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Letter

Inorganic polymers made directly from silica

Monika Kazancioglu[a], Bharath Krishnamurthi[a], Serena Mueller[a], Zhenni Lin[b], Sam Skran[b], Sarah Snyder[b], Christian Tabedzki[a], Richard Lehman[b], Masanori Hara[a,*]

[a] Department of Chemical and Biochemical Engineering, Rutgers, The State University of New Jersey, 98 Brett Rd, Piscataway, NJ 08854, USA
[b] Department of Materials Science and Engineering, Rutgers, The State University of New Jersey, Piscataway, NJ, USA

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ABSTRACT

A novel approach is presented in which silica is used as a source for the synthesis of decarbonized (silicate-based) inorganic polymers. Natural silica (e.g., sand) is envisaged as an assembly of polymer chains and these chains are "extracted" from silica. This is accomplished by using a two-step method: (1) silica is converted to silicate glass, (2) silicate glass is converted to silicate polymer. The resulting materials have T_g values as low as 150 °C and show various characteristics of polymers. The key to the success of this method is the use of ionic liquid, which works as an ionic "plasticizer."

Polymer science and engineering has exploded after the World War II due to application of rapidly-advanced organic chemistry [1]; as a result, polymer has been utilized extensively for various applications, ranging from daily goods to advanced composites, and are replacing traditional materials such as metals and ceramics [2,3] – we live in an age of "plastics." However, as organic polymers are practically made from carbon-based petroleum, depletion of fossil reserves is a serious concern: only 0.03 wt.% of earth's crust is C, in contrast to the first and second most abundant elements, O (47 wt.%) and Si (28 wt.%). Due to anthropogenic emission of CO_2 gas arising from combustion of fossil fuels, a fundamental shift to decarbonized energy source is under way [4,5]; similarly, a shift to decarbonized polymers will be desirable. Here, we report a novel approach by which Si–O based polymers are made directly from minerals (Si–O based silica). We can use practically-limitless Si and O atoms for polymer production, and resulting inorganic polymers are potentially more thermally-resistant, environmental-friendly, and non-toxic due to higher stability of Si–O bonds compared to C–C bonds [6,7]. Thus, silica-derived (Si–O) polymers provide tremendous advantages over oil-derived (C–C) polymers; and, direct production of silicate polymers from silica can contribute to the realization of decarbonized society. Since silica is envisaged as an assembly of Si–O based polymer chains that are connected by covalent bonds, "embedded" polymer chains may be "extracted" from silica. Our method will be extended to other minerals, such as natural clays and pyroxene, in which layers and chains are connected side-by-side via ionic bonds, respectively, and may be weakened and separated by ionic liquid, as we have shown in this work. The method used for these systems is somewhat reminiscent of the "scotch-tape method" that is used to extract graphene layers from natural graphite [8,9]. This approach is unique and more economical than the bottom-up approach by which silicones, such as poly(dimethyl siloxane), are made; i.e., through chemical reactions of basic elements (e.g., Si made via. heating silica with cokes at 2000 °C) with harsh chemicals [10]. In addition, poly(dimethyl siloxane) is a hybrid polymer made of organic and inorganic components (40 wt.% organic); thus, inherent problems associated with organic polymers, such as rather high flammability, cannot completely be avoided. Finally, newly developed polymers are ionic polymers as opposed to silicones, which are neutral polymers: introduction of ionic nature into polymer chains is known to cause dramatic changes in structure and properties [11]. Thus, we can expect advantages which lead to various applications, such as transducers, fuel cell membranes, and a template for making metal/semiconductor nanoclusters, which are not seen for neutral silicones. In a sense, new polymers are combinations of three unique characteristics, i.e., silicate, polymer, and ionic; thus, they provide interesting materials to study further.

The "extraction" of Si–O polymer chains is accomplished by developing a novel, two-step method (Fig. 1). In the first step, silica is converted to silicate glass by incorporating large metal ions (Fig. 1(a)). These ions weaken inter-segmental bonds and increase free volume, leading to a lower glass transition (processing) temperature (T_g). During this process, three-dimensional (highly cross-linked) structure of silica is converted to one-dimensional and two-dimensional structures; such structures are responsible for thermal processability of organic (thermoplastic) polymers. A specific example of the first step is seen for silicate glass made by the addition of potassium oxide, K_2O, to silica, where –Si–O–Si– bonds of silica were converted to $–Si–O^{-}K^{+}$ [12]. The K_2O to silica ratio, $[K_2O]/[SiO_2]$, was altered as 0.31, 0.56, 0.78, and 1.0: the higher the

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[*] Corresponding author.
E-mail address: mhara@rutgers.edu (M. Hara).

