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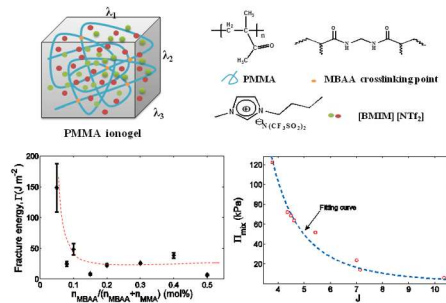
We demonstrate that the fracture energy of ionogels correlates inversely with cross-link density. The behavior of ionogels is well captured by the ideal elastomeric gel model.

Mechanical behavior of a poly(methyl methacrylate)-based ionogels

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Abstract

Ionogels are formed when a cross-linked polymer network absorbs an ionic liquid. Ionogels are ionic conductors and, as such, are being considered for use in stretchable electronics and artificial muscles or nerves. Use of ionogels in these applications is limited in part by their mechanical behavior. Here we present an ionogel prepared by swelling covalently cross-linked poly(methyl methacrylate) in 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide. The resulting ionogel is compliant, stretchable, and relatively tough. We demonstrate that the swelling ratio, elastic modulus, stretchability, and fracture energy of the ionogel depend sensitively on the cross-link density of the polymer network. The behavior of the ionogel is well captured by the model of the ideal elastomeric gel combined with the Flory-Huggins model for the energy of mixing.

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1. Introduction

When a cross-linked polymer network absorbs an ionic liquid, it forms an ionogel. Ionogels possess both the mechanical integrity of a cross-linked polymer, and the ion conductivity and non-volatility of an ionic liquid.[1] They are used in energy storage and conversion devices,[2,3-5] gate dielectrics for organic electronics,[6] gas and ion separation membranes,[7] and in sensors and actuators.[8,9] With recent developments in the nascent field of soft machines, ionogels also have great potential for use as ionic conductors in artificial muscles or nerves and in stretchable electronics.

Recently Keplinger et al fabricated a class of elastomeric actuators that use a hydrogel as a transparent, compliant, and stretchable ionic conductor. The long-term performance of these actuators is severely limited by evaporation of water: as water evaporates, the hydrogel conductor dries out and loses functionality.[10] Using an ionogel as an ionic conductor provides one potential solution to this problem: the ionic liquid in the gel enables ion transport and makes the ionogel non-volatile.[11] Ionogel-based conductors can potentially impact a large scope of applications, including transparent loudspeaker,[10] active-noise-cancellation windows, and transducers.[12] Along with good ion conductivity and non-volatility, ionogels used in these applications also need to be compliant, stretchable, and tough, so as to not constrain actuation, enable large deformation, and resist fracture. Many existing ionogels, however, have high stiffness[13, 14] and rupture at small strains.[15] Much attention has been paid to the thermal and ion transport properties of ionogels,[16,17,18] but the complex chemo-mechanical interaction between the polymer network and the ionic liquid has received little attention. Use of ionogels in applications where mechanical performance is critical requires models to describe and predict the mechanical behavior of these materials.

Here we present an ionogel prepared by swelling cross-linked poly(methyl methacrylate) (PMMA) in a 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([BMIM][NTf$_2$]) ionic liquid. This ionogel is representative of a larger class of ionogels based covalently cross-linked networks of neutral polymers swollen in ionic liquids. The resulting ionogels are compliant, highly stretchable, and relatively tough. We establish the effects of cross-link density on the swelling ratio, elastic modulus, stretchability, and toughness of the gels. We further demonstrate that the behavior of the ionogels is well captured by the model of the ideal

elastomeric gel and that their fracture energy correlates inversely with cross-link density, in agreement with Lake-Thomas theory.[19] Because the cross-link density and the Flory interaction parameter fully determine the equations of state, we expect that the mechanical behavior observed in this study is representative of a broader class of ionogels obtained by swelling covalently cross-linked polymer networks in ionic liquids with physico-chemical parameters similar to those of [BMIM][NTf2].

2. Experimental

2.1 Synthesis of the ionic liquid

The ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf$_2$]), was synthesized using an anion exchange reaction between 1-butyl-3-methylimidazolium chloride (BMIMCl, Sigma, 38899) and the lithium salt of bis(trifluoromethane)sulfonimide (LiNTf$_2$, Sigma, 449504). BMIMCl and LiNTf$_2$ were mixed together in equimolecular quantities in distilled water. The solution was kept at 70°C and stirred for 12 hours until it separated into two transparent layers: an aqueous solution on top and a hydrophobic oil-like ionic liquid at the bottom. The aqueous solution was removed and the ionic liquid was washed several times with distilled water. The ionic liquid was then dried at 100°C in a vacuum oven for 12 hours.

