



Dynamic polysulfide shape memory networks derived from elemental sulfur and their dual thermo-/photo-induced solid-state plasticity



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ABSTRACT

In this study, we demonstrate the synthesis of dynamic polysulfide networks through the solution polycondensation of pentaerythritol tetra(3-mercaptopropionate) (PTMP) with elemental sulfur by a reverse vulcanization process. Elemental sulfur content as high as 51% can be incorporated into the dynamic polysulfide networks. An important feature of the resulted polysulfide networks is their catalytic-free malleability, which implies that they have both thermo- and photo-induced solid-state plasticities to obtain a complex permanent shape due to the exchange of dynamic S–S bonds. These dynamic polysulfide networks have great potentials in fabricating complex three-dimensional shape memory devices for biological and mechanical applications.

1. Introduction

Polymeric materials play important roles in our daily life. In general, polymers are divided into two main classes depending on their responses to thermal stimuli: thermoplastics and thermosets. Leibler [1–4] introduced the third class of polymers called vitrimers. Vitriimer is a new type of polymeric network materials connected by dynamic covalent bonds, it combines the network structure of thermosets and the remoldability of thermoplastics, which considerably increases the application ranges of polymers. Interestingly, vitrimers possess two glass transition temperatures, T_g (transition temperature analogous to T_g observed in classical thermosets) and T_v (transition temperature of the freezing topology). At high temperatures, vitrimers can flow and behave like viscoelastic liquids because of the fast exchange of dynamic covalent bonds, while at low temperatures, exchange reactions of dynamic covalent bonds are frozen and they behave like classical thermosets. This unique property provides an innovative strategy to produce malleable thermoset materials, which can be remolded many times, and thus, it dramatically reduced the environmental impact of traditional thermoset. Various dynamic covalent bonds such as disulfide exchange [5–8], imine exchange chemistry [9–11], transesterification reaction [1,12–14], transcarbamylation [15,16], siloxane exchange [17,18], and alkoxyamine chemistry [19,20] have already been incorporated into polymeric materials to endow them with malleability or self-healing properties [21].

Shape memory polymers (SMPs) are a unique class of functional polymer materials in which externally programmed shapes can be temporarily fixed and later thermally recovered on demand [22–23]. In

general, SMPs are elastic polymer networks that consist of chemical (covalent bonds) cross-linking or physical (non-covalent bonding like hydrogen bonding) cross-linking [24–26]. However, recent studies have shown that shape memory networks with reversible cross-links, such as dynamic covalent [25], have more interesting properties. In particular, Xie et al. synthesized SMPs with thermally distinct elasticity and plasticity using dynamic covalent bonding connected reversible cross-link networks, which showed incredibly complex thermal deformation process [27–30].

In addition, the application of dynamic covalent chemistry to produce malleable vitrimers using elemental sulfur, which is an industrial by-product, as the monomer for the manufacture of functional polymeric materials is an alternative strategy to reduce the negative impact of thermoset to the environment. A large amount of elemental sulfur is generated annually from hydrodesulfurization in petroleum refining processes; however, it has a limited number of uses besides its use in the production of sulfuric acid and using as the cross-linking agent in vulcanized rubber. Pyun reported an innovative facile method (termed ‘inverse vulcanization’) to prepare chemically stable and processable sulfur-rich polymeric network materials through the direct copolymerization of elemental sulfur with vinylic monomers [31,32]. This methodology enabled the incorporation of large amounts of sulfur into processable copolymer forms with tunable thermomechanical properties. Bowman's group has obtained cross-linked polysulfide networks with photo-induced plasticity [33,34]. The polysulfide network can be rapidly plasticized by photo-cleavage of photo-initiator in polymer matrix through ultraviolet (UV) irradiation. However, both Bowman and Pyun have explored materials with thermo-stimulated plasticity or

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photo-stimulated plasticity. Furthermore, study on whether materials that have both thermo- and photo-induced plasticities simultaneously is worthy because these materials will have great potentials to be used in a broader range of applications.

In this study, we report the synthesis of novel dynamic polysulfide networks Poly(S-PTMP) through the polycondensation reaction of pentaerythritol tetra (3-mercaptopropionate) (PTMP) with elemental sulfur. The number of S – S bonds and the T_g of the dynamic polysulfide networks can be controlled by slightly varying the thiol/elemental sulfur feed ratios in the copolymerization process. An important feature of the resulted dynamic polysulfide networks is their catalytic-free malleability due to the dynamic sulfur-sulfur bonding. Thus, the single dynamic polymer network has both elasticity and plasticity properties. The complex thermo- and photo-stimulated shape memory properties of Poly(S-PTMP) were demonstrated and attributed to the reconstruction of cross-linked network by the breakage and re-bonding of sulfur-sulfur bonds. More interestingly, the T_g can be tailored to about 30 °C; thus, a polymer network with its thermal phase transition occurring close to the body temperature can be obtained, and thus, its shape recovery can be triggered in hand. This dynamic polysulfide network has a great potential in fabricating complex three-dimensional (3D) shape memory devices for biological applications.

2. Experimental

2.1. Chemicals

Pentaerythritol tetra(3-mercaptopropionate) (PTMP, 95%) was purchased from TCI (Shanghai) Development Company Limited. Sulfur (precipitated powder, 99.5%), toluene (99.5%), and ethanol (99.7%) were purchased from Chengdu Kelong Chemical Company Limited. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO, 97%) was obtained from Aladdin Industrial Corporation.