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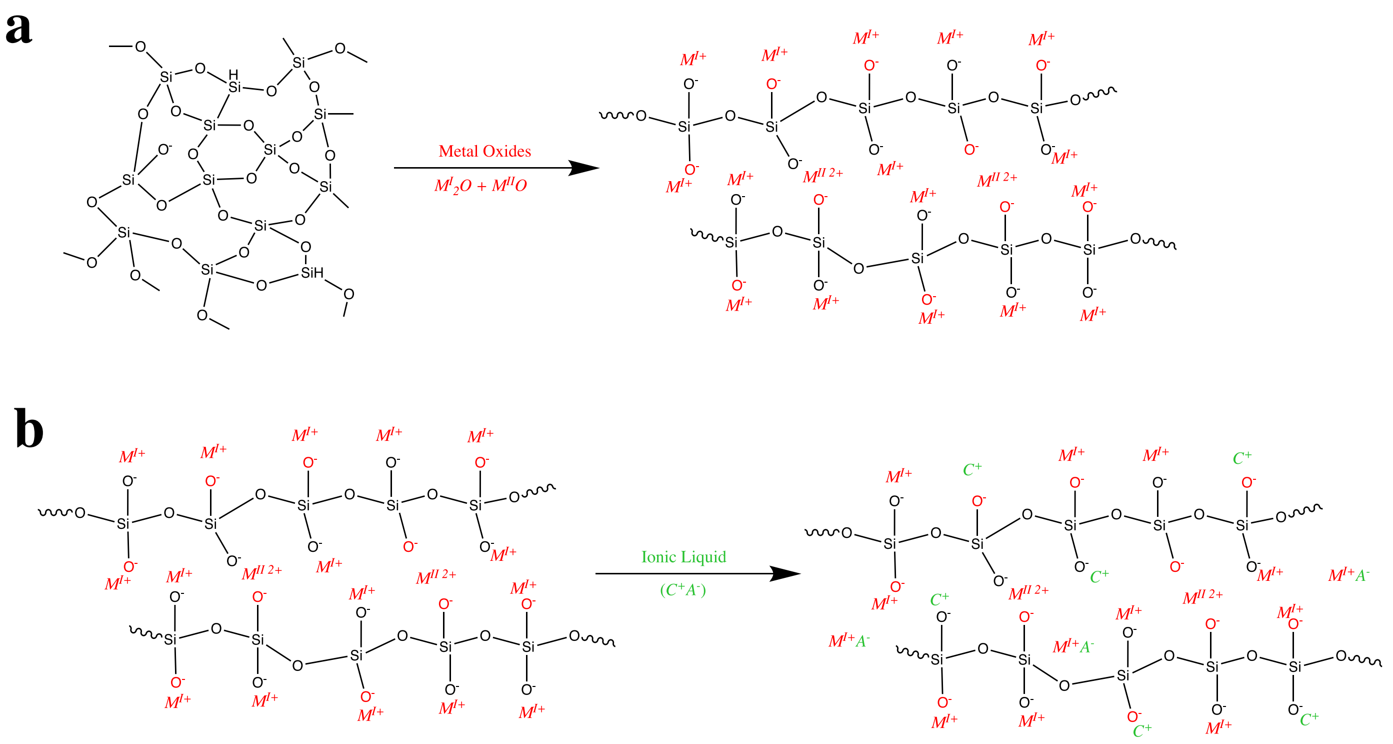

Fig. 1. Our approach for converting silica to silicate polymer. (a) Silica is converted to silicate glass by adding metal oxide modifiers. (b) Silicate glass is converted to silicate polymer by the addition of ionic liquid to silicate glass.

ratio, the higher the conversion to –Si–O^- K^+ (ionic groups). Since strong Si–O–Si covalent bonds are replaced with weaker Si–$O^-K^+\cdots{}^+K$–O–Si ionic bonds, local segmental motion and thus free volume is increased. This in turn decreases T_g; and, the higher the $[K_2O]/[SiO_2]$ ratio, the lower the T_g. The differential scanning calorimetry (DSC) thermograms clearly indicate this effect (Fig. S1(a)). Because the strength of ionic bonds decreases (or free volume increases) as the size of alkali metal ion increases [13], larger metal ions cause lower T_g than smaller ions (Fig. S1 (b)). In this paper, larger metal ions (K^+, Rb^+, Sr^{2+}) than those commercially used (Na^+, Ca^{2+}) [14] were chosen to be incorporated by using a well-established glass processing method to make silicate glass [15].

