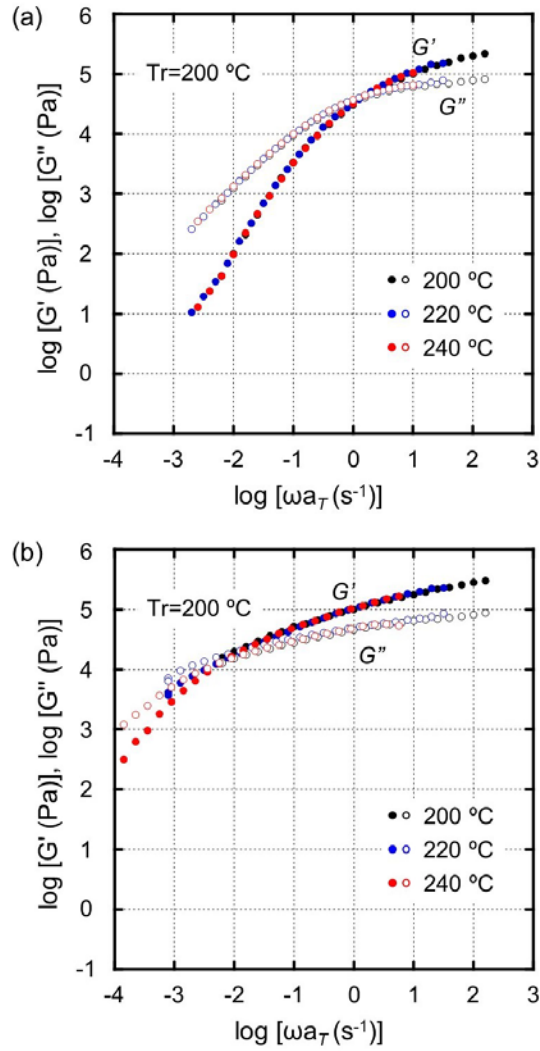
Figure 6. Master curves of frequency dependence of oscillatory shear moduli of (a) poly(methyl methacrylate) (PMMA)/LiCF$_3$SO$_3$ and (b) PMMA/LiBr with a [Li]/[C=O] ratio of 0.01 at the reference temperature T_r of 200°C; (black) 200°C, (blue) 220°C, and (red) 240°C.

208   The master curves of the oscillatory shear moduli are shown in Figure 6 at the

209   reference temperature (T_r) of 200°C. The time–temperature superposition principle was

210   not applicable for PMMA/LiBr. This is reasonable because the ion–dipole interaction

211   between the lithium cations and the carbonyl groups in PMMA decreased with

212   temperature, as demonstrated in our previous paper. However, the time–temperature

213   superposition principle was apparently applicable for PMMA/LiCF$_3$SO$_3$. This

214   phenomenon was detected because the contribution of the ion–dipole interaction to the

215   oscillatory moduli was much smaller than that of reptation motion. When the molecular

216   weight of PMMA is low, a thermorheological complex is observed, as shown in the

217   previous report[14]. Furthermore, the rubbery region of PMMA/LiBr was significantly

218   broad, demonstrating that the ion–dipole interaction prolongs the reptation motion of

219   polymer chains, even at 240°C. The longer relaxation of PMMA/LiBr is also suggested

220   quantitatively by the fact that the inverse of the angular frequency at the cross point of

221   G' and G'', i.e., ω_x, an average relaxation time of 180 s for PMMA/LiBr was

222   significantly longer than that for the other one, 0.63 s.

223   The steady-state shear stress at 240°C is shown in Figure 7 for pure PMMA

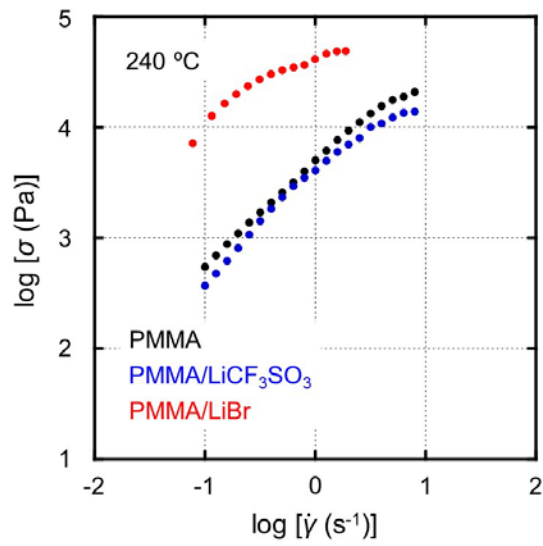224   and both blends at a [Li]/[C=O] ratio of 0.01.

225

Figure 7. Relationship between shear rate and shear stress at 240°C in poly(methyl methacrylate) (PMMA)/LiCF$_3$SO$_3$ and PMMA/LiBr with a [Li]/[C=O] ratio of 0.01 at 240°C; (black) PMMA, (blue) PMMA/LiCF$_3$SO$_3$, and (red) PMMA/LiBr.

226   The steady-state shear stress values for PMMA/LiBr were an order of magnitude higher

227   than those for the other blend. This indicates that the ion–dipole interaction persisted

228   and acted as a means of crosslinking, even at 240°C, as corroborated by the linear

229   viscoelastic properties. Furthermore, the shear stress of PMMA/LiCF$_3$SO$_3$ was slightly

230   lower than that of pure PMMA, indicating that LiCF$_3$SO$_3$ acts as a diluent for PMMA at

231   high temperatures, although it behaved like an antiplasticizer in the blend near the T_g.

232

233   **4. Conclusion**

234   We investigated the thermal and dynamic mechanical properties of PMMA containing

235   two lithium salts: LiCF$_3$SO$_3$ and LiBr. Both salts increased the T_g of PMMA owing to

236   ion–dipole interactions between the lithium cations and the carbonyl groups, and

237   LiCF$_3$SO$_3$ produced a marked increase in the T_g. However, the addition of salt also

238   increases moisture absorption. Because water acts as a plasticizer, an effect that was

239   more predominant in the case of LiCF$_3$SO$_3$, the T_g and modulus were depressed, even

240   in the glassy region of PMMA/LiCF$_3$SO$_3$. In contrast, plasticization due to moisture

241   absorption was hardly detected in the case of LiBr. The strong interaction between

242   PMMA and undissociated LiBr, which led to a prolonged relaxation mode, explains the

243   difference between PMMA/LiBr and PMMA/LiCF$_3$SO$_3$.

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