

Dynamics of Poly(methyl methacrylate) in Ionic Liquids with Different Concentration and Cationic Structures

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 Electronic Supplementary Information

Abstract The dynamic behavior of entangled poly(methyl methacrylate) (PMMA) chains in both the traditional monocationic ionic liquid (MIL) and synthetic dicationic ionic liquid (DIL) with the same anion bis[(trifluoromethyl)sulfonyl]imide ([TFSI][−]) has been examined over the wide composition range using differential scanning calorimetry and rheological measurements. PMMA/DIL and PMMA/MIL systems exhibit two glass transitions in the midrange of composition due to self-concentration effects. PMMA in DIL shows slower relaxation behavior, however, after the iso-free-volume correction, the terminal relaxation time τ_0 of PMMA in both the DIL and MIL presents the power law behavior $\tau_0 \sim \phi^\nu$ with exponent ν conforming to experimental results for conventional polymer solutions ($\nu=2.0 \pm 0.2$). At high ILs concentration (70%), the entanglement molecular weight M_e of PMMA/DIL system is lower than that of PMMA/MIL system owing to the formation of additional physical network in DIL, while the difference of M_e is reversed at low ILs content. The composition dependence might be related to the fact that the probability of formation of physical cross-linking points in linked double imidazolium ring increases with the increase of DIL content. The recovered creep strain of PMMA/DIL is almost 18 times of PMMA/MIL, exhibiting significantly better viscoelastic behavior.

Keywords Ionic liquids; Terminal relaxation time; Entanglement molecular weight; Creep-recovery behavior

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INTRODUCTION

Ionic liquids (ILs) as green solvents are expected to replace organic solvents due to their extremely low volatility, good chemical and thermal stability, relatively high ionic conductivity, and wide liquid temperature ranges.^[1,2] The combination of ILs with polymer exhibiting unusual phase behavior and chain dynamics provides a theoretical reference for the development and utilization of new materials. Currently, most of the ILs used in polymer/ILs systems are monocationic ILs (MILs) from imidazolium family. Recent experimental and theoretical works on polymer/MILs have shown that various self-assembly or phase separation behaviors could occur driven by intra- and inter-specific interactions including hydrogen bonding, cation- π interaction and electrostatic interaction, etc.^[1,3–6] Specifically, the phase separation kinetics, crystallization kinetics and special rheological responses for semi-crystalline poly(ethylene oxide) (PEO)/imidazolium-based MILs have been investigated in detail from the viewpoint of hydrogen bonding interaction.^[7–9]

Besides the studies of PEO and its derivatives in ILs, incorporation of ILs into amorphous poly(methyl methacrylate)

(PMMA) could also attract much attention due to the improved thermal stability and gel properties of the mixtures.^[10,11] It has been demonstrated that the imidazolium-based MILs interact with PMMA mainly *via* the hydrogen bonds between the H atoms on the C₂ position of the imidazolium rings and O atoms of polymer carboxylic.^[12] The hydrogen bonding interactions might have a significant effect on segmental dynamics of polymers in MILs. Lodge and Watanabe reported that two broad but distinct glass transitions appeared in PMMA/1-ethyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([C₂(mim)][TFSI]) system which indicates some local structures between PMMA and [C₂(mim)][TFSI] form at intermediate concentration range originated from the chain connectivity of PMMA.^[13,14] The rheological property covering from unentangled to entangled behavior in PMMA/[C₂(mim)][TFSI] system has been studied, in which the plateau modulus G_N^0 shows a concentration dependence of $G_N^0 \sim c^{2.2}$ at the PMMA concentrated regimes.^[13] Yan *et al.* found the intermolecular interaction between PMMA and MILs is too weak to change the nonlinear chain orientation/stretch under shear flow or large deformation.^[15] It is scarce to study the dynamics of PMMA/ILs systems with different ILs structures, especially with stronger interactions between the PMMA and ILs, because only a small variety of ILs exhibit good compatibility with PMMA.

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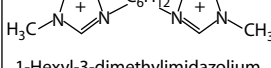
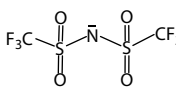
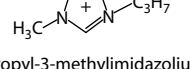
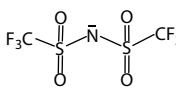
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Dicationic ionic liquids (DILs), composed of two monoanions and one dication linked by a molecular chain with variable length, have been designed and developed.^[16–20] Compared with MILs, DILs show the more favorable physicochemical properties including thermal stability, surface tension, shear viscosity, and so forth.^[16,17,21–23] Only a few reports focus on polymer/DILs systems, which exhibit higher viscoelasticity and thermal stability than those of polymer/MILs systems. It is attributed to the special double imidazolium ring structure of DILs that results in the formation of polymer-ionic network and the stronger electrostatic attraction between cations and anions.^[24–26] In our previous work, the relaxation and entanglement of PMMA chains in DILs and MILs were investigated only at low PMMA concentrations (no more than 35.3%). The result indicates that PMMA in DILs shows lower critical entanglement concentration, longer relaxation time, and a denser entanglement network than in their MILs counterparts.^[25] The focus of this work is to systematically examine the dynamic behaviors of PMMA chains in both the traditional MIL and new DIL over a wide composition range. The concentration dependence of the difference in entanglement between PMMA/MIL and PMMA/DIL systems is obtained. The relaxation of PMMA/ILs systems in the presence of hydrogen bonding interaction and physical cross-linking points is investigated by means of iso-free-volume correction in detail. The glass transition behavior of PMMA/ILs systems is studied at compositions from 20% polymer to pure polymer. Finally, a creep-recovery experiment is performed to quantitatively examine the viscoelastic behavior of PMMA/MIL and PMMA/DIL systems.

EXPERIMENTAL

Materials and Sample Preparation

PMMA was provided by Sigma-Aldrich with $M_w=80$ kg/mol ($M_w/M_n=1.76$). MIL was purchased from Shanghai Cheng Jie Chemical Co., Ltd. DIL was synthesized on the basis of our previous work,^[25] and chemicals required in the synthesis of DIL were obtained from Aladdin without further purification. The chemical structures of DIL and MIL are shown in Scheme 1. Some key characteristic properties of DIL and MIL including density (ρ), glass transition temperature (T_g) and viscosity (η) at room temperature are summarized in Table 1. Before use, the MIL and DIL were purified by rotary evaporation at 100 °C for 1 h, and PMMA was dried at 80 °C for at least 24 h in a vacuum oven.