In the second step, an ionic liquid (IL) is added to silicate glass, which further weakens inter-segmental (ionic) bonds (Fig. 1(b)), thereby increasing local segmental motion and adding extra free volume to polymer chains, which further reduces T_g and makes processing easier. In these inorganic polymers, IL is used as an ionic plasticizer and is not incorporated in the structure, i.e. the resulting polymer is 100% inorganic along the chain. This fascinating liquid has been studied recently and used for various applications [16–18]. Since IL is made of poorly coordinated ions, IL has low melting-temperature (often lower than room temperature) and is nonvolatile [19]. Although IL is reported to weaken or break ionic aggregates of ionomers (i.e., ion-containing organic polymers) [20–22], no work is reported about the interaction of IL with (ionic groups of) silicate glass. To the best of our knowledge, ours is the first report about the effect of IL on silicate glass. Although IL/silica system has been studied [23,24], silica is considered to be an inert material with pores that can hold IL (e.g., catalytic applications, ion gels) [25,26], whereas silicate is not inert and interact with IL molecules as we point out in this article. From a different perspective, IL works as an ionic plasticizer for silicate glass, as an organic compound, dioctyl phthalate, works as a plasticizer for organic poly(vinyl chloride) [27]. Plasticizer molecules incorporated into organic polymer chains weaken or break the inter-segmental bonds and increase segmental mobility, thus decreasing T_g [28].

Fig. 2 shows the fabrication process and what samples look like during the fabrication of silicate polymers from silicate glass and IL. Rubidium silicate glass ($RbSiO_2$) is mixed with IL, EMIM ES (Table S1 and S2), at various IL ratios (Fig. 2(a)). The IL ratio is defined as the charge ratio of IL to metal ions (see Supplementary Material); thus, IL ratio = $[IL]/[Rb^+]$ for the $RbSiO_2$ /IL system. $[IL]/[Rb^+] = 1/4$ means that 1/4 mol of IL is mixed with 1 mol of Rb^+ ions (or O^- Rb^+ ion pairs). As Fig. 2(a) shows, a sherbet-like mixture was made at $[IL]/[Rb^+] = 1/16$, and a gel was formed when the amount of IL was increased to $[IL]/[Rb^+] = 1/4$. Eventually, the silicate glass was dispersed completely in the IL at $[IL]/[Rb^+] = 1$. Fig. 2(b) shows that a plastic sample is made by applying heat and pressure (i.e., compression molding) to the silicate glass mixed with IL. Our inorganic polymer samples are soft at temperatures above T_g and return to their glassy state below T_g, including room temperature. At temperatures higher than T_g, a sample bent when bending force was applied (Fig. 2(c)) and fibers were formed upon stretching (Fig. 2(d)). The sample showed flow at room temperature, thus a cylindrical sample deformed under gravity (Fig. 2(e)). These observations confirm that inorganic polymers fabricated possess processing characteristics similar to those of organic polymers [1]. In short, selected silicate-glass and IL show good compatibility, where ionic groups of IL preferentially interact with ionic groups of silicates, weakening or breaking ionic bonds. The polymeric materials made by compression molding indeed show properties that are closer to those of organic polymers rather than those of inorganic glass and minerals. Typical T_g values in our process are ~1200 °C for pure silica, ~400 °C for silicate glass, and ~150 °C for silicate polymer.