2.2 Preparation of cross-linked PMMA film

The polymer network of the ionogel was synthesized using methyl methacrylate (MMA; Sigma, M55909) as monomer, N, N'-methylenebisacrylamide (MBAA, Sigma, M7279) as cross-linker, and benzoyl peroxide (BPO, Sigma, 33581) as initiator. MBAA, in quantities from 7.2 mg (0.05 mol %) to 72.8 mg (0.5 mol %), was dissolved in 10 ml MMA inside a 20 ml glass bottle. After bubbling nitrogen through the mixture of MBAA and MMA for 10 minutes, 0.033 g (0.1 mol%) BPO was added. The solution was then heated to 90°C and kept at this temperature for 15-20 minutes to initiate the polymerization reaction. As soon as the solution turned into a viscous liquid, the solution was cooled to room temperature by immersing the bottle in water and poured into a glass mold with dimensions of 80×80×0.1 mm³. The mold was then kept at 50°C

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for 5 hours, after which the temperature was increased to 90°C for one hour to finish the polymerization process. This protocol produced stiff, transparent films of cross-linked PMMA.

2.3 Swelling of PMMA

The PMMA films were submerged in [BMIM] [NTf$_2$] at 120°C until equilibrium was established. The mass of dry PMMA films was measured using an analytical scale before the swelling, and at various times during the swelling process. Typically, the swelling process reached equilibrium after 24 hours. The swelling ratio of the resulting gels, *J*, was calculated from

$$J = 1 + \frac{(m_{gel} - m_{dry}) / \rho_{IL}}{m_{dry} / \rho_{PMMA}} \, , \tag{1}$$

where the density of [BMIM] [NTf$_2$], ρ_{IL} , is 1.43 g cm^{-3} and that of poly(methyl methacrylate), ρ_{PMMA}, is 1.17 g cm^{-3} .[20]

2.4 Mechanical testing

A series of mechanical tests were carried out at room temperature using an Instron tensile machine with a 50-N load cell. Samples were attached to polyacrylate grips with UV-curing acrylic glue (Loctite^{R} 3106 light cure adhesive). No debonding was observed during tensile testing of the ionogels using this type of glue. By contrast, glues based on cyanoacrylate (Krazy^{R} glue) or epoxy (Devcon^{R} epoxy 5 minute) did not provide adequate adhesion between the ionogels and the polyacrylate grips. The section of the tensile specimens between the grips was 5 mm in length and 30 mm in width. During the tests, the stretch rate was kept constant at 5 mm min^{-1}. All samples were stretched to rupture.

The fracture energy of the ionogels was measured using the pure shear test.[21] The samples had a gauge section of 5 mm, a width of 30 mm, and a thickness in the 0.2-0.4 mm range. For each ionogel, two samples were tested: an un-notched sample and a notched sample with a 10 mm edge crack in the middle of specimen. The un-notched sample was used to record the load-

extension curve. The notched sample was used to determine the critical extension l_c at which the crack started to propagate. The fracture energy of the ionogel was then calculated using

$$\Gamma = \frac{U(l_c)}{wt},$$ (2)

where $U(l_c)$ is the work done by the applied force for the un-notched sample to reach the critical extension l_c; w and t are the width and thickness of the specimen gauge section, respectively. The work $U(l_c)$ is readily determined by integrating the load-extension curve of the un-notched sample up to an extension l_c.

3.Result and discussion

3.1 Ionogel preparation

In this study, we selected PMMA as host polymer, MBAA as cross-linker, and [BMIM][NTf$_2$] as ionic liquid (Fig. 1a). The covalently cross-linked polymer network was selected because of its greater chemical and thermal stability compared to networks based on physical crosslinks.[22] The ionic liquid [BMIM][NTf$_2$] was selected because of its good miscibility with PMMA, low melting point, vanishing vapor pressure, low viscosity, and good ionic conductivity (3.9 mS cm^{-1}).[23] Furthermore, both PMMA and [BMIM][NTf$_2$] are hydrophobic and immiscible with water; the resulting ionogel absorbs less than 1% water by mass in a high-humidity environment (Supporting information, Fig. S1). By contrast, ionogels formed by combining hydrophobic ionic liquids with hydrophilic polymers like polyethylene glycol readily absorb water, which may result in volume changes, phase separation, and a reduction in transparency.[24]

Ionogel are generally prepared in one of two ways: monomers can be polymerized in the presence of an ionic liquid,[16, 23, 24] or the polymer network can be formed first in a different medium and then swollen in an ionic liquid.[25] Using *in-situ* polymerization, it is difficult to synthesize ionogels with large swelling ratios and some ionic liquids have been shown to disrupt the polymerization process.[16, 24] By contrast, the ex-situ approach allows independent

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optimization of the polymerization process using established chemistries and the resulting networks have fewer defects,[26] but the swelling process can take a long time for a gel in bulk form. The ionogels in this study were synthesized using the ex-situ method. The resulting ionogels were highly transparent to the full spectrum of visible light (Supplementary Information, Fig. S2) and no phase separation was observed, confirming that PMMA and [BMIM][NTf$_2$] are highly compatible.