ILs	Cations	Anion
DIL	 1-Hexyl-3-dimethylimidazolium, abbreviated as $[C_6(mim)_2]^{2+}$	 Bis(trifluoromethyl)sulfonyl anion, abbreviated as $[TFSI]^-$
MIL	 1-Propyl-3-methylimidazolium, abbreviated as $[C_3(mim)]^+$	 Bis(trifluoromethyl)sulfonyl anion, abbreviated as $[TFSI]^-$

Scheme 1 Structures of cations and anion for the ILs studied in this work.

Table 1 Physicochemical Properties of DIL and MIL.^[16]

ILs	ρ (g/cm ³)	T_g (°C)	η (cP)	Miscibility with water
$[C_6(mim)_2][TFSI]$	1.52	−60.6	649.5	No
$[C_3(mim)][TFSI]$	1.45	−90.0	42.8	No

PMMA and ILs with different volume ratios were mixed using ethyl acetate as cosolvent under continuous stirring to homogeneous solution. Then, solvent was evaporated slowly by a natural volatilization process in a fume cupboard. The as prepared film samples were further dried at 60 °C in a vacuum oven for 1 week to remove any residue solvent and stored in the glove box. The PMMA/ILs systems were hot-pressed at 150 °C in vacuum into disks (25 mm × 1.0 mm) for rheological measurements. PMMA/DIL and PMMA/MIL systems were labeled as D_nAx and M_nAx respectively, where “A” stands for PMMA, “n” represents the alkyl chain lengths and “x” is volume fraction of PMMA (ϕ) in the mixture.

Rheological Measurements

The viscoelastic properties of the PMMA/ILs systems were implemented by a stress-controlled (TA-DHR-3) rheometer with the 25 mm parallel plate geometry and the 0.8 mm gap. Dynamic frequency sweeps from 100 rad/s to 0.1 rad/s were performed on using strain amplitude of 2% or less to guarantee the linear response of the measured samples. To further characterize and quantify the viscoelastic difference of PMMA/DIL and PMMA/MIL systems, creep-recovery experiments were carried out at given temperatures. In the creep test a constant shear stress of 10 Pa was applied and the resulting time-dependent creep compliance (J_c) was obtained. As the J_c reached the terminal flow zone, the shear stress was set to zero and the creep stopped. The entire creep process occurred in linear viscoelastic deformation regime. Subsequently, the recoverable compliance (J_r) was measured as a function of the recovery time. All experiments were carried out under a nitrogen atmosphere and the sample was allowed to equilibrate for 10 min before starting any testing.

Differential Scanning Calorimetry (DSC)

DSC measurements were taken on a DSC250 (TA instruments, USA) to investigate the T_g of PMMA/ILs systems under a flowing nitrogen atmosphere. Samples (~4–10 mg) were firstly annealed at 150 °C for 10 min to eliminate the thermal history and subsequently cooled to −80 °C, after which the samples were heated to 150 °C for the second time. Both the cooling and heating rates were 10 °C/min. Measurements were obtained in the secondary heating scan, and the T_g values were obtained from the derivative heat flow curves.

RESULTS AND DISCUSSION

Glass Transition of PMMA/DIL and PMMA/MIL Systems

Fig. 1 shows the DSC heat flow curves and the corresponding derivative curves of PMMA/DIL and PMMA/MIL systems. The glass transition is traditionally associated with the step change of heat flow versus temperature which appears as a peak in the derivative curve.^[27] Each T_g value could be taken from the peak position in the derivative curve. A monotonical decrease in the T_g occurs as the ILs concentration increases. The transition is

