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Description	

Enhancement of Glass Transition Temperature for Poly(methyl methacrylate) by Salt

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Abstract

We investigated the effects of two metal salts—lithium trifluoromethanesulfonate ($LiCF_3SO_3$) and lithium bromide (LiBr)—on the glass transition temperature of poly(methyl methacrylate) (PMMA). Both $LiCF_3SO_3$ and LiBr greatly enhanced the glass transition temperature (T_g) of PMMA in dry conditions. However, once the sample films were exposed to humidity, PMMA containing $LiCF_3SO_3$ absorbed a large amount of water, which acts as a plasticizer. As a result, the T_g shifted to a lower temperature, which restricts the usefulness of the polymer in industrial applications. In contrast, the T_g of PMMA containing LiBr was barely affected by the absorption of water. This phenomenon can be explained by an ion–dipole interaction with a small number of dissociated lithium cations.

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

Highlights:

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

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

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 absorption of salts has a marked effect.

In the present study, we focused on the effects of the addition of metal salts—i.e., lithium trifluoromethanesulfonate ($LiCF_3SO_3$) and lithium bromide (LiBr)—on the T_g of PMMA under dry and humid conditions.

2. Experimental Section

2.1. Materials

The polymer used in this study was a commercially available PMMA (ACRYPET V; Mitsubishi Chemical Corp.). The number- and weight- average molecular weights, which were determined by size-exclusion chromatography (HLC-8020; Tosoh Corp.) using chloroform as a solvent, were M_n = 8,900 and M_w = 15,000, respectively. Two lithium salts—lithium bromide (LiBr > 99.0 %; Tokyo Chemical Industry Co., Ltd.) and lithium trifluoromethanesulfonate ($LiCF_3SO_3$ ≥ 98.0 %; Kanto Chemical Co., Ltd.)—were used without further purification.

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2.2. Sample preparation

The PMMA and the metal salt were completely dissolved in a mixture of dichloromethane and methanol in 9-to-1 weight ratio, and stirred for 1 h. The molar ratios of lithium ions to PMMA carbonyl groups were 0, 0.01, 0.03, and 0.07, which corresponded to 0, 2, 6, and 10 wt.% $LiCF_3SO_3$, and 0, 1, 3, and 6 wt.% LiBr in the blends. The solutions were cast in petri dishes and dried at 160°C for 30 h under vacuum. The samples were then compression molded into 350-µm-thick films. After heating at 200°C for 10 min, the samples were quenched at 25°C in a compression molding machine. Some of the sample films were investigated immediately after compression molding. The other films were kept at 25°C and 50% relative humidity (RH) or 50°C and 50% RH in a temperature- and humidity-controlled chamber.

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2.3. Measurements

The thermal properties of the polymer were measured by differential scanning calorimetry (DSC) using a DSC 8500 calorimeter (PerkinElmer Co., Ltd.) at a heating rate of 10°C/min from room temperature. The samples (approximately 10 mg each) were encapsulated in an aluminum pan.

The temperature dependence of oscillatory tensile moduli, such as storage modulus E' and loss modulus E'', were measured between 30°C and 200°C using a Rheogel-E4000 dynamic mechanical analyzer (UBM Co., Ltd.). The frequency and heating rate were 10 Hz and 2°C/min, respectively. The frequency dependences on the oscillatory shear moduli were measured using an AR2000ex cone-and-plate rheometer (TA Instruments

Co., Ltd.) under nitrogen flow at 200, 220, and 240°C. The steady-flow properties were also measured using the same plate under nitrogen flow at 240°C.

Infrared spectra were evaluated by attenuated total reflection (ATR) measurements using a KRS-5 ATR prism under nitrogen flow. The accumulation count and the resolution were four times and 4 cm^{-1}, respectively.

3. Results and Discussion

The DSC heating curves of the dried samples, i.e., immediately after compression molding, are shown in Figure 1. The molar ratio of the salt to the carbonyl groups in the PMMA was 0.07 in both blends. Glass-to-rubber transition was obvious in pure PMMA and PMMA/$LiCF_3SO_3$. The glass transition temperature was increased by the addition of $LiCF_3SO_3$. In the case of the PMMA/LiBr blend, glass transition occurred over a broad temperature range.