The DSC thermogram of a silicate polymer (Fig. 3(a)) shows a single T_g in the entire temperature range studied, from −100 °C to 300 °C. This may reflect the formation of a single silicate/IL phase at the given scale, indicating good miscibility between the silicate glass and the IL. By contrast, if miscibility is poor, there appear two T_g's which reflect an IL-rich (or IL-only) phase and a silicate-rich (or silicate-only) phase. Miscibility judgement through T_g values is well established for glassy polymer blends (mixtures) [29]. However, it should be added that a single T_g is

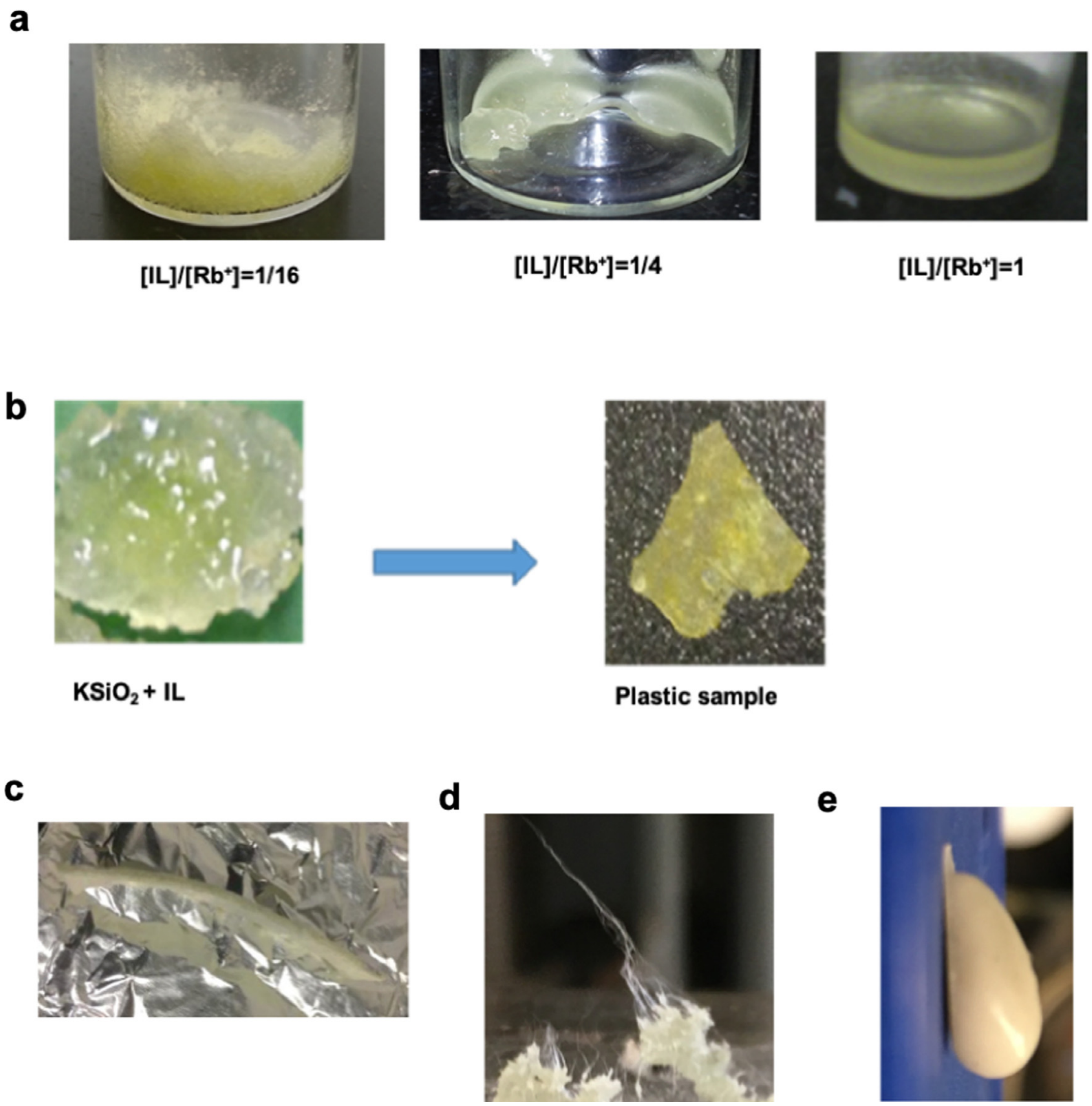

Fig. 2. Appearances of silicate polymers fabricated in this work. (a) Mixtures of $RbSiO_2$ with IL, EMIM ES, at various IL ratios, $[IL]/[Rb^+]$. $[Rb_2O]/[SiO_2] = 0.78$. (b) Compression molding of the silicate polymer ($KSiO_2$ with 1/8 EMIM ES). $[K_2O]/[SiO_2] = 1.0$. (c) Silicate polymer (10% $SrRbSiO_2$ with 1/12 EMIM TF) is bent at temperature higher than T_g. (d) Silicate polymer (10% $SrRbSiO_2$ with 1/12 EMIM TF) forms fibers upon stretching at temperature higher than T_g. (e) Silicate polymer (10% $SrRbSiO_2$ with 1/6 EMIM TF) flows under gravity.