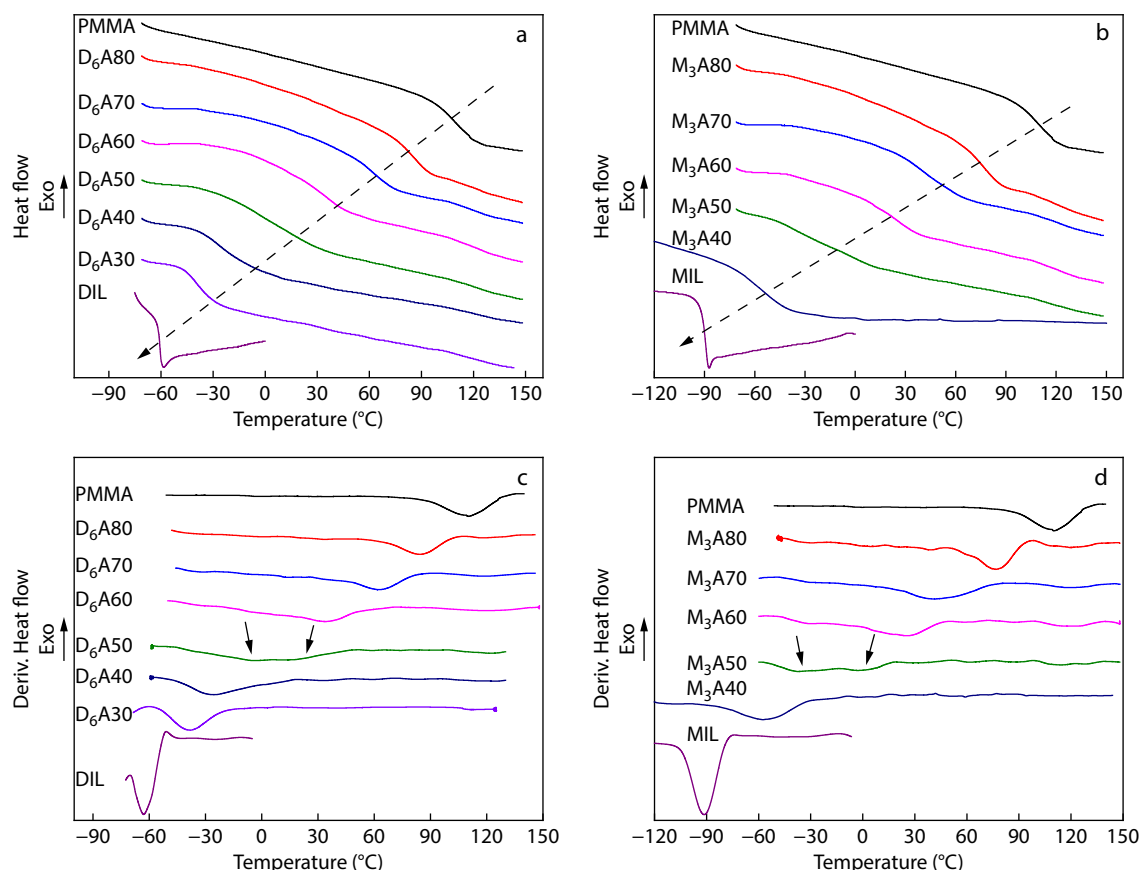


Fig. 1 DSC heating curves (a, b) and corresponding derivative curves (c, d) of PMMA/ILs systems with different ILs concentrations.

remarkably broad in the mid-composition range, especially for M₃A50 and D₆A50, where a bimodal corresponding to two T_g values appears in the derivative curves. Even though the signature of D₆A50 and M₃A50 in Figs. 1(c) and 1(d) is not obvious due to the limitation of the Y-axis scale, the derivative heat flow curves are presented in Fig. S1 (in the electronic supplementary information, ESI) for D₆A50 and M₃A50 with a bimodal clearly observed. This result was also reported in some miscible polymer blend system,^[27] which could be explained by the Lodge-McLeish model that based on the effective local compositions caused by self-concentration effects.^[28] Therefore, the appearance of two T_g values in M₃A50 and D₆A50 indicates the inherent compositional heterogeneity rather than phase separation in the mixture.

The T_g values determined in the analysis described above for PMMA/ILs systems are plotted against the volume fraction of PMMA in Fig. 2. Two glass transitions are clearly shown for D₆A50 and M₃A50 systems, in which the lower T_g is assigned to ILs-rich regions and the higher T_g to PMMA-rich regions. It is noteworthy that ILs-rich or PMMA-rich regions here refer to the presence of effective local concentrations at length scales of relevance to T_g dynamics instead of the phase regions, as shown in Fig. S2 (in ESI). The concentration dependence of T_g in miscible blend system could be predicted using Gordon-Taylor equation (Eq. 1) and Fox equation (Eq. 2):^[29,30]

$$T_g = v_A T_{g,A} + v_B T_{g,B} \quad (1)$$

$$\frac{1}{T_g} = \frac{v_A}{T_{g,A}} + \frac{v_B}{T_{g,B}} \quad (2)$$

where v_A and v_B ($v_A + v_B = 1$) are volume fractions and $T_{g,A}$ and $T_{g,B}$ are glass transition temperatures corresponding to PMMA and ILs, respectively. The fitting results are the same for the PMMA/DIL and PMMA/MIL systems. Obviously, the composition dependence of T_g at higher PMMA content could be fitted by using Gordon-Taylor equation, while Fox equation is more suitable for fitting the data at lower PMMA content. Theoretically, the physical meaning of the Gordon-Taylor

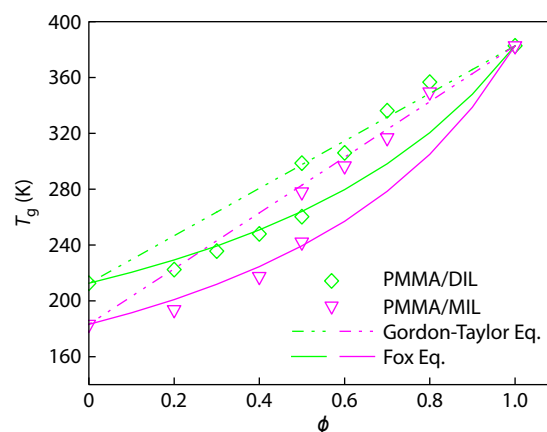


Fig. 2 T_g of PMMA/ILs systems as a function of the volume fraction of PMMA. Noted that the dash and solid lines are fitting results by Gordon-Taylor equation and Fox equation, respectively.

equation is based on a weighted average of various macroscopic properties associated with T_g (e.g., viscosity), while the Fox equation describes microscopic properties related to T_g (e.g., activation energy). The space scale of polymer dynamics (on the order of 10 Å) is longer than that of solvent molecules. That is to say, for PMMA/ILs systems with large amounts of PMMA, the glass transition is influenced by the averaged interaction of several ILs molecules around the PMMA chain, while the T_g of the mixtures with higher ILs content is related to the distribution of PMMA-ILs distances due to a higher self-concentration in the more flexible small molecule ILs.^[13,14] Thus, the composition dependence of T_g in mixtures with higher PMMA volume fractions or the PMMA-rich regions of D₆A50 (M₃A50) system is consistent with the Gordon-Taylor equation corresponding to the plasticizing effectiveness of ILs on PMMA chain motion; T_g at higher ILs content or the ILs-rich regions of D₆A50 (M₃A50) could be described by the Fox equation related to the motion of ILs.

