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Re-healable polyimine thermosets: polymer composition and moisture sensitivity†

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Moisture sensitivity of polyimines is systematically studied by incorporating various diamine moieties into the polymer networks. Significant variations in moisture responsiveness and property changes were observed. Hydrophilic polyimines can be re-healed at ambient conditions, whereas more hydrophobic polyimines require heat to be healed.

Covalently cross-linked polymer networks are traditionally described as thermosets,[1,2] obtaining this name from the fact that they cannot flow upon heating and thus cannot be reshaped or recycled.[1] Very recently, this picture has been changed by incorporating dynamic covalent bonds[3–7] into polymer networks.[8–21] Such polymers, referred as "covalently adaptable networks"[9,12,22,23] are still covalently cross-linked, but the presence of dynamic covalent bonds[24–26] allows the rearrangement of the polymer network through bond breaking and reformation, which results in macroscopic stress relaxation and ultimately material flow.[12–15,27–30] Covalently adaptable networks represent an exciting breakthrough in novel polymer development as they open the door to new material processing paradigms for thermosets including thermoforming,[13] welding,[28] self-healing,[8,10] and recycling.[30]

The imine-linked polymers,[31,32] which form through Imine condensation,[33,34] are attractive for the development of dynamic covalent networks. Since imine condensation simply requires an amine and an aldehyde or ketone, there is a wide variety of suitable monomers commercially available. In addition, the reaction can take place at reasonable rates at elevated temperatures even in the absence of a catalyst.[35] We have demonstrated that polyimines fundamentally behave like a classic thermoset at ambient conditions yet can be reshaped and molded by the application of either water or heat in the absence of any catalyst.[29] We showed that heat or water greatly

facilitates imine exchange reactions, leading to the malleability and rehealability of polyimines.[29] Although polyimines hold a great potential for developing simple, easily accessible, truly green, and inexpensive malleable polymer networks, there have been only few reports on this interesting type of materials.[36,37] One interesting feature of polyimine materials is their moisture sensitivity. Although they can be stable against hydrolysis and retain their structural integrity even when soaked in water, the mechanical and malleable properties of the networks can be strongly influenced by water and atmospheric moisture, which needs to be evaluated for practical applications. Herein, we demonstrate the moisture sensitivity of polyimines can be modulated through judicious selection of monomers. Highly hydrophilic to hydrophobic polyimines with a broad range of mechanical/thermal properties and moisture sensitivity have been obtained by simply varying amine-containing monomers. We also sought to understand to what extent highly hydrophilic polymers are more susceptible to hydrolysis. We also found rehealability of polyimines is directly influenced by their hydrophilicity.

Polyimine networks were prepared from diamine and dialdehyde monomers combined with triamine crosslinkers (Scheme 1). Because of the relative abundance of inexpensive commercially available diamines, we chose to investigate the impact of changing the composition of diamine monomers. A

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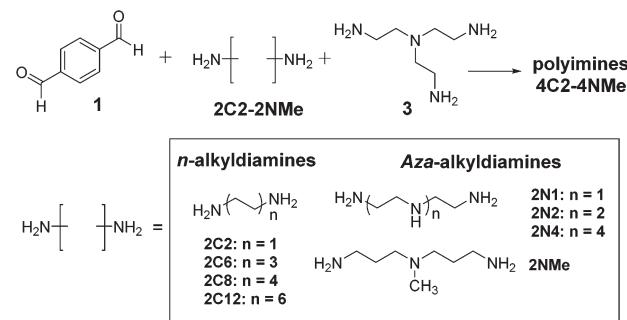
Scheme 1 Preparation of polyimine networks consisting of various diamine moieties.

