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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 .

52 1. Introduction

53 Amorphous plastics are widely used in various applications, and they inevitably affect
54 people's daily lives. For practical reasons, it is necessary that such plastics have high
55 glass transition temperatures (T_g s). Therefore, various means of increasing the T_g have
56 been proposed, such as decreasing the number of chain ends—i.e., increasing the
57 molecular weight¹⁻⁴—adding miscible polymers with high T_g s,^{5,6} and suppressing
58 molecular motion by introducing chemical/physical crosslink points.⁷⁻¹¹ Apart from the
59 chemical crosslinking generally used in rubber processing, other crosslinking structures
60 include hydrogen bonding,^{6,10,11} π - π stacking,¹² and electrostatic interactions¹³.

61 We have recently reported that the T_g of poly(methyl methacrylate) (PMMA) is greatly
62 increased by the addition of lithium trifluoromethanesulfonate (LiCF_3SO_3).¹⁴
63 Although the metal salt addition was known to enhance T_g of an ionomer,¹⁵⁻¹⁷ this
64 should be noted because PMMA does not contain any acid/base functions like carboxyl
65 group. The ion-dipole interaction between dissociated lithium cations and oxygen
66 atoms in the carbonyl groups of PMMA causes reduced segmental motion in the
67 glass-to-rubber transition region, leading to an increase in T_g .¹⁴ This phenomenon has a
68 large impact on industry. Therefore, the hygroscopic nature of polymers, and the effect
69 of moisture on their T_g s 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 ($\text{LiBr} > 99.0\%$; Tokyo Chemical Industry Co., Ltd.) and
82 lithium trifluoromethanesulfonate ($\text{LiCF}_3\text{SO}_3 \geq 98.0\%$; 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.% LiCF₃SO₃, 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- μ m-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.

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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

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/LiCF₃SO₃. The glass transition temperature was increased by the addition
116 of LiCF₃SO₃. In the case of the PMMA/LiBr blend, glass transition occurred over a
117 broad temperature range.

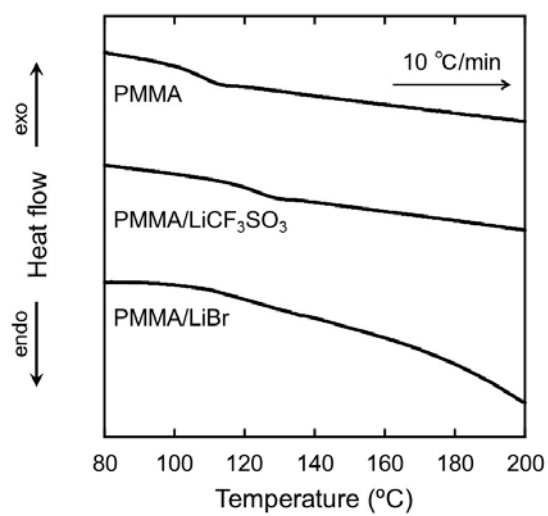


Figure 1. Differential scanning calorimetry (DSC) heating curves obtained at 10°C/min for pure poly(methyl methacrylate) (PMMA), PMMA/LiCF₃SO₃ ([Li]/[C=O] ratio of 0.07), and PMMA/LiBr ([Li]/[C=O] ratio of 0.07).

118 Figure 2 shows the temperature dependencies of the dynamic tensile moduli of
119 PMMA/LiCF₃SO₃ 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 LiCF₃SO₃ 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/LiCF₃SO₃
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 LiCF₃SO₃ reduces the
135 service temperature of PMMA, especially at high temperatures.