Entanglement and Relaxation Behaviors of PMMA/DIL and PMMA/MIL Systems

Time-temperature superposition (TTS) is a well-known methodology integral based on the thermorheological simplicity that combines the effects of temperature and time.^[31] Fig. 3(a) presents the master curves of PMMA/DIL and PMMA/MIL with different polymer concentrations at a reference of 100 °C. It clearly demonstrates that the TTS principle works well for the blend melts, indicating the miscibility of PMMA/DIL and PMMA/MIL systems at the experimental temperature range. One can see that for the reference temperature, the dynamic moduli decrease gradually with the increase of ILs concentration owing to the dilution of ILs small molecules. In addition, the storage modulus G' and loss modulus G'' of PMMA/DIL are higher than those of PMMA/MIL at the same ILs content, respectively. It is mainly attributed to a relatively small dilution effect of DIL due to the additional physical cross-links that could be formed by the special double imidazolium ring structure of DIL as the “cross-linking point” interacting with different PMMA chains.^[25]

To further quantify the temperature dependence of viscoelastic properties for PMMA/ILs systems, the values of horizontal shift factor a_T are shown in Fig. 3(b). The Williams-Lan-

del-Ferry (WLF) equation is used to describe a_T as a function of T .^[32]

$$\text{Log} a_T = -\frac{C_1 (T - T_{\text{ref}})}{C_2 + (T - T_{\text{ref}})} \quad (3)$$

where C_1 and C_2 are WLF parameters, T_{ref} represents the reference temperature to construct the master curve by the TTS principle. Through fitting, one can see that the temperature dependence of a_T is stronger in PMMA/DIL system than in PMMA/MIL system, which relates to the temperature dependence of the diffusion coefficient of the polymer chain.^[33] In more detail, the fractional free volume f/B could be determined by C_1 :

$$f/B = \frac{1}{2.303C_1} \quad (4)$$

where B is a constant. The value of f/B related to monomeric friction factor ζ_0 by $\zeta_0 \approx \exp(B/f)$ as a measure of segmental dynamics is summarized in Table 2.^[34] The fractional free volume ($f/B=0.037$) of D₆A80 is slightly higher than that ($f/B=0.035$) of M₃A80, while the difference is reversed with the further increase of ILs content. It might be attributed to the special double imidazolium ring structure of DIL, on the one hand, physical cross-links form by the contribution of two interaction sites linked by alkyl chain between PMMA and DIL resulting in the larger the friction coefficient, but on the other hand, the fewer total interaction sites for PMMA/DIL system at the same ILs content due to the smaller freedom of imidazolium ring constrained by alkyl chain and relatively bulkier based on the folded form existing. Thus, the competition between physical cross-links restriction of PMMA chains and the decrease of interaction sites reducing interaction of PMMA and DIL contributes to the multiple relaxation of PMMA.

For brevity, the master curves of PMMA/ILs systems and pure PMMA at a reference of 150 °C are presented in Fig. S3 (in ESI). The terminal relaxation time τ_d could be determined by the inverse of the cross-over frequency at low frequencies of master curves.^[35] Fig. 4(a) shows the volume fraction ϕ dependence of the τ_d , in which τ_d decreases with the increase of ILs content. It can also be observed that τ_d is longer in the PMMA/DIL system than in the PMMA/MIL system at the same ϕ (for example, τ_d of PMMA in DIL reduces to nearly 7 times of that in MIL at $\phi=50\%$). The change of τ_d is attributed to the co-

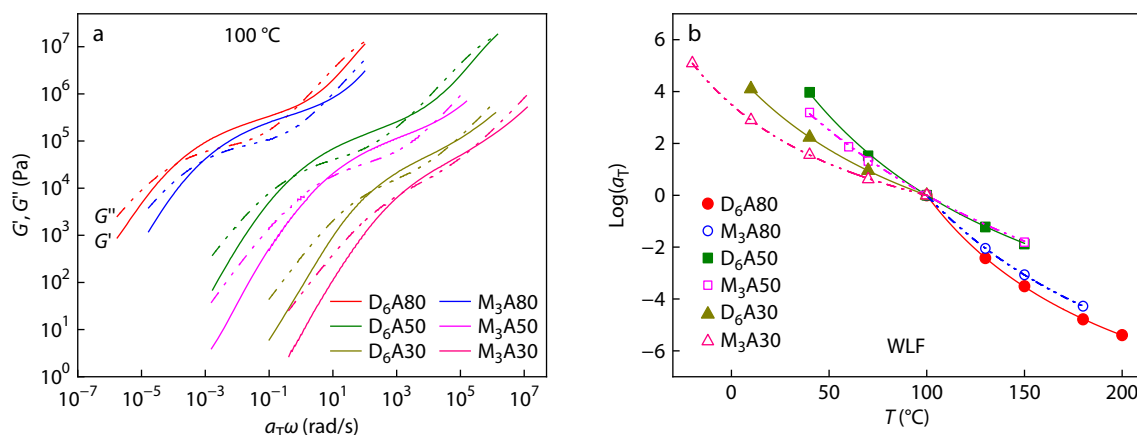


Fig. 3 Master curves of G' , G'' (a), and horizontal shift factor a_T (b) for PMMA/ILs systems with varying compositions at a reference temperature of 100 °C. The line through the data represents the WLF fit.

operation from dilution, plasticizing effectiveness and special interactions between the PMMA and ILs. Generally, τ_d of polymer chains in entangled concentrated polymer solutions could be simply related to these factors as:

$$\tau_d = K(M) \phi^\nu \zeta_0(\phi, T) \quad (5)$$

where $K(M)$ is the structure factor indicating the global relaxation of the long chain M , and $\zeta_0(\phi, T)$ decreases with increasing temperature T and decreasing ϕ of PMMA.^[36] ϕ^ν and $\zeta_0(\phi, T)$ could be separable experimentally through the iso- ζ_0 (iso-free-volume) correction in order to investigate the terminal relaxation time of PMMA in DIL and MIL in detail. The terminal relaxation time in the iso- ζ_0 state is denoted by τ_0 .

The procedure of the isomonomeric friction adjustment is based on Yan's work.^[37] The fractional free volume f/B of each system could be calculated by the method in the previous section, in which the f/B of the same system varies linearly with the reference temperature, as shown in Figs. 4(c) and 4(d). At a given reference temperature T' , the f/B of the same mixture with different PMMA content is not equal, i.e., $f(\phi_2, T')/B_2 \neq f(\phi_1, T')/B_1$.

Generally, T' could be regarded as the T_{ref} of the undiluted polymer and the concentration ϕ_1 often represents the undiluted state. In order to be adjusted to the same frictional state as the ϕ_1 mixture, the ϕ_2 mixture requires a new temperature T'' to make $f(\phi_2, T'')/B_2 = f(\phi_1, T')/B_1$. Therefore, the different T'' of PMMA/DIL systems with the same f/B could be seen in Fig. 4(c), and the τ_0 is further obtained through the master curves at different T'' .