series of diamines (**2C2-2NMe**) were explored, which include alkyl diamines (**2C2–2C12**) consisting of alkyl chains of varied length and the aza-analogues (**2N1–2N4**) consisting of oligoethyleneimine or oligo-propyleneimine of varying length. In order to examine the effect of possible hydrogen bonding, we also chose to use **2NMe**, in which the secondary amine group in the backbone of diamine monomer is methylated. The polyimines (**4C2-4NMe**) were obtained from a diamine (**2C2-2NMe**), terephthaldehyde (**1**), and tris(2-aminoethyl)amine (**3**), as shown in Scheme 1. In a typical procedure, diamine **2**, dialdehyde **1** and crosslinker **3** in a stoichiometric ratio of 0.450 : 1.000 : 0.367 were mixed in solvent (EtOH for **4N1-4NMe**, EtOH/CH$_2$Cl$_2$/H$_2$O for **4C2–4C12**) in a tray made from silicone-coated release paper. The volatiles were then slowly evaporated to yield the polyimine (**4C2-4NMe**) as a transparent film. Prior to the property measurement, the resulting uncured film was heat pressed for 3 h at 78 °C, 1 h at 95 °C, and finally 1 h at 105 °C using a top platen-heated hand-operated heat press under nominal pressure. The crosslinking amine moieties constitute approximately 55 mol% of primary amines in the network, thus the resulting polymers can be described as 55% crosslinked. Polyimine **4N1** was prepared as 70% crosslinked using a 0.300 : 1 : 00 : 0.467 (**2N1 : 1 : 3**) ratio for the sake of easy comparison with the properties of the previously reported polyimine.[29]

Mechanical properties of these polyimines were then investigated. Tensile testing revealed a great variation in elongation at break and tensile strength among these polyimines (Table 1, Fig. S4†). With the increase of chain length of the diamines, we observed greater elongation at break and lower tensile strength of the resulting polyimines. Tensile strength decreases in the order of **4N1** > **4N2** > **4N4, 4NMe** and **4C2** > **4C6** > **4C8, 4C12**, whereas elongation at break increases in the order of **4N1** < **4N2** < **4N4** < **4NMe** and **4C2, 4C6** < **4C8** < **4C12**. Polyimine **4C2** consisting of short ethylene chain exhibits the highest tensile strength at 65 ± 2 MPa, and a modulus of approximately 1 GPa, which are similar to previously reported **4N1**.[29] The polyimine **4C12** consisting of dodecyl diamine exhibits the highest percent elongation (112 ± 34% elongation at break) among polyimines consisting of alkyl diamine moieties. We found analogous polyimine **4N4** composed of aza-alkyl diamine components with the same chain length as those in

4C12 is far less elastomeric, showing ~40% elongation at break. This result indicates the replacement of CH$_2$ with NH group in the polyimine chain and the presence of extra hydrogen bonding have a negative effect on the elastic properties of polyimines. When the hydrogen bonding sites are removed by using *N,N*-bis(3-aminopropyl)methylamine (**2NMe**), the resultant polyimine **4NMe** exhibits dramatically increased elastomeric behavior (162 ± 22% elongation at break).

The thermal properties of the polyimines were characterized by dynamic mechanical analysis (DMA) and thermal gravimetric analysis (TGA). The glass transition temperatures of polyimines were determined by the maximum Tan delta in DMA curves and first heating run data were used (Fig. S1 and S2†). Polyimines with short diamines exhibit higher T_g, *e.g.* 120 °C for **4C2** and 110 °C for **4N1**. The T_g trend of polyimines containing alkyl diamines (**4C2** > **4C6** > **4C8** > **4C12**) is in line with the decreasing rigidity of diamine monomers, which agrees well with the notion that T_g is associated with the molecular packing density and rigidity of the polymer backbones. The T_g of polyimines containing aza-alkyl diamines with multiple amine groups does not follow an obvious trend, likely due to the combined effect of rigidity of polymer chain and inter-chain hydrogen bonding. We observed the lowest T_g (57 °C) for **4NMe**, which might be attributed to the decreased hydrogen bonding density. This result indicates that interchain hydrogen bonding has a significant impact on the glass transition of polymers. Correspondingly, polyimine **4N2** (T_g = 80 °C) and **4N4** (T_g = 95 °C) with multiple NH groups exhibit higher glass transition temperatures compared to the analogous **4C8** (T_g = 61 °C) and **4C12** (T_g = 47 °C) in which NH groups were replaced by CH$_2$. The thermal stabilities of the polyimines were evaluated by TGA in nitrogen atmosphere at a heating rate of 10 °C min^{-1}. TGA analysis shows that all polyimines lose less than 5% weight at 200 °C, and the temperatures for 10% weight loss in nitrogen atmosphere were in the range of 294–326 °C for polyimines (**4C2–4C12**) and 238–314 °C for aza-analogues (**4N1–4N4**). At 600 °C, the residue weight % of **4C2** was about 66%, which was the highest among all the polyimines. The char yields of other polyimines at 600 °C were in the range of 34–47%.