a necessary, but not a sufficient condition for homogeneous structure. A single T_g may be observed for special cases, such as formation of a very small domain or low intensity of the glass transition process [30]. The thermograms in Fig. 3(b) show drops in T_g values for the $RbSiO_2$ upon addition of the IL. The trend of the T_g drop with increasing the amount of IL is clearly seen for a concave up curve in Fig. 3(c) (i.e., a sharp drop in the beginning and a gradual decrease later), which is typically observed for organic-polymer/plasticizer systems [28]. With such low-T_g values, these inorganic polymers can be processed by conventional polymer processing equipment [31]. A drop in T_g upon addition of IL is also observed for the divalent/monovalent system (10% $CaKSiO_2$ ($Ca_{0.1}K_2Si_{1.1}O_{3.3}$) + EMIM TF) (Fig. 3(d)). For simplicity, we use the designation of the silicate as follows in this article: 10% $CaKSiO_2$ means silicate (SiO_2) with Ca^{2+} and K^+ metal ions, where the charge ratio of divalent ions (Ca^{2+}) to monovalent ions (K^+), $2[Ca^{2+}]/[K^+]$, is 0.1 or 10% (see Supplementary Material for details). A small fraction of divalent ions was added to monovalent ones to make the silicate glass less hygroscopic and non-crystalline. In this case, an increase in T_g due to divalent ions (Fig. S2(a) and S2(b)) is more than compensated for the drop in T_g due to the addition of IL (Fig. S2(c)). The T_g value for RbSiO2 + 1/8 EMIM ES was 204 °C (Fig. 3a), whereas that of the material of the same composition was 237 °C (Fig. 3b): the difference between these samples was molding temperature used for making samples (150 °C vs 200 °C). Obviously, this suggests the importance of a kinetic factor in addition to a thermodynamic factor. Importance in the kinetic factor for processing polymeric samples is well known [32], since "real" thermodynamic state is often difficult to achieve under practical processing conditions. In order to minimize the effect of molding temperature, most of the samples used in this work were molded at 180–200 °C.

Fig. 4 shows the characterization results of the silicate polymers. Scanning electron microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) images were collected to study sample topography (Fig. S3(a)) and elemental distribution (Fig. 4(a)). With each color representing a different element, EDS images show that IL is distributed uniformly, i.e. well mixed at the scale of 0.1 mm; however, local heterogeneity exists in nanometer scale, as seen in TEM micrograph (Fig. S3(b)). Electron diffraction pattern (Fig. 4(b)) shows only concentric rings without any reflections, indicating that polymer structure is amor-