The related parameters including the fractional free volume, the iso- ζ_0 temperatures and the corresponding friction correction factor ($\zeta_0(\phi, T'')/\zeta_0(\phi, T')$ ratio) are summarized in Table 3. The ϕ dependence of τ_0 of PMMA/DIL and PMMA/MIL systems in the iso- ζ_0 state exhibits power law relationship, as shown in Fig. 4(b). Interestingly, the f/B of D₆A80 is slightly larger than that of M₃A80 at 150 °C, but the terminal relaxation time of the former is longer before and after the iso- ζ_0 correction. At low ILs content, a small number of physical cross-links are formed in PMMA/DIL retarding the relaxation of PMMA chains, which have little effect on the ζ_0 . However, ζ_0 is very sensitive to the details of local structure through the special interaction between the PMMA and ILs, which results in the slightly smaller f/B of M₃A80 due to the more interaction sites.^[38]

To further verify the effect of ILs structure on the dynamic behavior of PMMA, the plateau modulus G_N^0 and entanglement molecular weight M_e are obtained as shown in Fig. 5. Al-

Table 2 The fractional free volume f/B at 100 °C for PMMA/ILs systems.

	D ₆ A80	D ₆ A50	D ₆ A30
f/B	0.037	0.050	0.070
	M ₃ A80	M ₃ A50	M ₃ A30
f/B	0.035	0.058	0.109

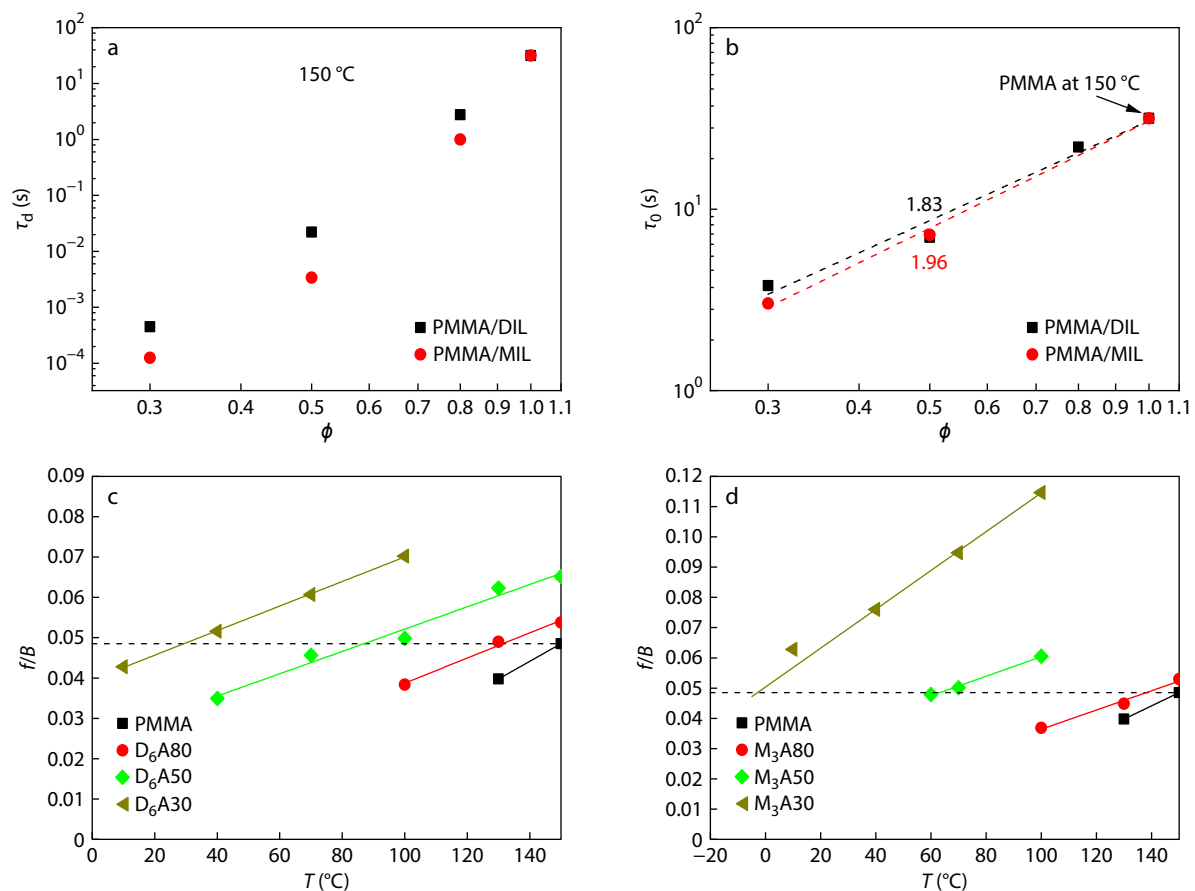


Fig. 4 The terminal relaxation time τ_d at isothermal state (a) and the terminal relaxation time τ_0 in the iso- ζ_0 state (b) as a function of PMMA content for PMMA/ILs systems. Temperature dependence of fractional free volume f/B for PMMA/DIL (c) and PMMA/MIL (d).

though it has been reported that G_N^0 is independent of polydispersity,^[39,40] the correct value of G_N^0 is extracted from the data with caution. In this study, G_N^0 is determined by the MIN method for the slightly poly-disperse polymer (1.76).^[41]

$$G_N^0 = G'(\omega)_{\tan\delta \rightarrow \text{minimum}} \quad (6)$$

The G_N^0 for PMMA is 3.7×10^5 Pa that is slightly lower than the values of $G_N^0 = 4.7 \times 10^5 - 8.0 \times 10^5$ Pa reported by previous work.^[13,42] This might arise from the different plateau moduli determination methods. Fig. 5(a) shows the volume fraction ϕ dependence of the G_N^0 on double logarithmic scale. Obviously, G_N^0 decreases with the increase of ILs content, and exhibits an approximately linear relationship. For PMMA/MIL system, the power law fitting result is a slope of 2.26 ± 0.13 that is consistent with conventional concentrated polymer solutions.^[36,42,43] However, a smaller exponent around 1.87 ± 0.11 is observed in PMMA/DIL system, which is attributed to dilution of entanglement network partially compensated by the formation of physical network in DIL with the double imidazolium ring structure.