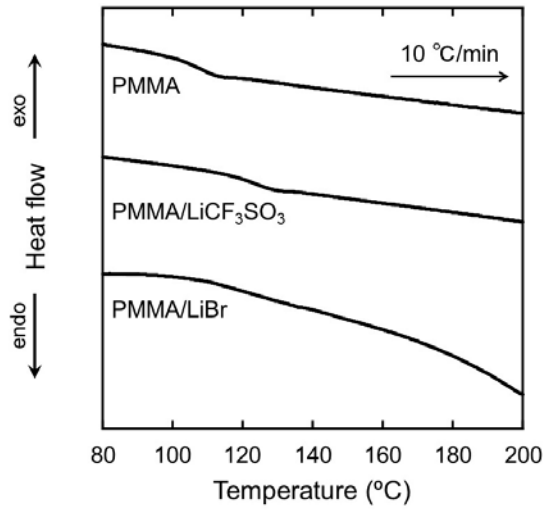

Figure 1. Differential scanning calorimetry (DSC) heating curves obtained at 10°C/min for pure poly(methyl methacrylate) (PMMA), PMMA/LiCF3SO3 ([Li]/[C=O] ratio of 0.07), and PMMA/LiBr ([Li]/[C=O] ratio of 0.07).

Figure 2 shows the temperature dependencies of the dynamic tensile moduli of PMMA/$LiCF_3SO_3$ and PMMA/LiBr with the same molar ratios, i.e., [Li]/[C=O] of 0.07. The data for pure PMMA are also represented in the figure as gray symbols for comparison.

As demonstrated in the previous study, the addition of $LiCF_3SO_3$ extended the glassy region to high temperatures, i.e., increased the T_g. Furthermore, E' was high and insensitive to temperature in the glassy region at high temperatures. Consequently, the peak ascribed to T_g was located at high temperatures. However, after storing for 5 days in a temperature- and humidity-controlled chamber (25°C and 50% RH), the E' in the glassy region decreased. Furthermore, besides the peak at 133°C, there was an ambiguous broad peak in the E'' curve at 94°C, which is indicated by an arrow in the figure. The low-temperature peak represents the T_g in the region containing a large amount of water, as described later. In other words, water molecules act as a plasticizer.[18–20] As a result, following moisture absorption the E' of PMMA/$LiCF_3SO_3$ was much lower than that of pure PMMA over a wide temperature range. Moreover, it was impossible to define the rheological glassy and transition regions. This demonstrates that, following moisture absorption, the addition of $LiCF_3SO_3$ reduces the service temperature of PMMA, especially at high temperatures.

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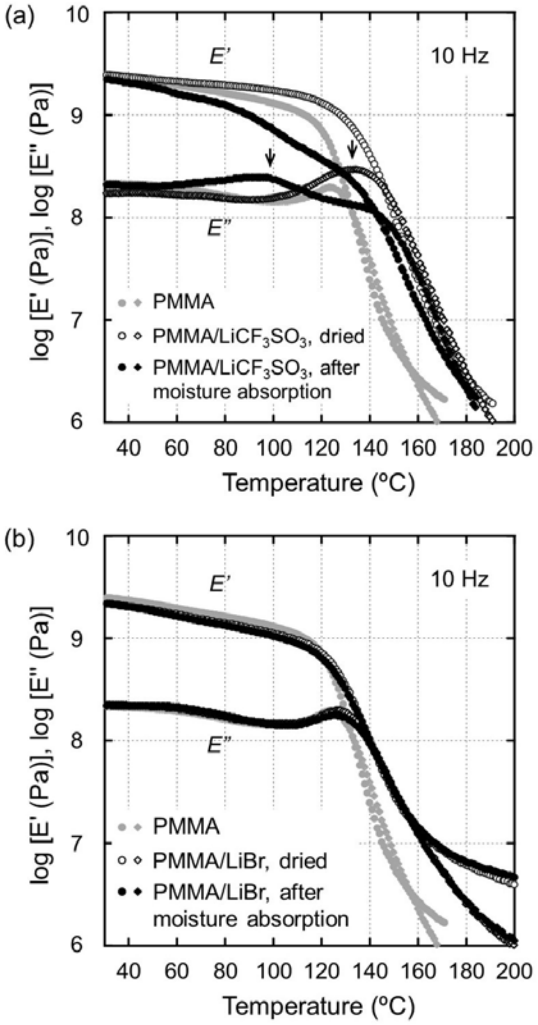