Figure 1b illustrates the swelling process schematically: a unit block of dry PMMA absorbs a large amount of ionic liquid, [BMIM][NTf$_2$] and forms a block of ionogel with dimensions ($\lambda_1, \lambda_2, \lambda_3$). The swelling ratio, *J*, denotes the ratio of the volume of the swollen ionogel to that of the dry network. Since the dry network is homogeneous and isotropic, the stretch ratio for the free swelling is independent of the direction, $\lambda_1 = \lambda_2 = \lambda_3 = J^{1/3}$. Figure 1c depicts the swelling ratio of the ionogels as a function of MBAA concentration. Evidently the swelling ratio is very sensitive to the cross-link density of the PMMA network. As the MBAA content increases, the equilibrium swelling ratio, *J*, decreases. At low cross-link densities, the volume fraction of ionic liquid is as high as 90 %.

3.2 Mechanical behavior

The stress-stretch curves of the ionogels are shown in Fig. 2a for different MBAA concentrations. The nominal stress is the loading force divided by the cross-sectional area of the undeformed sample. The stretch ratio is the current length divided by the initial length of the undeformed sample. The figure clearly illustrates that the ionogels exhibit lower stiffness and larger stretchability with decreasing MBAA content. The most compliant ionogel can sustain a stretch ratio of 280% before rupture. On the time-scale of the experiments, the ionogels behave as elastic elastomers with negligible hysteresis between loading and unloading (Supplementary information Fig. S3).

The plane-strain elastic moduli (M) of the ionogels can be determined as the slopes of the initial portions of the stress-stretch curves of the ionogels. The Young's moduli (E) were calculated from equation $E = M \times (1 - v^2)$, where *v* is Poisson's ratio. Because the ionic liquid is non-volatile and tests were performed in less than two minutes to prevent any re-distribution of

the ionic liquid inside the sample, the ionogels behave like incompressible solids and Poisson's ratio can be taken as 0.5. The calculated Young's moduli of ionogels are shown in Fig. 2b. As the MBAA concentration increases, the elastic modulus increases from 38 kPa to 729 kPa. The cross-link density N of the PMMA network is related to the elastic modulus and the swelling ratio of the ionogel by

$$NkT = \frac{E}{2(1+v)} J^{1/3},$$
(3)

where v is Poisson's ratio, kT the temperature in units of energy, and N is the cross-link density referred to the volume of the dry polymer.[27] Using the experimental values of the swelling ratios and elastic moduli, the cross-link densities of the ionogels can be calculated from Eq. (3). The results are shown in Fig. 2c as a function of MBAA concentration and, not surprisingly, the crosslink density increases with increasing MBAA concentration (Fig. 2c). Compared to the hydrogels used as ionic conductors on elastomeric actuators by Keplinger et al,[10] the ionogels in this work exhibit similar stretchability and stiffness, indicating that the ionogels can be used in the same application, but without the risk of desiccation.

3.3 Fracture energy

The fracture energy of ionogels is critical in many applications involving soft machines. Ionic conductors, for example, often undergo large and frequent deformation. The fracture energy quantifies the resistance of a material to crack propagation, independent of the presence of any defects in the material; it is a material property that is independent of the test method.[28] Other parameters that are sometimes used to describe the resistance to fracture, such as fracture strain, work of loading before rupture, or breaking stress, depend on the flaws present in a particular sample, and are therefore less appropriate.[29,30,31] Many methods for measuring facture energy have been established, including the trouser tear test, the single-edge notch test, and the pure-shear test. Here we used the pure-shear test to measure the fracture energy. The pure-shear test was developed by Thomas to measure the fracture energy of elastomers. J. Y. Sun et al recently demonstrated this method on hydrogels.[32]

Figures 3a and b depict schematic load-extension curves of samples with and without pre-crack, respectively, and illustrate how the fracture energy is determined. Figure 3c shows as a function of MBAA content the stretch ratio at which the pre-crack starts to propagate. It is clear from the figure that the critical stretch ratio is large for low cross-link densities and decreases with increasing cross-link density. The fracture energy of the ionogels follows a similar trend and is shown in Figure 3d. The inverse dependence on cross-link density is in agreement with the Lake-Thomas model for the fracture toughness of elastomers, and indeed the fracture energy of these ionogels is quite comparable to the threshold toughness of rubber, 40-80 J m^{-2}.[33] In accordance with the Lake-Thomas model, this fracture energy is associated mainly with the breaking of carbon-carbon bonds, without any other energy dissipation mechanisms. To the best of our knowledge, this is the first measurement of the fracture energy of an ionogel. While the fracture energy of these ionogels is already relatively high, the fracture energy can be improved further through inclusion of energy dissipation mechanisms such as the rupture of sacrificial bonds or the unzipping of crystallites. These strategies have been used to increase the fracture energy of hydrogels significantly, [32, 34,35, 36] but further development is needed to adapt them to ionogels.