Fig. 5(b) shows the value of M_e that could be deduced from the G_N^0 , as the following relationship:

$$M_e = \frac{4 \phi \rho R T}{5 G_N^0} \quad (7)$$

where ρ denotes the density of the polymer solution, T is the absolute temperature and R is the gas constant.^[44] Obviously, M_e of PMMA/DIL and PMMA/MIL samples are both smaller than their ideal values. This might be due to the cohesive entanglement induced by hydrogen bonding interactions

between the PMMA and ILs. In particular, it has been reported that the hydrogen bonding between polymers and solvent could greatly influence the chain entanglement by the formation of cohesive entanglement, which is the site with local parallel alignment of neighboring segments.^[45] Strictly speaking, cohesive entanglement could also be regarded as physical cross-link to render the linear polymer to behave as a network, distinguished here only from the physical cross-link formed by linked double imidazolium ring between PMMA and DIL. When ILs content is below 50%, there is a little difference in M_e between PMMA/MIL and PMMA/DIL systems. And the M_e value of D₆A80 becomes slightly higher than that of M₃A80. It might be ascribed that the DIL has a low probability to form physical cross-linking points between PMMA chains at low DIL content. At the same time, D₆A80 exhibits a slightly larger the f/B as mentioned in Table 2, resulting in the stronger entanglement network dilution than that in M₃A80 system. The physical cross-linking point between PMMA and DIL increases with the increase of DIL content. As a result, the M_e value of D₆A30 is lower than that of M₃A30, in accordance with our previous work.^[25] The interchain cross-links will contribute to the formation of the denser entanglement network structure in D₆A30, that is, the number of “entanglements” per PMMA chain in DIL is larger than that in MIL. Thus, the multiple relaxation of PMMA exhibits the nontrivial concentration dependence.

Creep and Recovery Studies of PMMA/DIL and PMMA/MIL Systems

Based on above discussion, one can see that a denser

Table 3 WLF parameters, fractional free volume, and isomonomeric friction adjustment results for PMMA/DIL and PMMA/MIL systems.

PMMA/ILs systems	ϕ	T_{ref} (°C)	T^* (°C)	C_1	$f(\phi, T_{\text{ref}})/B$	T^* (°C)	$\zeta_0(\phi, T^*)/\zeta_0(\phi, T)$
PMMA/DIL	1	150	150	8.86	0.049	150	1.0
	0.8	150		8.04	0.054	132	7.9
	0.5	150		6.68	0.065	87.1	3.2×10^2
	0.3	150		5.11	0.085	29.6	8.4×10^3
PMMA/MIL	1	150	150	8.86	0.049	150	1.0
	0.8	150		8.19	0.053	139	3.4
	0.5	150		5.87	0.074	63.8	2.1×10^3
	0.3	150		3.06	0.142	-2.7	2.4×10^4

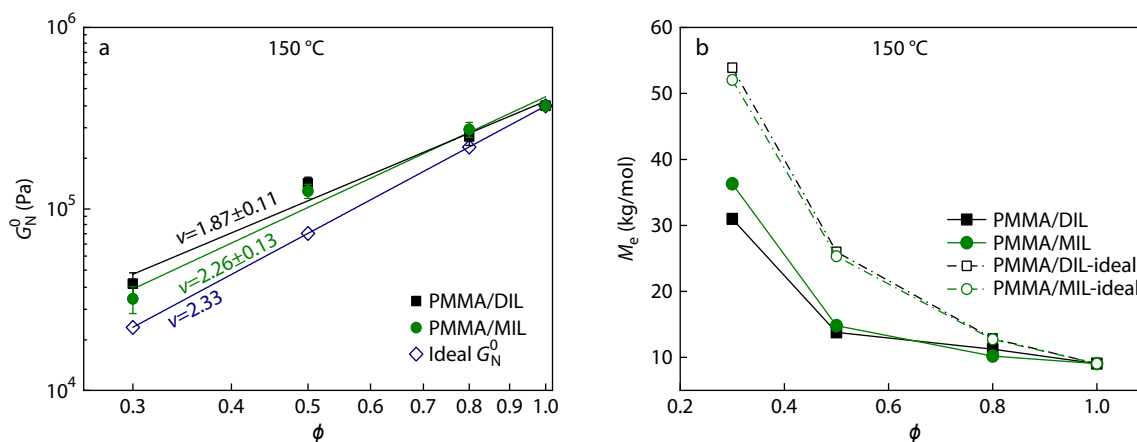


Fig. 5 Variation of plateau modulus G_N^0 (a) and average entanglement molecular weight M_e (b) for PMMA/ILs with different compositions at a reference temperature of 150 °C.

entanglement network forms in PMMA/DIL system at $\phi=30\%$, which might exhibit the stronger recovery or self-healing ability than the M_3A30 system. To further characterize and verify the viscoelastic behavior of PMMA/DIL and PMMA/MIL materials, J_c and J_r as a function of time are shown in Fig. 6. For all the creep curves, J_c continuously increases and reaches the constant slope 1 within a linear range of deformation.^[46] The lower curves of Fig. 6 represent the J_r that grows with the increase of recovery time and finally remains constant value J_e^0 at longer times. The linear steady-state recoverable compliance J_e^0 is found to be independent of temperature, as well known in the literature,^[47,48] and reaches a value of about 0.023 Pa^{-1} and 0.061 Pa^{-1} for M_3A30 and D_6A30 , respectively. Fig. 6(c) shows the master curves for M_3A30 and D_6A30 at 60°C , which expand test times at a reference temperature, and demonstrate that the

TTS principle works well for the blend melts indicating the creep-recovery experiments performed in the linear viscoelastic region.