Figure 2. Temperature dependence at 10 Hz of the dynamic tensile moduli of (a) poly(methyl methacrylate) (PMMA)/$LiCF_3SO_3$ ([Li]/[C=O] ratio of 0.07) and (b) PMMA/LiBr ([Li]/[C=O] ratio of 0.07) films; gray symbols, pure PMMA; open symbols, dried blends; closed symbols, moisture-absorbed blends.

In the case of PMMA/LiBr (Figure 2(b)), the dynamic mechanical properties were different from those of PMMA/$LiCF_3SO_3$, although PMMA/LiBr also had a higher T_g than pure PMMA. In the glassy region, E' decreased slightly with temperature in a trend similar to that of pure PMMA. However, beyond the glass-to-rubber transition the E' was significantly higher than that of pure PMMA. Furthermore, the E'' peak became broad, especially in the high-temperature region, suggesting a relaxation mode. These results correspond to the DSC heating curves, and indicate that ion–dipole interactions in the PMMA/LiBr system were significant and provided a prolonged relaxation mechanism. Finally, it should be noted that the dynamic mechanical properties of PMMA/LiBr were barely affected by moisture absorption. This is a very important phenomenon because it implies that LiBr can be used to increase the T_g of PMMA in industrial applications.

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

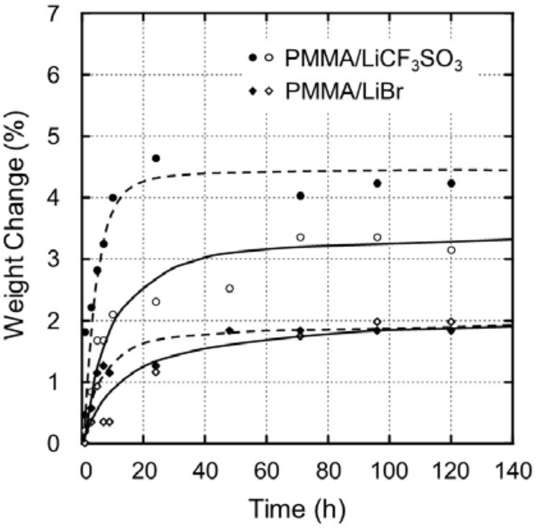

Figure 3. Growth curves of the weight change for (circles) poly(methyl methacrylate) (PMMA)/LiCF3SO3 ([Li]/[C=O] ratio of 0.07) and (diamonds) PMMA/LiBr films ([Li]/[C=O] ratio of 0.07); open symbols, 25°C and 50% relative humidity (RH); closed symbols, 50°C and 50% RH.

The figure reveals that water adsorption occurred immediately over a short period, and the moisture content became constant, i.e., reached equilibrium. The moisture content of PMMA with $LiCF_3SO_3$ was approximately 4%. In contrast, the PMMA containing LiBr had a moisture content of only 2%. Although the values were both larger than that of pure PMMA (approximately 1%), the result demonstrates that the species of salt strongly affects the hygroscopic property of the polymer.

The difference in the moisture content of the polymer compositions containing the two types of salt, which greatly affects the T_g, presents a fundamental question about the interaction between the salt and the PMMA. The dissociation and ionization of the salts in the PMMA are described using the binding energy based on coulombic interaction, as defined by the following equation:[21]

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

where Q_1 and Q_2 are charges, $\varepsilon = 3.6$ and ε_0 are the dielectric constants of the medium and vacuum, respectively,[22,23] and r is the distance between the cation and the anion. Here, we can assume that r is equal to the sum of the radii of the cation and anion (where a_+ is the radius of the cation[24] and a_- is the radius of the anion,[25] which are shown in Table 1). Based on this equation, dissociation occurs readily when the sum of 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}