2.2. Synthesis of poly(S-PTMP) powders and films

Sulfur (3.2070 g, 0.100 mol) was dissolved in toluene (60 ml), which was previously deoxygenated with bubbling argon for 10 min. The solution was heated to 80 °C under stirring. When the sulfur was totally dissolved, PTMP (1.5271 g, 0.003 mol) was added to the solution. The reaction was maintained at 80 °C for 12 h under stirring. The product was then filtered immediately and washed with ethanol three times. After drying under vacuum, a light yellow powdered product was obtained.

Because of the dynamic S–S bonding, the resulted Poly(S-PTMP) powders can be readily compression molded at 200 °C at 10 MPa for 30 min to afford flexible transparent films.

2.3. Complex shape memory behavior of dynamic polysulfide networks

A: Elasticity-based shape memory behavior: The dynamic polysulfide network film was cut into strips and folded into U shape at 40 °C. The U shaped sample was then cooled at – 10 °C for 90 min to fix its shape. Subsequently, the U shaped sample was placed in an oven at 40 °C or on a person's palm to observe the recovery process.
 B: Thermo-plasticity-based shape memory behavior: The polymer film was cut into strips, folded into O shape and heated at 200 °C for 30 min to fixing their shapes. Subsequently, the O shaped sample was recovered to its initial shape at 40 °C, which was then cooled at – 10 °C for 90 min to fix its shape. The O shaped sample was placed in the oven at 40 °C, and the recovery process was recorded.
 C: Photo-induced plasticity-based shape memory behavior: The polymer film was cut, folded into a complex shape, and stereotyped at 360 nm UV light for 2 h under various temperatures. Subsequently, the sample was cooled at – 10 °C for 90 min to fix its shape. The sample was then placed in the oven at 40 °C, and the

recovery process was recorded.

2.4. Characterization

Infrared (IR) spectra were recorded using a Nicolet 560 spectrometer. Solid-state nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker Avance III 500 MHz with a standard 4-mm Bruker MAS probe at a sample spinning rate of 8.0 kHz. Scanning electron microscopy (SEM) was performed using an Inspect F SEM at an accelerating voltage of 20 kV. Differential scanning calorimeter (DSC) characterization was performed using a Q2000 DSC calorimeter (TA Instruments). The measurements were made under nitrogen atmosphere in the temperature range of – 50 to 150 °C at a heating rate of 5 °C/min. Dynamic mechanical analysis (DMA) was taken from a TA Q800 apparatus at a heating rate of 5 °C/min and a load frequency of 1 Hz in film tension geometry (sample size 30 mm × 5 mm). TGA was taken from a Netzsch TG 209 F1 instrument at a heating rate of 10 °C/min from 30 to 800 °C under nitrogen flow. The tensile test was carried out using a universal material testing machine (AGS-J, SHIMADZU Corporation) with test speeds of 2 mm/min at room temperature.

Electron paramagnetic resonance (EPR) experiments were conducted using an EPR spectrometer (Bruker EMX EPR). The sample was placed into a glass bottle (10 ml). It was then irradiated with 360 nm UV light to initiate the generation of sulfur radicals. After 1 h, 1 ml DMPO solution in toluene (0.1 M) sparged by argon was injected into the bottle and quenched in ice bath quickly. The solid part of the sample was then put into a quartz EPR tube (4-mm OD), and the liquid part was sucked up by a capillary to conduct EPR experiment.

3. Results and discussion

The reaction of thiols with elemental sulfur is well known in organic chemistry [32]; however, it has found little use in polymer preparation, and only limited polysulfide materials have been reported so far. We try to extend this traditional reaction for the facile preparation of dynamic polysulfide networks. The elemental sulfur can be dissolved in toluene upon heating up to 80 °C, when PTMP was added to the solution, pale yellow powders gradually precipitated (Scheme 1).

To interrogate the presence of sulfur in poly(S-PTMP) samples, copolymers with different molar ratios of sulfur to PTMP in raw material (nS: n-HS = 0.4:1, 0.8:1, 1.65:1, 3.76:1, 8:1, and 16:1) were prepared and characterized by elemental analysis (EA). Data from EA showed that the sulfur content in poly(S-PTMP) (nS: n-HS = 0.4:1) was 34.84% and that in poly(S-PTMP) (nS: n-HS = 0.8:1) was 44.43%. However, with the further increase in sulfur to thiol ratio, the sulfur content gradually increased: in poly(S-PTMP) (nS: n-HS = 1.65:1), the sulfur content was 46.90%, while in poly(S-PTMP) (nS: n-HS = 3.76:1, 9:1, and 15:1), it was only slightly increased from 48.51% to 49.79% and 50.65%. By further increasing the sulfur to thiol ratio, the sulfur content in the polymer remained constant, while some unreacted elemental sulfur precipitated from the reaction solution when the solution was cooled to room temperature. Thus, in the following work, polysulfide copolymers with nS: n-HS = 0.4:1, 0.8:1, and 15:1 were chosen to be tested further. These copolymers were named poly(S-PTMP)-35, poly(S-PTMP)-44, and poly(S-PTMP)-51, respectively, and the numbers indicate their corresponding sulfur content in the polymer network.

The FTIR and ^{13}C NMR spectra both confirmed that the poly(S-PTMP)s were successfully synthesized. Fig. 1A shows a peak at 2568 cm^{-1} that can be attributed to the characteristic peak of the –HS group in monomer PTMP. The gradually disappearance of the 2568 cm^{-1} peak with the increase in sulfur to thiol ratio indicates that there were no unreacted –SH groups in poly(S-PTMP)-44 and poly(S-PTMP)-51 polymer networks. Moreover, the ^{13}C NMR data shown in Fig. 1B further confirm the structure of the product. The chemical shift at 33 ppm can be ascribed to the C–S carbon connected with sulfur, while the chemical shifts at 171, 63, and 41 ppm can be attributed to

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