In order to further compare the viscoelastic behavior of M_3A30 and D_6A30 in a popular way, the creep strain and unrecovered strain are plotted in Fig. 7 as a function of time in the creep and recovery process. The creep strain of systems increases with the increase of creep time at a given stress until reaches the terminal flow zone, then recovery process occurs without the stress. On the basis of the previous work by other researchers, the final percentage recovery X_R can be defined as following:^[24,49]

$$X_R = \left[\frac{\varepsilon_{\max} - \varepsilon_{\infty}}{\varepsilon_{\max}} \right] \times 100\% \quad (8)$$

where $\varepsilon_{\max}$ denotes the maximum deformation corresponding

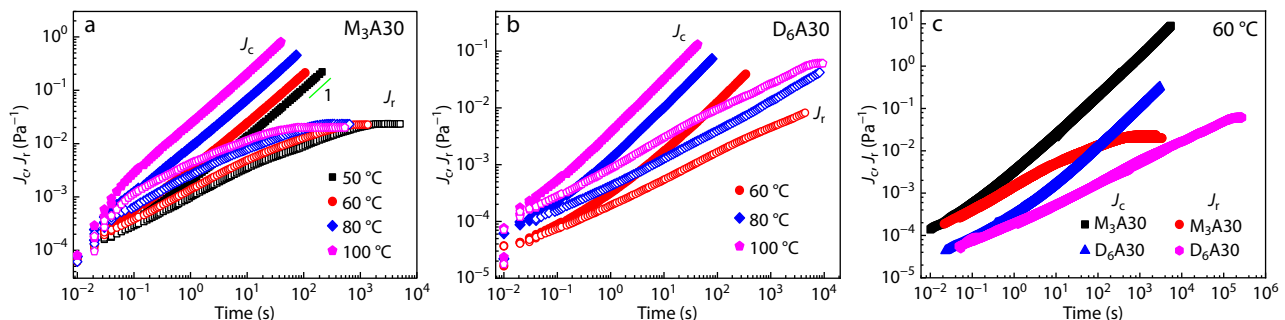


Fig. 6 Creep compliance J_c and recoverable compliance J_r for M_3A30 (a) and D_6A30 (b) at different temperatures. Master curves of the J_c and J_r for M_3A30 and D_6A30 at a reference temperature of 60°C (c).

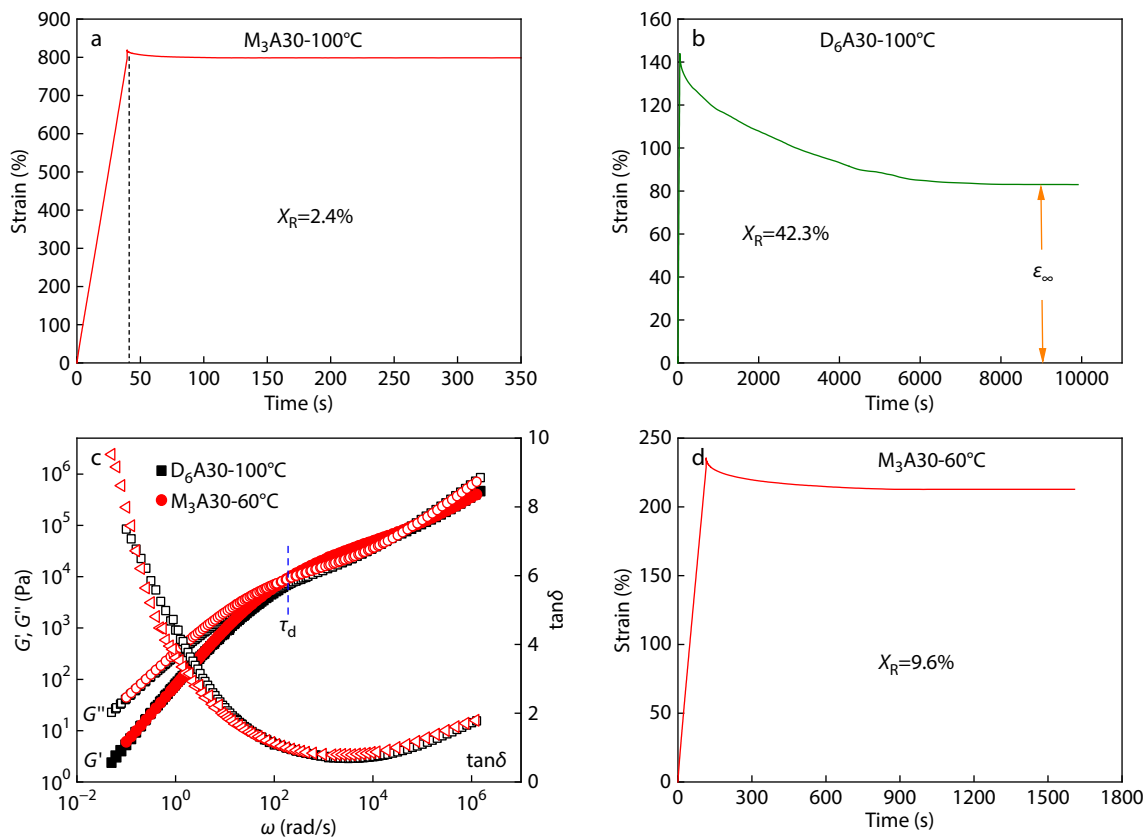


Fig. 7 Creep-recovery curves for M_3A30 at 100°C (a) and 60°C (d), and for D_6A30 at 100°C (b). The master curves of G' , G'' for M_3A30 and D_6A30 are compared at different temperatures in order to have an overlapped terminal regime (c).