In order to characterize the hydrophilicity of polyimines, we immersed each sample in deionized water for 24 h and

Table 1 Summary of mechanical and thermal properties of polyimines

Polyimines	Tensile strength (MPa)	Elastic modulus (GPa)	Elongation at break (%)	T_g[b] (°C)	Nitrogen content[c] (mol%)	Weight gain (%)
4N1[a]	40	1.0	4	110	19	63
4N2	25	0.93	5	80	20	71
4N4	11	0.21	40	95	22	90
4NMe	11	0.013	162	57	17	52
4C2	65	1.05	19	120	18	7
4C6	41	1.01	22	76	16	11
4C8	17	0.014	50	61	15	6
4C12	20	0.027	112	47	13	6

[a] 70% crosslinked. [b] T_g was obtained from Tan delta peak in the first scan DMA curve. [c] Nitrogen content (mol%) on the backbone of the polymers.

measured the weight increase of the fully swelled sample. The swelling data provides the most relevant insight into the effects of moisture on each polyimine, as the weight increase provides a reasonably accurate estimation of the water content within the polymer matrix. We found weight gains of the polyimines are mostly proportional to the density of amine/imine bonds in the polymer matrix in most cases, *e.g.* the order of weight gains in polyimines (**4N4** > **4N2** > **4N1** > **4NMe**) agrees well with the order of nitrogen mol% in polyimines (**4N4** > **4N2** > **4N1** > **4NMe**) (Table 1). More hydrophilic polyimines (**4N1**, **4N2**, and **4N4**), which have imine/amine bonds for every two carbons, absorb considerable amount of water, showing greater than 60% weight increase. Polyimines (**4C2–4C12**) with alkyl diamines show less than 11% weight gain after immersion in water. Polyimine **4C12** consisting of hydrophobic docecyldiamine moieties absorbs only 6 wt% of water upon saturation. Our results clearly show the water sensitivity of polyimines can be tuned by judicious selection of monomers, and both hydrophilic and hydrophobic polymers can be accessible.

Next, the mechanical properties of the wet polyimine films were examined after 24 h immersion in water. After absorbing water, most of the polyimines become more elastomeric with the exception of polyimine **4NMe** (>2 fold decrease), which was originally the most elastic. The polyimines made critical gains in elongation ranging from 150% (**4C2**, or **4N4**) to approximately 20 fold in the case of polyimine **4N1**. The polyimine **4C2** consisting of ethylenediamine moieties shows the least change of elongation at break (50%). We found that polyimines (**4C2–4C12**) retain considerable toughness (∼50% original tensile strength) in the wet state, whereas polyimines (**4N1–4N4**) lose >90% original tensile strength (Fig. 1b). Our study suggests that for most polyimines water mainly acts as plasticizer, reducing the stiffness and increasing the elongation at break by interposing itself between polymer chains and reducing their intermolecular bond strength, which is consistent with plasticizing effect of water on many other polymers.[38] It is interesting to note that wet sample of polyimine **4NMe** consisting of *N*-methyldipropylenetriamine essentially loses all mechanical strength, showing only 45% of its original elongation, and 2% of its initial tensile strength.

In order to gauge the impact of hydrophilicity on the hydrolytic stability of the polymers, the solid-state ^{13}C-NMR of the polyimines **4N4** and **4C12** were measured in the wet and dry state. Hydrolysis of imine bonds in the polymer matrix was determined by measuring the change in the ratio of imine to aldehyde carbon peaks (159 ppm and 192 ppm, respectively). As shown in the ^{13}C-NMR spectra (Fig. S5–S9†), there is no observable decrease in the intensity of the imine carbon peak (159 ppm) when either of the polymers is completely saturated with water. This means that even very hydrophilic polyimine, which readily absorbs nearly 90% of its weight in water, does not exhibit any measureable hydrolysis in the swollen state. In order to further test whether any decomposition of polyimines occurs during the soaking process, we measured the weight change of samples before and after soaking. Polyimine **4N1** was soaked in aqueous solutions of three different pH values (pH = 4, 7, and 10) for 24 h. Nearly no weight loss was observed for all the samples after drying, which indicates polyimine **4N1** is stable and does not undergo any decomposition under a broad range of pH conditions (pH = 4–10).