3.4 Equations of state for an ionogel

We next derive the equations of state for ionogels based on the model of the ideal elastomeric gel. This model provides a simple, robust, and general approach to characterize a gel and has been applied successfully to several types of hydrogels, including neutral hydrogels,[37] temperature-sensitive hydrogels,[38] and polyelectrolyte hydrogels.[38,39] The model does not assume any particular mechanical model a priori, and can be calibrated via a set of straightforward experiments.

Recall the two basic assumptions of the ideal elastomeric gel. First, the individual polymer chains and solvent molecules are taken to be incompressible; their volumes remain nearly unchanged on mixing. Consequently, we assume that the volume of the ionogel is equal to the volume of the polymer network plus the volume of the ionic liquid. There then exists a simple relationship between J and C.[40] Subject to charge balance, i.e., the number of cations must equal

the number of anions $C_+ = C_- = \frac{1}{2}C$, where C is the total number of cations and anions divided

by the volume of dry polymer network, the swelling ratio is given by[40]

$$J = 1 + \frac{1}{2}C(\Omega_- + \Omega_+),\tag{4}$$

where Ω_+ and Ω_- refer to the atomic volumes of the cation and anion of the ionic liquid,

respectively. Second, the density of crosslinks in the gel is assumed to be sufficiently low, that

the effect of the cross-links on the molecular interactions between polymer and solvent is

negligible.

As an idealization, the Helmholtz free energy of the ionogel is taken as the sum of the free

energy due to stretching of the network and the free energy due to mixing of the polymer network

and the ionic liquid:

$$W = W_{stretch}\left(\lambda_1, \lambda_2, \lambda_3\right) + W_{mix}(J).\tag{5}$$

The free energy of the gel, W, is defined as the excess energy of the gel relative to the sum of its

constituents—that is, W is the free energy of the gel minus that of the dry polymer and that of the

pure ionic liquid. The free energy due to the stretching of the network, $W_{stretch}(\lambda_1, \lambda_2, \lambda_3)$, is a

function of the stretches and depends solely on the cross-link density. The free energy due to the

mixing of the polymer and the ionic liquid, $W_{mixing}(J)$, is a function of the swelling ratio, but is

independent of the cross-link density. The polymer backbone carries no charge; besides the

mixing and stretching contributions, there are no additional energy terms.

Consider a block of ionogel subjected to Cauchy stresses σ_1, σ_2, and σ_3 (Fig. 1a) in an

ionic liquid. If the gel is in equilibrium with its surroundings, the Helmholtz free energy of the

ionogel satisfies the equation

$$dW = \sigma_1 \lambda_2 \lambda_3 d\lambda_1 + \sigma_2 \lambda_3 \lambda_1 d\lambda_2 + \sigma_3 \lambda_1 \lambda_2 d\lambda_3 + \mu_+ dC_+ + \mu_- dC_-,\tag{6}$$

where μ_+ and μ_- are the chemical potentials of the cations and anions in the ionic liquid,

respectively. A combination of (4)-(6) then yields

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$$\left[\frac{\partial W_{stretch}}{\partial \lambda_1} - \left(\sigma_1 + \Pi_{mix}(J) + \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}\right)\lambda_2\lambda_3\right]d\lambda_1$$

$$+\left[\frac{\partial W_{stretch}}{\partial \lambda_2} - \left(\sigma_2 + \Pi_{mix}(J) + \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}\right)\lambda_3\lambda_1\right]d\lambda_2 \qquad (7)$$

$$+\left[\frac{\partial W_{stretch}}{\partial \lambda_3} - \left(\sigma_3 + \Pi_{mix}(J) + \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}\right)\lambda_1\lambda_2\right]d\lambda_3 = 0$$

where the osmotic pressure due to mixing is given by

$$\Pi_{mix}(J) = -\frac{dW_{mix}(J)}{dJ}. \qquad (8)$$

For the ionogel to be in equilibrium with its surroundings, Eq. (7) must hold for arbitrary and independent changes in the three stretches, λ_1, λ_2 and λ_3. Consequently, the coefficients of the variations of the stretches must vanish, giving three independent equations,

$$\sigma_1 = \frac{\partial W_{stretch}}{\lambda_2\lambda_3\partial \lambda_1} - \Pi_{mix}(J) - \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}, \qquad (9a)$$

$$\sigma_2 = \frac{\partial W_{stretch}}{\lambda_1\lambda_3\partial \lambda_2} - \Pi_{mix}(J) - \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}, \qquad (9b)$$

$$\sigma_3 = \frac{\partial W_{stretch}}{\lambda_1\lambda_2\partial \lambda_3} - \Pi_{mix}(J) - \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}. \qquad (9c)$$