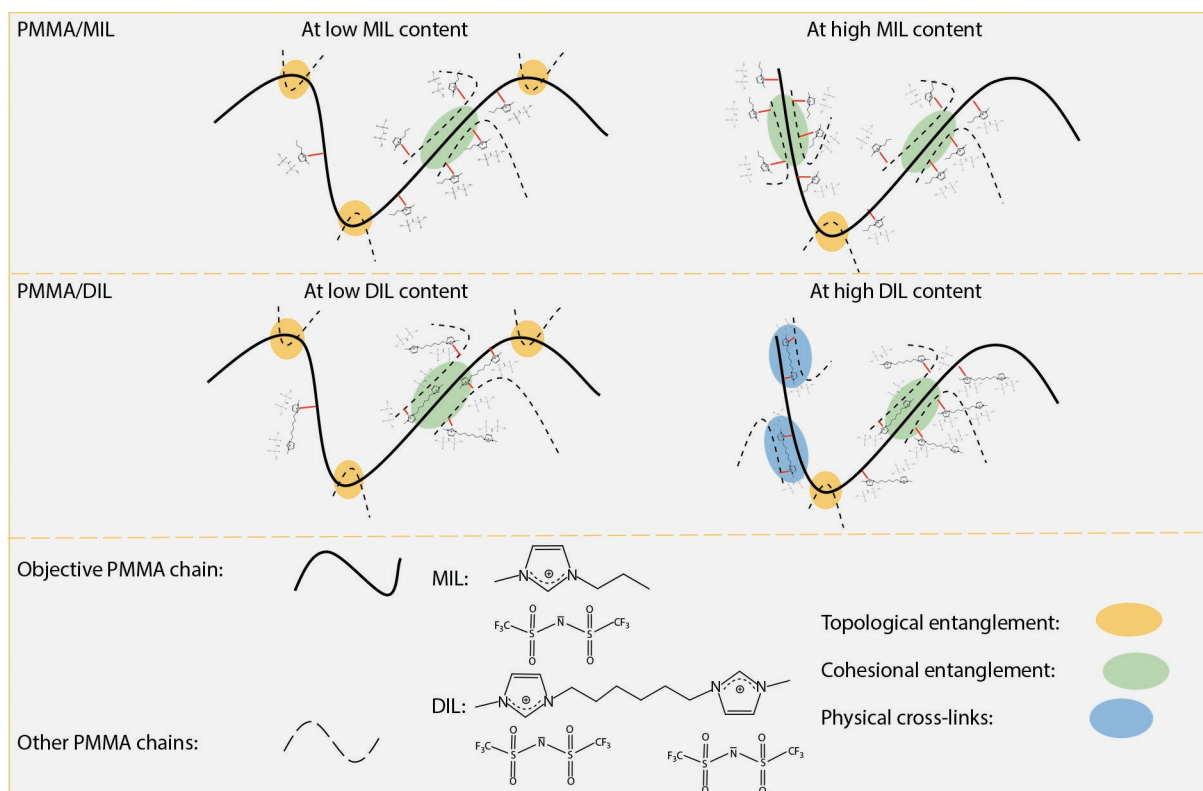


Fig. 8 Schematic mechanism of entanglement behavior of PMMA for PMMA/MIL and PMMA/DIL systems at different IL contents.

to the strain value for the longest creep time, and ε_{∞} is the permanent strain from viscous flow effects. Clearly, X_R for D₆A30 system as the 42.3% is significantly higher than that of M₃A30 (2.4%) at 100 °C, which is attributed to the dense entangled network forming in D₆A30. Even though the strain value of M₃A30 at 100 °C is relatively larger, it is still within the linear viscoelastic region, as shown in Fig. S4 (in ESI). Meanwhile, X_R for D₆A30 and M₃A30 systems is also compared for identical Weissenberg number based on the same τ_d at different temperatures,^[50] and a similar result could be obtained. Note that the discrepancy of X_R between D₆A30 and M₃A30 systems might be larger at a lower reference temperature due to increasing temperature breaking the physical cross-links between the DIL and PMMA chains.

As mentioned above, the possible mechanism illustrating the entanglement and relaxation of PMMA in MIL and DIL with the increase of ILs content is proposed in Fig. 8. The H atom on the C₂ position of the ILs imidazolium ring could form hydrogen bonding interaction with the O atom of PMMA carboxylic group. Thus, the cohesive entanglement exists in both PMMA/MIL and PMMA/DIL systems. For PMMA/DIL system, additional physical cross-links form by PMMA chain and linked double imidazolium ring of DIL. However, at low DIL content, the probability of cross-links formation is low due to the smaller freedom of imidazolium ring constrained by alkyl chain. And the fewer total interaction sites lead to fewer the amount of the cohesive entanglement in PMMA/DIL system than that in PMMA/MIL system. At high DIL content, the combination of significant physical cross-links and cohesive entanglement results in a denser

entanglement network in PMMA/DIL system.

CONCLUSIONS

In this study, the relaxation and entanglement of PMMA in both DIL and their MIL counterparts have been examined over the wide composition range. PMMA/ILs systems exhibit two glass transitions in the midrange of composition corresponding to PMMA-rich regions and IL-rich regions. The composition dependence of T_g at higher and lower PMMA content could be fitted by using Gordon-Taylor equation and Fox equation respectively, which indicates that T_g of the ILs-rich systems is weaker in composition dependence than the PMMA-rich systems. PMMA in DIL shows slower relaxation behavior, such as τ_d reduces to nearly 7 times of that in MIL at $\phi=50\%$. After the iso-free-volume correction, the ϕ dependence of τ_0 of PMMA in both DIL and MIL shows the power law behavior $\tau_0 \sim \phi^{\nu}$ with exponent of $\nu=2.0 \pm 0.2$ consistent with conventional polymer solutions.

In terms of entanglement of PMMA/ILs systems, G_N^0 of PMMA/MIL system exhibits a concentration dependence of $G_N^0 \sim \phi^{2.26 \pm 0.13}$, and the smaller exponent (1.87 ± 0.11) for PMMA/DIL system implies that dilution of entanglement network is partially compensated by the formation of physical network in DIL with the double imidazolium ring structure. At the ILs concentration of 20%, the M_e value of PMMA/DIL system is slightly higher than that of PMMA/MIL system which might be ascribed that the DIL has the lower probability to form physical cross-linking point between PMMA chains at low DIL content. For D₆A30 and M₃A30, the M_e value of the

former is relatively lower due to the formation of the denser entanglement network structure originated from the physical cross-links. As a result, introducing DIL instead of MIL into PMMA could enhance the creep recovery ratio to a large extent.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

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