The reversibility of dynamic imine bonds allows these polyimines to be rehealed at the molecular level when pressed together at room temperature. We found hydrophobic and hydrophilic polyimines exhibit different rehealability. As shown in Fig. 2, when two broken pieces of hydrophilic polyimine **4N4** was pressed together with 200 g loading for 1 h, they were physically inseparable (Fig. 2d). When the two broken pieces were covered with a piece of moist paper towel and pressed together with 200 g loading, we obtained better re-healed materials with no discernible interface, which could hold 50 g of weight (Fig. 2c and e). This result indicates water catalyzes the bond exchange reaction in the polyimine, and atmosphere moisture might be enough to heal polyimines under extended time and higher pressure. On the contrary, more hydrophobic polyimine **4C12** cannot be re-healed at room temperature under the same conditions even in the presence of water. However, when the two broken pieces of **4C12** were pressed together under heat (77 °C) for 1 h, we obtained a completely healed piece that can hold 50 g of weight. Our study indicates polymer composition and hydrophobicity directly influence the rehealability of these polyimines.
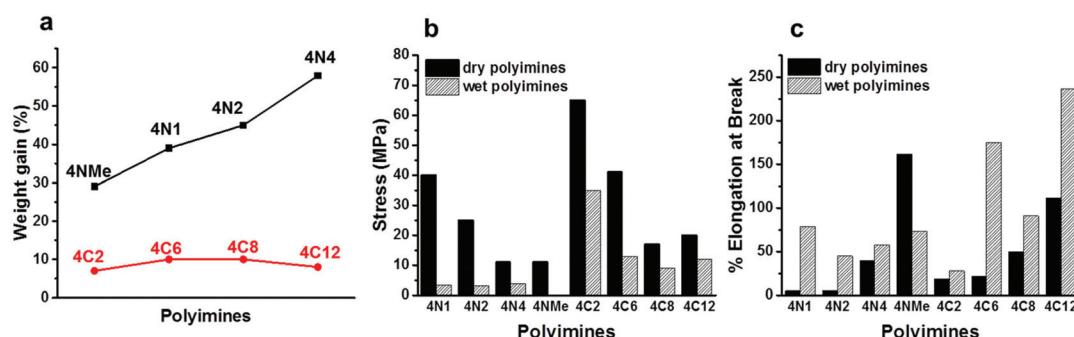

Fig. 1 Comparison of tensile testing results of wet/dry samples of polyimines **4C2-4NMe**.
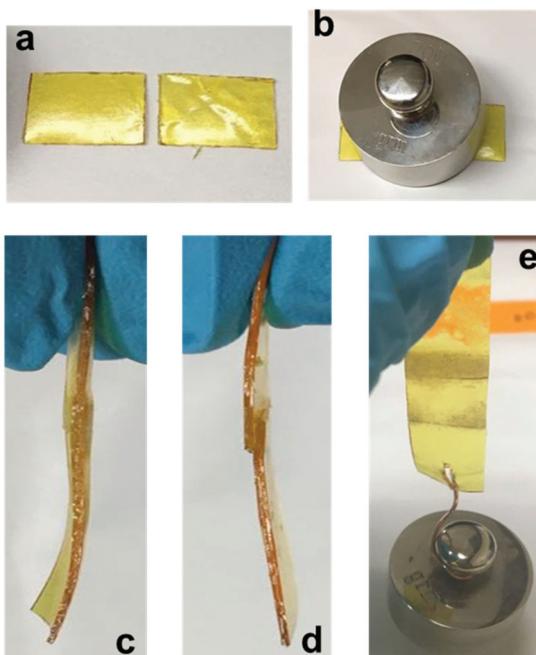
Fig. 2   Re-healing broken samples: (a) two broken pieces of polyimine 4N4; (b) the two broken pieces were pressed together with 200 g loading at room temperature; (c) the re-healed sample when pressed with a piece of moist paper towel on the top of the two overlapping pieces; (d) the re-healed sample when pressed in the absence of moist paper towel; (e) the sample shown in (c) holding 50 g weight.

In conclusion, we have demonstrated that the moisture-sensitivity of polyimines can be modulated by the incorporation of hydrophilic and hydrogen bonding amine moieties into their backbones. Simple variation of monomers among commercially available diamines can produce malleable polyimine networks with a wide range of thermal, mechanical, and moisture-induced properties, such as semicrystalline polymers with high strength and thermal stability, and tough elastomeric materials with low temperature malleability. Some of these polyimines are re-healable at ambient temperature using only water or even atmosphere moisture, which represents a highly green approach for materials processing and repair. With easy means of tuning the mechanical, thermal, and moisture-induced properties, polyimine vitrimers serve as a novel class of catalyst-free malleable thermosets with great potential to be adapted to a large number of potential applications.

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