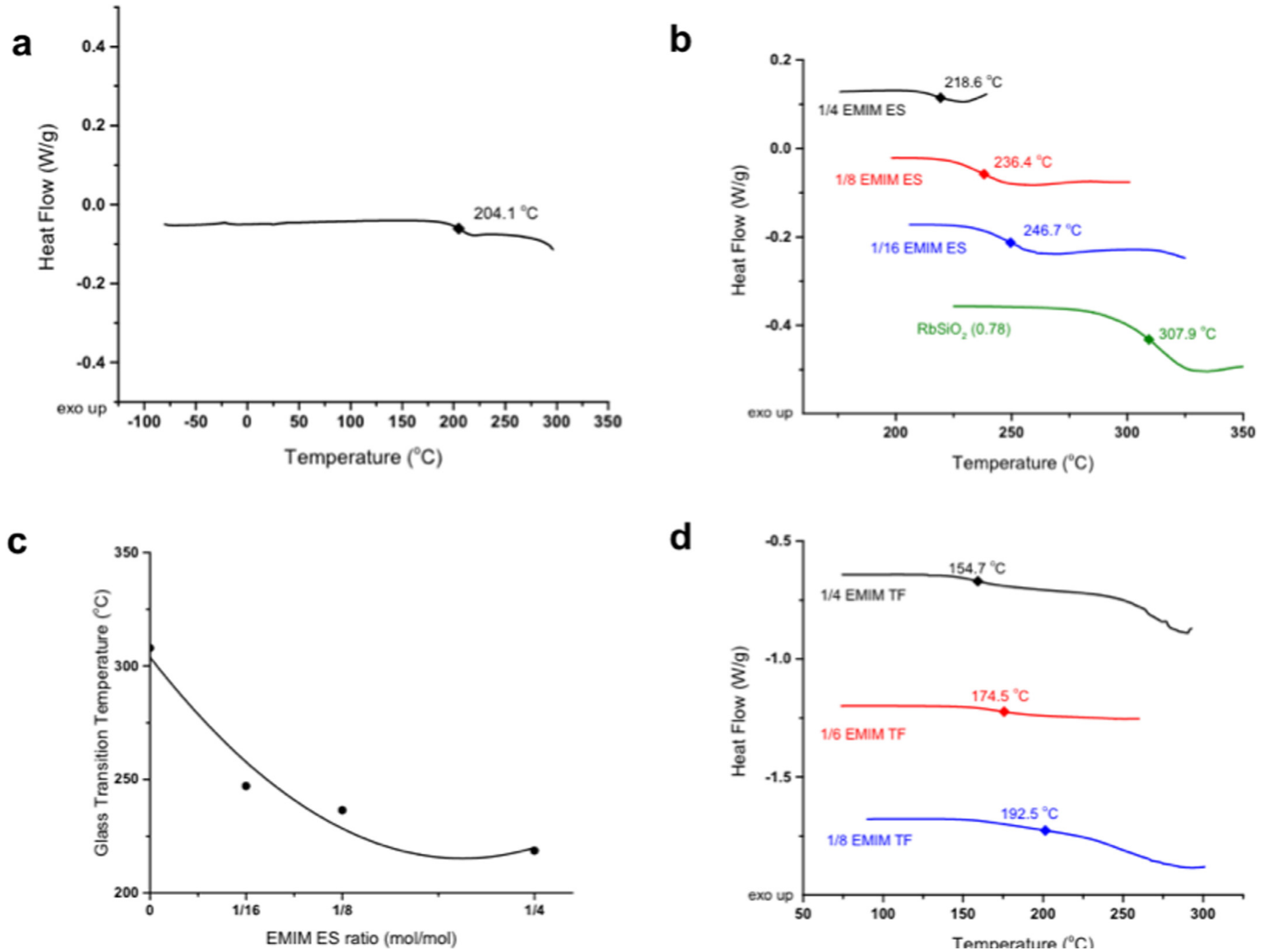

Fig. 3. DSC data for silicate polymers. (a) DSC thermogram of silicate polymer ($RbSiO_2$ + 1/8 EMIM ES), showing a single T_g. Compression molded at 150 °C. (b) DSC thermograms for silicate polymers ($RbSiO_2$ + EMIM ES) at various IL ratios. Compression molded at 200 °C. (c) Glass transition temperature vs IL ratio for silicate polymer ($RbSiO_2$ + EMIM ES). (d) DSC thermograms for silicate polymers (10% $CaKSiO_2$ + EMIM TF) at IL ratio of 1/8, 1/6, and 1/4.

phous without long-range ordered (crystalline) structure. This diffraction pattern is a proof that our inorganic polymers are amorphous, since it is important to avoid any crystallization for the successful synthesis of inorganic polymers. The X-ray Photoelectron Spectroscopy (XPS) data (deconvoluted functions from N1s orbital photoelectron spectrum) (Fig. 4(c)) reveal a new peak at 399 eV upon mixing of silicate glass with IL, in addition to the original peak at 402 eV, which is observed for the imidazole-ring of pure IL. The emergence of this new peak reflects the interactions occurring between IL and silicate glass; more specifically, between $BMIM^+$ion of the IL which contains N atoms and a –Si–O^-ion of the silicate. Note that silicate glass shows no peaks because of the lack of N atoms.