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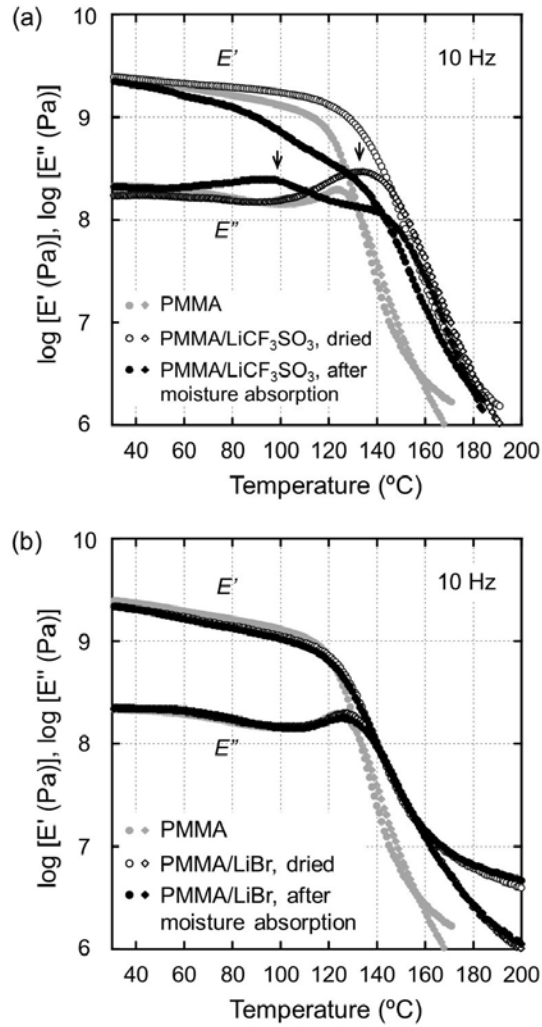


Figure 2. Temperature dependence at 10 Hz of the dynamic tensile moduli of (a) poly(methyl methacrylate) (PMMA)/LiCF₃SO₃ ([Li]/[C=O] ratio of 0.07) and (b) PMMA/LiBr ([Li]/[C=O] ratio of 0.07) films; gray symbols, pure PMMA; open symbols, dried blends; closed symbols, moisture-absorbed blends.

136 In the case of PMMA/LiBr (Figure 2(b)), the dynamic mechanical properties were
137 different from those of PMMA/LiCF₃SO₃, 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.

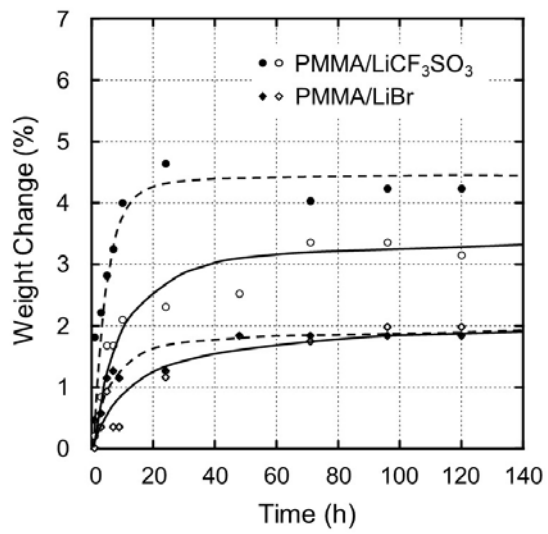


Figure 3. Growth curves of the weight change for (circles) poly(methyl methacrylate) (PMMA)/LiCF₃SO₃ ([Li]/[C=O] ratio of 0.07) and (diamonds) PMMA/LiBr films ([Li]/[C=O] ratio of 0.07); open symbols, 25°C and 50% relative humidity (RH); closed symbols, 50°C and 50% RH.

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 LiCF₃SO₃ 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

$$161 \quad U(r) = \frac{Q_1 Q_2}{4\pi\epsilon_0\epsilon r} \quad (1)$$

162 where Q_1 and Q_2 are charges, $\epsilon = 3.6$ 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 cation²⁴ 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.