For polymer networks with relatively low cross-link density, the Gaussian chain model provides a good description of the mechanical behavior. The free energy for stretching derived from the Gaussian-chain model is given by [41]

$$W_{stretch}(\lambda_1, \lambda_2, \lambda_3) = \frac{1}{2}NkT\left[\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 - 2\log(\lambda_1\lambda_2\lambda_3)\right]. \qquad (10)$$

The chemical interaction between a polymer and an ionic liquid can be very complex. Thus, for the time being, we do not specify the function $W_{mix}(J)$. Instead, we will show that $W_{mix}(J)$ is readily determined experimentally. With Eq. (10), the expressions for the stresses finally become

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$$\sigma_1 = \frac{NkT}{J}\left(\lambda_1^2 - 1\right) - \Pi_{mix}(J) - \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}, \tag{11a}$$

$$\sigma_2 = \frac{NkT}{J}\left(\lambda_2^2 - 1\right) - \Pi_{mix}(J) - \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}, \tag{11b}$$

$$\sigma_3 = \frac{NkT}{J}\left(\lambda_3^2 - 1\right) - \Pi_{mix}(J) - \frac{\mu_+ + \mu_-}{\Omega_+ + \Omega_-}. \tag{11c}$$

Thus, the ionogel is fully characterized by the scalar quantity NkT and a single-variable function $\Pi_{mix}(J)$. Once NkT and $\Pi_{mix}(J)$ are known, the four equations of state, (3), (11a), (11b) and (11c) connect eight thermodynamic variables: λ_1, λ_2, λ_3, C, σ_1, σ_2, σ_3, and $\mu = \mu_+ + \mu_-$.

3.5 The energy of mixing and the osmotic pressure

Under free-swelling conditions in an ionic liquid, the stretches of the ionogel are isotropic, $\lambda_1 = \lambda_2 = \lambda_3 = J^{1/3}$, and all applied stress components vanish, $\sigma_1 = \sigma_2 = \sigma_3 = 0$. If the ionic liquid is pure, the chemical potentials of the ionic species in the liquid are equal to zero, $\mu_+ = \mu_- = 0$. Substituting these expressions into Eq. (11a) yields

$$\Pi_{mix} = \frac{NkT}{J}(J^{\frac{2}{3}} - 1). \tag{12}$$

from which the osmotic pressure Π_{mix} can be calculated once J and NkT have been measured experimentally. Figure 4 shows the osmotic pressure as a function of the swelling ratio for the various ionogels synthesized in this study. Under the assumption that the cross-link density is sufficiently low that the cross-links do not affect the chemical interaction between polymer and ionic liquid, the graph in Fig. 4 provides a complete description of the energy of the interaction between PMMA and [BMIM][NTf$_2$]. Evidently, the osmotic pressure decreases as the concentration of the [BMIM][NTf$_2$] in the PMMA increases. This behavior is also observed for hydrogels. [36]

We next adopted the Flory-Huggins approach to derive an expression for the mixing contribution to the free energy of ionogels.[42,43] The ionic liquid is treated as a two-component solvent containing cations and anions. According to the regular solution model, the free energy

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(per site occupied by an ion) of the ionic liquid, F_{IL}, containing cations and anions in equimolecular quantities is given by

$$\frac{F_{IL}}{kT} = \ln\frac{1}{2} + \frac{1}{4}\chi_{+-}, \tag{13}$$

where χ_{+-} is the Flory interaction parameter for the anions and cations. The free energy F (per site) of a mixture of the ionic liquid and the polymer network is

$$\frac{F}{kT} = \Phi_{+}\ln\Phi_{+} + \Phi_{-}\ln\Phi_{-} + \frac{\Phi_{p}}{n}\ln\Phi_{p} + \chi_{+-}\Phi_{+}\Phi_{-} + \chi_{+}\Phi_{+}\Phi_{p} + \chi_{-}\Phi_{-}\Phi_{p} \tag{14}$$

where n is the number of sites occupied by the network, and where Φ_{+}, Φ_{-}, and Φ_{p} are the volume fractions of the cations, anions, and polymer in the ionogel, respectively. The Flory interaction parameters between the polymer and the cations, and between the polymer and the anions are denoted by χ_{+} and χ_{-}. The mass and charge balances require that $\Phi_{+} = \Phi_{-} = \frac{1}{2}\Phi$ and $\Phi_{p} = 1 - \Phi$, so that