The coulombic interaction energies of the ionic crystals in the PMMA are estimated as shown in the table. Because the sum of the ionic radii of $LiCF_3SO_3$ is relatively large owing to the large ionic radius of the triflate anion, the dissociation of $LiCF_3SO_3$ occurs more readily than that of LiBr in the same solvent. Furthermore, smaller ions tend to be more easily solvated by the surrounding molecules because of their higher charge density. Therefore, lithium cations are strongly solvated, whereas marked solvation is not expected for triflate ions. Considering both dissociation and solvation states, LiBr is expected to associate more closely with PMMA because of the difficulty of dissociation due to the stronger coulombic interaction between the lithium cations and the bromide anions. This explains the wide glass-to-rubber transition region of the dynamic tensile moduli of PMMA/LiBr, as shown in Figure 2(b).

Moreover, water adsorption by the lithium cation and bromide anion was prevented by the strong dipole interaction between them. However, the triflate anion was “naked”, which increased its solvation by water molecules. This is reasonable because metal trifluoromethanesulfonates act as Lewis acids in water,[26] and are therefore stable in aqueous media.

The ATR spectra of each film suggest that the lithium ions and the PMMA carbonyl groups interacted with each other, as shown in Figure 4.

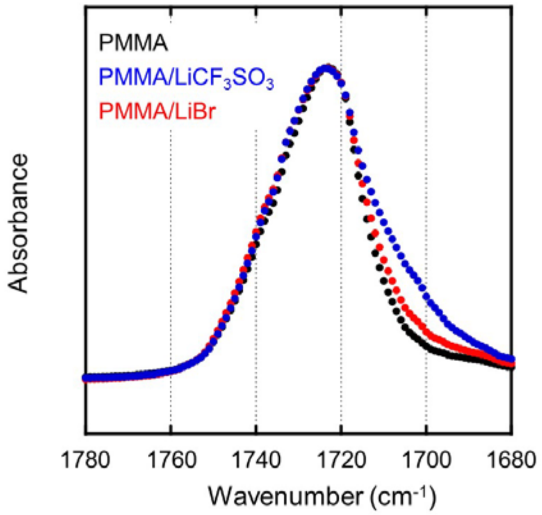

Figure 4. Attenuated total reflection (ATR) spectra of (black) poly(methyl methacrylate) (PMMA), (blue) PMMA/LiCF$_3$SO$_3$, and (red) PMMA/LiBr with a [Li]/[C=O] ratio of 0.07.

The samples were measured immediately after compression molding at 200°C to eliminate the effect of water absorption on the surfaces of the samples. The spectra were normalized using the peak height at 1724 cm^{-1}, which is attributed to the stretching vibration of the C=O bonds. In the case of PMMA/$LiCF_3SO_3$, the peak was broadened to the lower wavenumber region, i.e., the higher energy region. In contrast, the PMMA/LiBr peak was located at the same wavenumber as that of PMMA. This suggests that the ion–dipole interaction between the lithium cation and the carbonyl groups in PMMA/$LiCF_3SO_3$ was stronger than that in PMMA/LiBr on average. This may be attributed to the greater number of lithium cations due to the larger degree of dissociation of $LiCF_3SO_3$.

The dynamic tensile moduli of PMMA/$LiCF_3SO_3$ and PMMA/LiBr with different salt concentrations are shown in Figures 5(a) and (b), respectively.