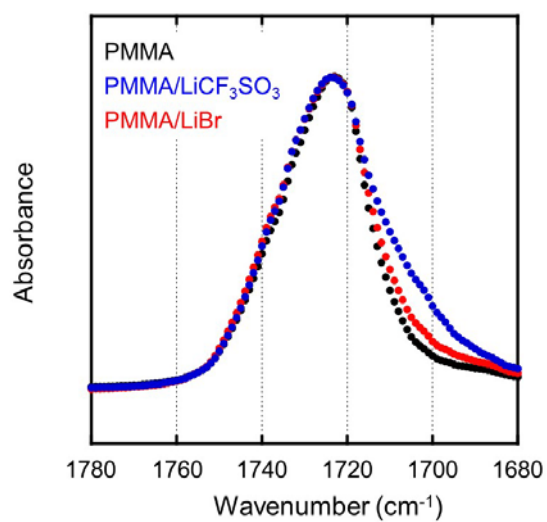


Figure 4. Attenuated total reflection (ATR) spectra of (black) poly(methyl methacrylate) (PMMA), (blue) PMMA/LiCF₃SO₃, and (red) PMMA/LiBr with a [Li]/[C=O] ratio of 0.07.

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/LiCF₃SO₃, 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/LiCF₃SO₃ 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 LiCF₃SO₃.

196 The dynamic tensile moduli of PMMA/LiCF₃SO₃ and PMMA/LiBr with different salt
197 concentrations are shown in Figures 5(a) and (b), respectively.