$$\frac{F}{kT} = \Phi\ln\frac{\Phi}{2} + \frac{(1-\Phi)}{n}\ln(1-\Phi) + \chi(1-\Phi)\Phi + \chi_{+-}\frac{\Phi^{2}}{4}, \tag{15}$$

where $\chi = \frac{1}{2}(\chi_{+} + \chi_{-})$. The free energy of mixing, F_{mix}, is then

$$F_{mix} = F - F_{IL} = kT\left[\Phi\ln\Phi + \frac{1-\Phi}{n}\ln(1-\Phi) + \chi'(1-\Phi)\Phi\right], \tag{16}$$

where $\chi' = \chi - \frac{1}{4}\chi_{+-}$. For a cross-linked network, $n \to \infty$ and

$$F_{mix} = kT\left[\Phi\ln\Phi + \chi'(1-\Phi)\Phi\right]. \tag{17}$$

From the definition of J, it follows that $\Phi = 1 - \frac{1}{J}$. Writing F_{mix} as a function of J and per unit volume, we eventually find

$$W_{mix}(J) = \frac{kT}{\Omega}[(J-1)\ln(1-\frac{1}{J}) + \chi'(1-\frac{1}{J})]\,, \tag{18}$$

leading to the following equation for the osmotic pressure

$$\Pi_{mix} = -\frac{kT}{\Omega}[\frac{1}{J} + \ln(1-\frac{1}{J}) + \frac{\chi'}{J^2}]\,, \tag{19}$$

where $\Omega = \frac{1}{2}(\Omega_+ + \Omega_-)$. This expression for the osmotic pressure is shown as a dashed curve in Fig. 4, where χ' was used a fitting parameter and where $\Omega_+ = 1.26 \times 10^{-28}$ m^{-3} and $\Omega_- = 3.54 \times 10^{-28}$ m^{-3} were calculated from the respective ionic radii in references.[44, 45] The experimental data in the figure is well captured by the Flory-Huggins model; evidently, the only materials parameters required for the equations of state of this class of ionogels are the elastic modulus and the Flory interaction parameter $\chi' = 0.48$.

4.Concluding remarks

We have prepared ionogels by swelling covalently cross-linked poly(methyl methacrylate) in 1-butyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide. The resulting ionogel is transparent, compliant, stretchable, and relatively tough. The inverse dependence of the fracture energy on the cross-link density agrees with the Lake-Thomas model and suggests that energy dissipation during fracture arises mainly from the fracture of carbon-carbon bonds. We anticipate that the toughness of these ionogels may be further improved by including other energy dissipation mechanisms. The chemo-mechanical behavior of the ionogels is well described by the model of the ideal elastomeric gel combined with the Flory-Huggins model for the free energy of mixing. Only two material parameters are required for the equations of state for these ionogels: the elastic modulus of the gel and a single Flory interaction parameter. Thus we expect that the mechanical behavior of the ionogel in this work is representative of a larger class of ionogels based on covalently cross-linked networks of neutral polymers.