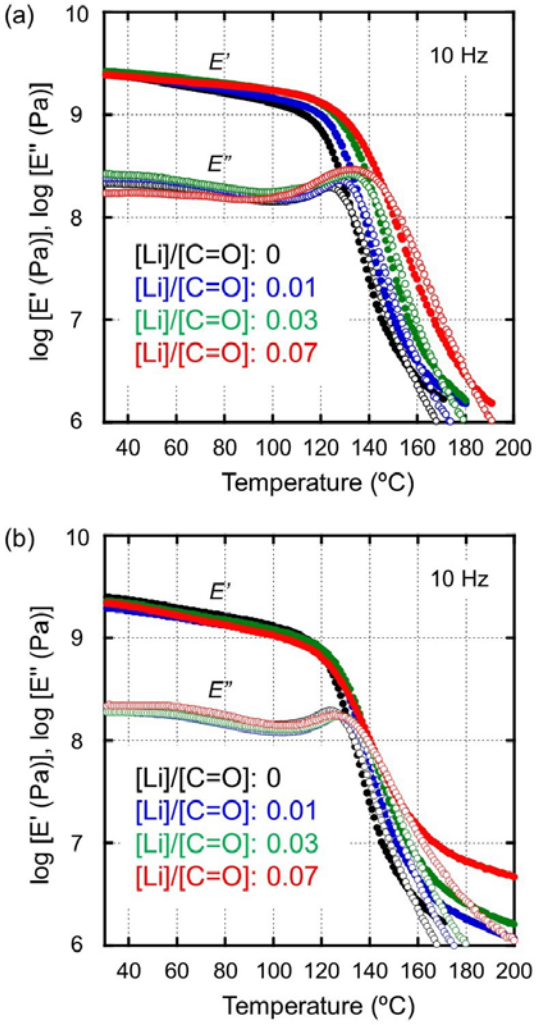

Figure 5. Temperature dependence of the dynamic tensile modulus at 10 Hz of (a) poly(methyl methacrylate) (PMMA)/$LiCF_3SO_3$ and (b) PMMA/LiBr films with different salt concentrations. The salt concentrations were 0–0.07 mol/mol of molecular weight of PMMA monomer; (black) 0 molar fraction, (blue) 0.01 molar fraction, (green) 0.03 molar fraction, and (red) 0.07 molar fraction of each salt to PMMA monomers.

The peak temperature of the E'' curve of PMMA/$LiCF_3SO_3$, ascribed to the glass-to-rubber transition, increased dramatically with the salt content. The E'' peak of PMMA/LiBr is located at a lower temperature than that of PMMA/$LiCF_3SO_3$ at the same molar ratio of the salt content in PMMA. Furthermore, it is highly significant that the E'' peak position did not change as the LiBr content increased at a [Li]/[C=O] ratio of greater than 0.01, i.e., only 1 wt.% in PMMA. Moreover, the E'' peak became broad, especially in the high temperature region.

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To investigate the rheological properties in the molten state, the frequency dependence of the oscillatory shear moduli was evaluated for pure PMMA and both blends at a [Li]/[C=O] ratio of 0.01 at various temperatures.

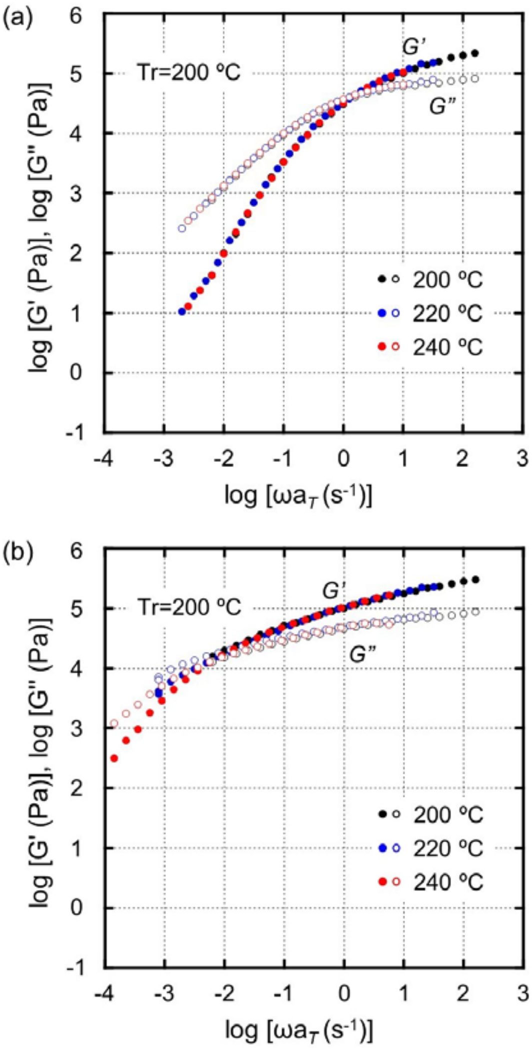

Figure 6. Master curves of frequency dependence of oscillatory shear moduli of (a) poly(methyl methacrylate) (PMMA)/$LiCF_3SO_3$ and (b) PMMA/LiBr with a [Li]/[C=O] ratio of 0.01 at the reference temperature T_r of 200°C; (black) 200°C, (blue) 220°C, and (red) 240°C.