To demonstrate the advantageous effect of the silicate polymer fabricated, flammability was tested (Fig. 4(d)). When exposed to high-temperature flames from a torch, exposed area of the inorganic polymer sample turned white and no smoke was observed. This flammability characteristics is similar to that of the silicate glass used as a reference, as seen in Fig. 4(d). By contrast, poly(dimethyl siloxane) turned black with smoke coming out. This clearly indicates the inflammability of our polymer, i.e., inorganic nature of silicate polymer, as opposed to the more organic nature of poly(dimethyl siloxane), which is a hybrid of organic/inorganic polymers. Mechanical properties of silicate polymers were tested (Fig. 4(e)). Because tensile testing is most sensitive to material flaws and microscopic cracks, and because compression testing tends to be characteristic to polymers [33,34], we conducted compression stress-strain testing. Initial results show that compressive modulus of the inorganic polymer is in the range of 0.41–0.63 GPa, which is comparable to that of polystyrene sample we also measured (0.63 GPa). The modulus of another widely used conventional polymer, high density polyethylene (HDPE), is reported to be in the range of 0.5–1.4 GPa [35]. These results indicate that the modulus data of prototype silicate polymers are comparable to those of typical conventional polymers. When synthesis conditions and processing methods are further improved, as has been witnessed in the development of many organic polymers used today, silicate polymers with better mechanical properties will be developed. One potential improvement is an increase in ductility. This may be achieved by suppressing crack formation through an increase in yield stress, which may be possible through an increase in ionic cross-links. This is expected from our previous work on mechanical properties of ionic polymers (ionomers) [36,37], in which a small number of ionic cross-links formed work as junction points that can increase the total strand density of the system, leading to suppression of crazing in favor of shear yielding. Based on the results on ionomers, we can expect an increase in strength and ductility, if a proper number of ionic