Acknowledgements

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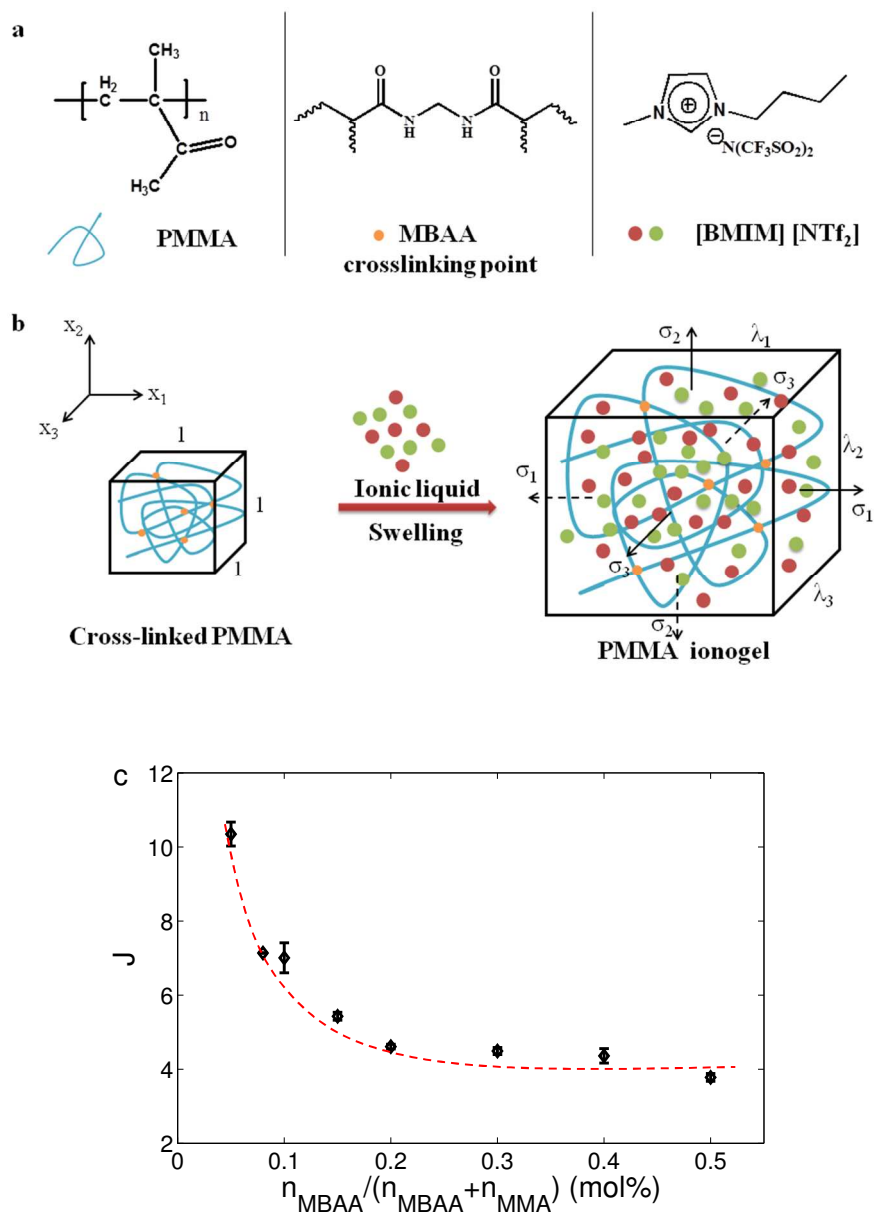
Fig. 1. a) Chemical structures of ionogel components. b) Schematic diagram of the formation of the ionogels; c) Swelling ratio of ionogels as a result of MBAA content. Error bars show one standard deviation; sample size N=3. The curve in the graph is a guide to the eye.

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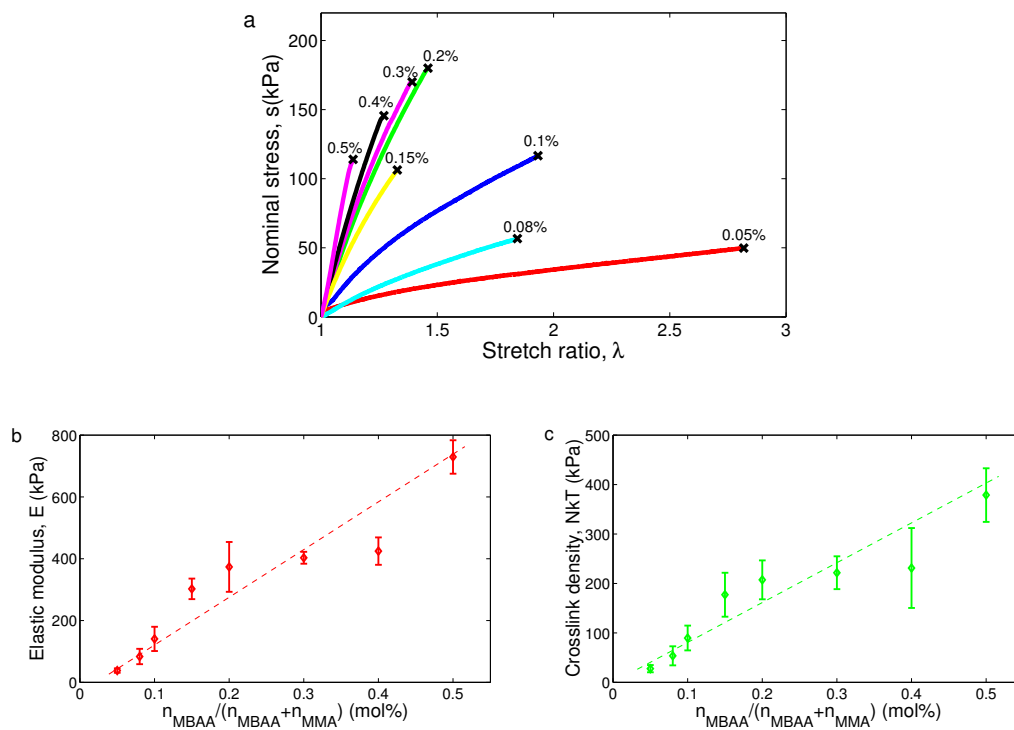
Fig. 2. a) Tensile curves of ionogels with various MBAA molar percentages as illustrated in the figure. b) Young's Modulus as a function of MBAA content; c) cross-link density. Error bars show one standard deviation; sample size N=3. The dashed lines are guides to the eye.