The master curves of the oscillatory shear moduli are shown in Figure 6 at the reference temperature (T_r) of 200°C. The time–temperature superposition principle was not applicable for PMMA/LiBr. This is reasonable because the ion–dipole interaction between the lithium cations and the carbonyl groups in PMMA decreased with temperature, as demonstrated in our previous paper. However, the time–temperature superposition principle was apparently applicable for PMMA/$LiCF_3SO_3$. This phenomenon was detected because the contribution of the ion–dipole interaction to the oscillatory moduli was much smaller than that of reptation motion. When the molecular weight of PMMA is low, a thermorheological complex is observed, as shown in the previous report[14]. Furthermore, the rubbery region of PMMA/LiBr was significantly broad, demonstrating that the ion–dipole interaction prolongs the reptation motion of polymer chains, even at 240°C. The longer relaxation of PMMA/LiBr is also suggested quantitatively by the fact that the inverse of the angular frequency at the cross point of G' and G'', i.e., ω_x, an average relaxation time of 180 s for PMMA/LiBr was significantly longer than that for the other one, 0.63 s.

The steady-state shear stress at 240°C is shown in Figure 7 for pure PMMA and both blends at a [Li]/[C=O] ratio of 0.01.

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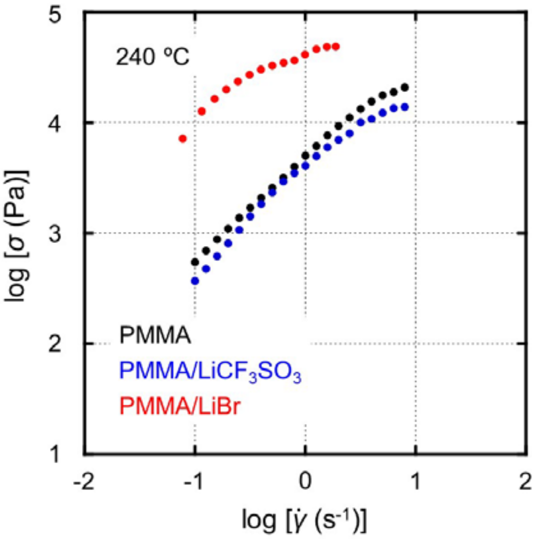

Figure 7. Relationship between shear rate and shear stress at 240°C in poly(methyl methacrylate) (PMMA)/$LiCF_3SO_3$ and PMMA/LiBr with a [Li]/[C=O] ratio of 0.01 at 240°C; (black) PMMA, (blue) PMMA/$LiCF_3SO_3$, and (red) PMMA/LiBr.

The steady-state shear stress values for PMMA/LiBr were an order of magnitude higher than those for the other blend. This indicates that the ion–dipole interaction persisted and acted as a means of crosslinking, even at 240°C, as corroborated by the linear viscoelastic properties. Furthermore, the shear stress of PMMA/$LiCF_3SO_3$ was slightly lower than that of pure PMMA, indicating that $LiCF_3SO_3$ acts as a diluent for PMMA at high temperatures, although it behaved like an antiplasticizer in the blend near the T_g.

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4. Conclusion

We investigated the thermal and dynamic mechanical properties of PMMA containing two lithium salts: $LiCF_3SO_3$ and LiBr. Both salts increased the T_g of PMMA owing to ion–dipole interactions between the lithium cations and the carbonyl groups, and $LiCF_3SO_3$ produced a marked increase in the T_g. However, the addition of salt also increases moisture absorption. Because water acts as a plasticizer, an effect that was more predominant in the case of $LiCF_3SO_3$, the T_g and modulus were depressed, even in the glassy region of PMMA/$LiCF_3SO_3$. In contrast, plasticization due to moisture absorption was hardly detected in the case of LiBr. The strong interaction between PMMA and undissociated LiBr, which led to a prolonged relaxation mode, explains the difference between PMMA/LiBr and PMMA/$LiCF_3SO_3$.

Acknowledgements

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