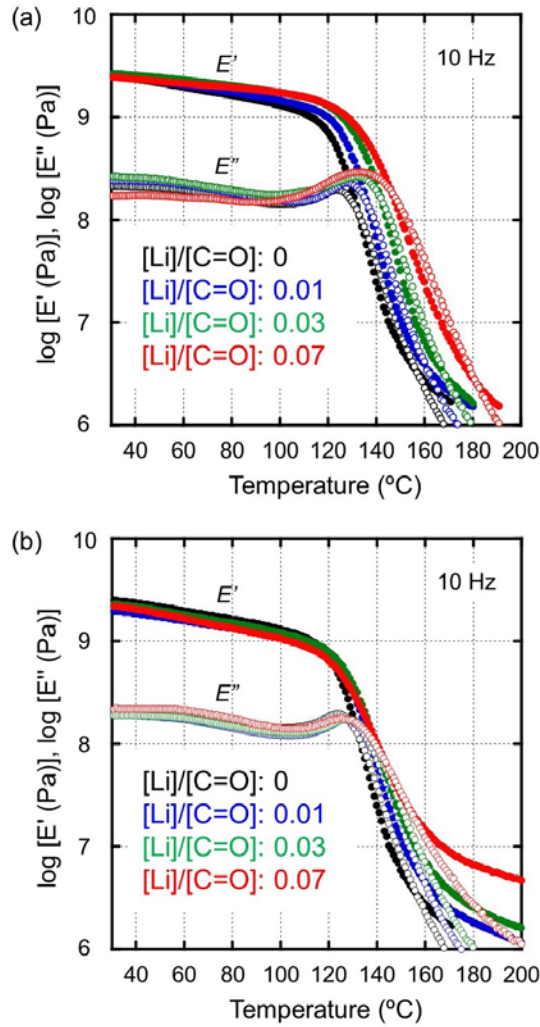


Figure 5. Temperature dependence of the dynamic tensile modulus at 10 Hz of (a) poly(methyl methacrylate) (PMMA)/LiCF₃SO₃ and (b) PMMA/LiBr films with different salt concentrations. The salt concentrations were 0–0.07 mol/mol of molecular weight of PMMA monomer; (black) 0 molar fraction, (blue) 0.01 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/LiCF₃SO₃, 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/LiCF₃SO₃ 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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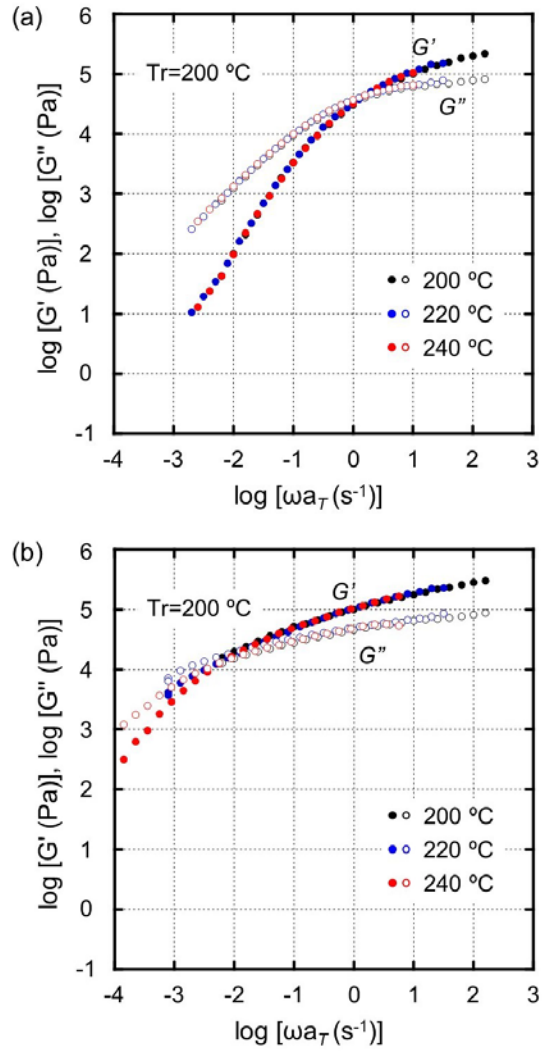


Figure 6. Master curves of frequency dependence of oscillatory shear moduli of (a) poly(methyl methacrylate) (PMMA)/LiCF₃SO₃ and (b) PMMA/LiBr with a [Li]/[C=O] ratio of 0.01 at the reference temperature T_r of 200°C; (black) 200°C, (blue) 220°C, and (red) 240°C.

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/LiCF₃SO₃. 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 report¹⁴. 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.

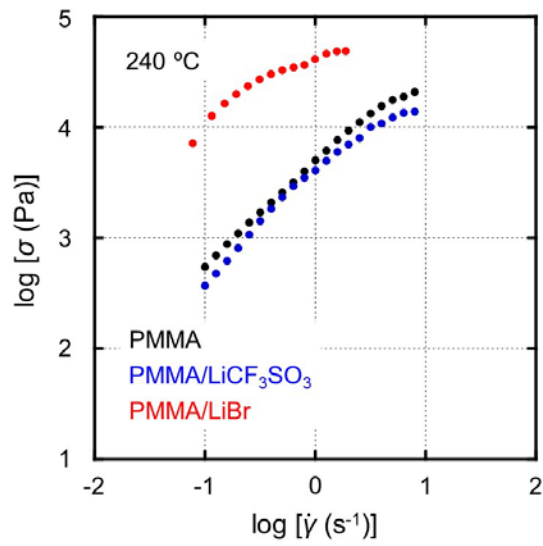


Figure 7. Relationship between shear rate and shear stress at 240°C in poly(methyl methacrylate) (PMMA)/LiCF₃SO₃ and PMMA/LiBr with a [Li]/[C=O] ratio of 0.01 at 240°C; (black) PMMA, (blue) PMMA/LiCF₃SO₃, and (red) PMMA/LiBr.

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/LiCF₃SO₃ was slightly
230 lower than that of pure PMMA, indicating that LiCF₃SO₃ acts as a diluent for PMMA at
231 high temperatures, although it behaved like an antiplasticizer in the blend near the T_g .

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233 4. Conclusion

234 We investigated the thermal and dynamic mechanical properties of PMMA containing
235 two lithium salts: LiCF₃SO₃ 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 LiCF₃SO₃ 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 LiCF₃SO₃, the T_g and modulus were depressed, even
240 in the glassy region of PMMA/LiCF₃SO₃. 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/LiCF₃SO₃.

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250 Science and technology Agency (JST).

251

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256 technology Agency (JST).

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