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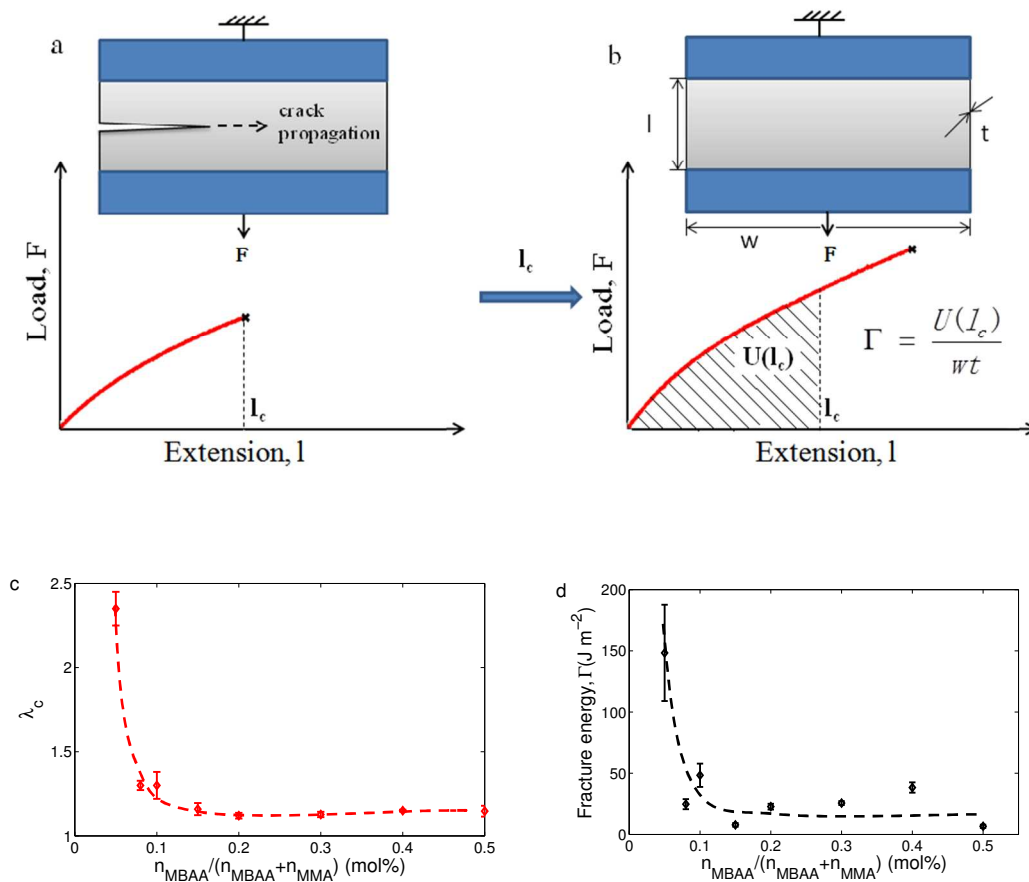
Fig. 3. Illustration of pure-shear fracture energy measurement. a) Load-extension curve for notched sample; b) Load-extension curve for un-notched sample; c) Stretch ratio at which pre-crack propagation starts as a function of MBAA content; d) Fracture energy of ionogels as a function of MBAA content. Error bars show one standard deviation; sample size N=3. The dashed lines in c and d are guides to the eye.
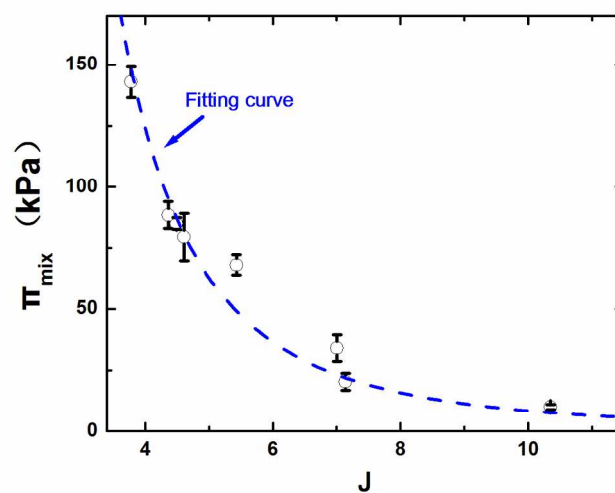
Fig. 4. The experimental osmotic pressure as a function of swelling ratio (open circles); the dashed curve represents the Flory-Huggins model, Eq. (19), with $\chi' = 0.48$, yielding a correlation coefficient $R^2 = 0.97$.

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