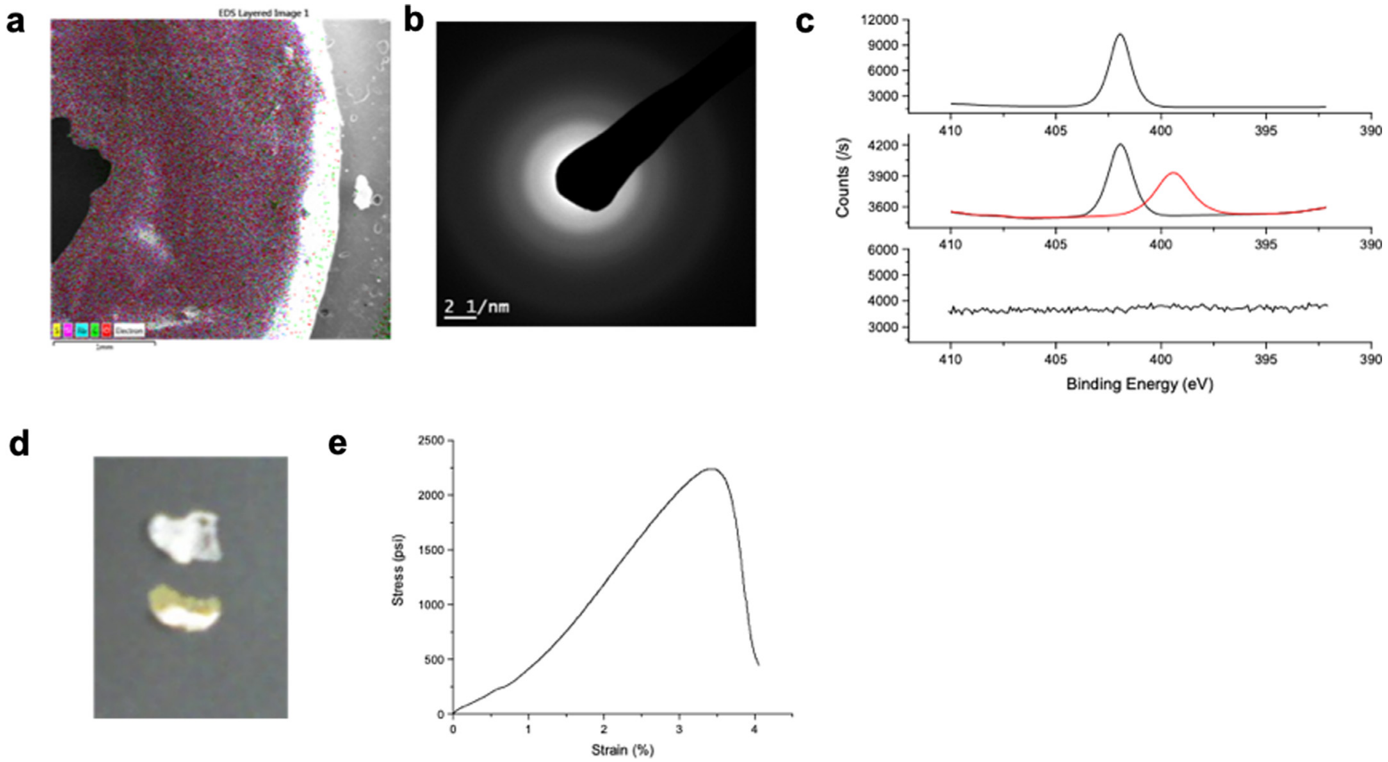

Fig. 4. Characterization of silicate polymers. (a) EDS/SEM picture for silicate polymer (30% $SrRbSiO_2$ with 1/8 EMIM TF). (b) Electron diffraction pattern for silicate polymer (10% $CaKSiO_2$ with 1/10 EMIM TF). (c) Deconvoluted functions from the high-resolution XPS spectrum at N1s orbital binding energy for: (i) BMIM PF_6; (ii) silicate polymer (30% $SrRbSiO_2$ with 1/3 BMIM PF_6); (iii) 30% $SrRbSiO_2$ glass. (d) $KSiO_2$ glass (top) and silicate polymer ($KSiO_2$ glass with 1/8 EMIM ES) (bottom), after exposed to a torch frame. $[K_2O]/[SiO_2] = 1.0$. Specimens were made by compression molding. (e) A typical compressive stress-strain curve for silicate polymers (5% $CaKSiO_2$ with 1/8 EMIM TF). Compression molded at 180 °C and 1500 psi.

cross-links are retained, although majority of ionic cross-links should be weakened (or broken) to make the material behave as a polymer. This is an interesting subject of our future research. Overall, novel inorganic (silicate) polymers are comparable to conventional polymers for modulus; comparable to silicate glass for non-flammability (much better than poly(dimethyl siloxane)); and, better than glass for ductility.

We speculate the molecular-level mechanism of interactions between silicate glass and IL. As depicted in Fig. 1(b), a cation from IL ($EMIM^+$) interacts with an O^-ion of silicate glass, forming an ion pair ($EMIM^{+\cdots}{}^-O$); and an anion from IL (TF^-) interacts with a cation (K^+) from silicate glass, forming an ion pair K^+TF^-. Similarly, for inorganic polymer made of $SrRbSiO_2$ glass and IL (EMIM TF), ion pairs ($EMIM^{+\cdots}{}^-O$) are formed, which are dispersed throughout the sample; and Rb^+ TF^- ion pairs are formed, which may form clusters that show crystalline structure. XRD data of this sample (Fig. S4) indeed shows the formation of crystal structure, which is comparable to the literature data of RbTF crystal [38]. Also, FTIR data (Fig. S5) suggest that the molecular mechanism described above is reasonable. Specifically, the peak height at 640 cm^{-1} increases with addition of EMIM TF. This peak is assigned to $O^{-\cdots}{}^+EMIM$ cation motion vibration. When IL (EMIM TF) is mixed with silicate glass ($CaKSiO_2$), alkali ions (K^+) are replaced with the cation (^+EMIM) from IL, forming $O^{-\cdots}{}^+EMIM$ ion pairs; hence the peak height increases when EMIM TF is added to the silicate glass, as seen in the figure. Note that aforementioned $O^{-\cdots\cdot}{}^+Cation$ interaction was confirmed before by the XPS data of BMIM PF_6 + $SrRbSiO_2$ silicate polymer.

In summary, silicate polymers were made directly from silica by using a top-down approach. Since natural silica (sand) is made of Si-O based polymer chains, polymer chains from silica were “extracted” by using a novel approach, involving Si-O bond modification (i.e., glass formation) and subsequent incorporation of ionic liquid. We have found that ionic liquid works as an ionic plasticizer which can weaken or break ionic bonds in silicate glass. These polymers can be processed at ~150 °C, a much lower temperature than those needed to process silica (~1350 °C) and silicate glasses (~400 °C). Silicate polymers reported in this article are prototypes of silica-derived (Si–O) polymers; silicate polymers that have better processability and properties than those reported in this article will be found when many combinations of silicates (with different kinds and amounts of metal ions) and ionic liquids (with the combinations of hundreds of cations and anions) are explored by using our general method. Since newly developed polymers possess three characteristics, i.e., silicate, polymer, and ionic nature, various applications are expected to be found. Potential applications include transducers (e.g., for artificial muscles, soft robotics, and sensors) [21,39], fuel cell membranes [40], a template for making metal/semiconductor nanoclusters [41], and biocompatible materials [42].

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mtla.2019.100486.

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