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Photohealable ion gels based on the reversible dimerisation of anthracene†

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We report a photohealable ion gel based on the photodimerisation of anthracene as a dynamic covalent bond. A tetra-arm poly(ethylene glycol) terminally functionalised with anthracene was synthesised and combined with an ionic liquid to form an ion gel. The photodimerisation reaction was utilised to realise photohealing of the ion gels.

One of the unique functions of living systems is their responsiveness to the surrounding environment.[1] More specifically, living matter can change its shape and mechanical properties in response to external stimuli. Thus, inspired by living systems, synthetic stimuli-responsive soft materials that can respond to external stimuli such as temperature, light, pH, and chemicals have been intensively investigated in recent decades.[2–5] Such responsive materials have versatile applications including drug delivery systems,[6] injectable gels,[7] cell culturing materials,[8] artificial muscles,[9] and self-healing materials.[10,11] Among the various stimuli-responsive systems reported to date, light-responsive materials have attracted significant attention because of their beneficial properties, such as high spatial and time resolutions, contactless manipulation, and non-invasiveness.[12–14] In this context, light responsiveness can be imparted to soft materials by the introduction of photochromic molecules into their molecular frameworks. For example, azobenzene is a particularly well-known photochromic molecule that exhibits light-induced *cis–trans* isomerisation. The polarity and molecular shape of azobenzene are modulated through this *cis–trans* isomerisation, and so azobenzene-containing materials exhibit unique photoinduced structural transitions in both dry and wet systems.[15–17]

One obvious drawback of wet systems such as hydrogels is the solvent volatility, which renders their use challenging in an open atmosphere. However, ion gels, which are polymer networks swollen with ionic liquids (ILs), can overcome this defect due to the intrinsic nonvolatility of ILs. In this context, we recently developed a new class of photoresponsive ion gels by introducing azobenzene moieties into thermoresponsive block copolymers[18–20] and ionic liquids.[21] In these systems, the polarity change induced by the photoisomerisation of azobenzene modulates the interaction strength between the polymers and the ILs. Consequently, differences were observed in the sol–gel transition temperatures (T_{gel}) of block copolymers in ILs between the *cis* (*cis*-T_{gel}) and *trans* (*trans*-T_{gel}) forms of azobenzene. This difference could be exploited to achieve photohealing of the ion gel by a light-induced sol–gel transition of the damaged segment.[19] However, the nature of the physical cross-linking of the ion gel resulted in the gel failing to endure large strains, due to the chain pullout from the physical association.[22] In this regard, the photodimerisation reaction can introduce chemical cross-linking into molecular frameworks, which can then be reversibly dimerised and dissociated by light irradiation.[14,23,24] The dynamic covalent bonds formed by photodimerisation have been previously utilised for the photohealing of dry polymers[25,26] and hydrogels;[27] however, to date, the photohealing of ion gels through dimerisation reactions has yet to be reported.

Thus, we herein describe the first report into photohealable ion gels *via* the photodimerisation of anthracene (Fig. 1). In this system, anthracene undergoes a photo-induced reversible [4+4] cycloaddition reaction, since anthracene dimerises upon irradiation at wavelengths >350 nm, whereas the dimer is dissociated by heating or by irradiation at wavelengths <300 nm.[14] In this study, the end group of tetra-arm poly(ethylene glycol) (tetraPEG) was functionalized with anthracene through the reaction between isocyanate and hydroxyl groups.[28] In the initial step of this reaction, the amino group of 2-aminoanthracene was converted into an isocyanate group using triphosgene at ambient temperature (Scheme S1a, ESI†). In the second step, the hydroxyl-terminated tetraPEG (M_n = 40 kDa) was reacted with an excess of the anthracene isocyanate in the presence of a dibutyltin dilaurate catalyst to yield the anthracene-terminated tetraPEG (tetraPEG–Ant) (Scheme S1b, ESI†).

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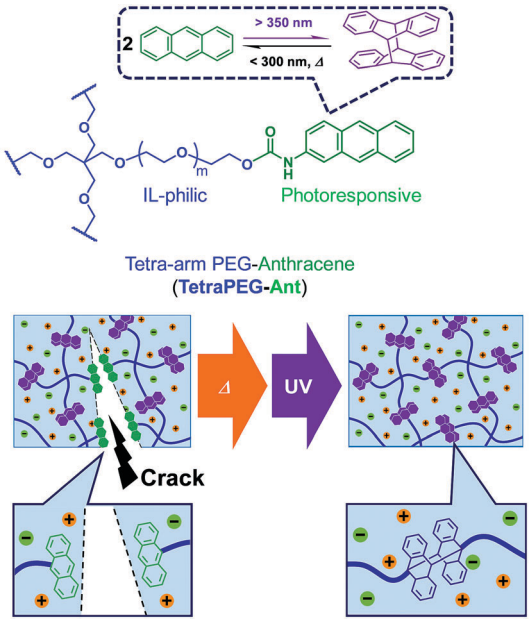

Fig. 1 The chemical structure of tetraPEG–Ant and a conceptual illustration of photohealing of the tetraPEG–Ant ion gel.

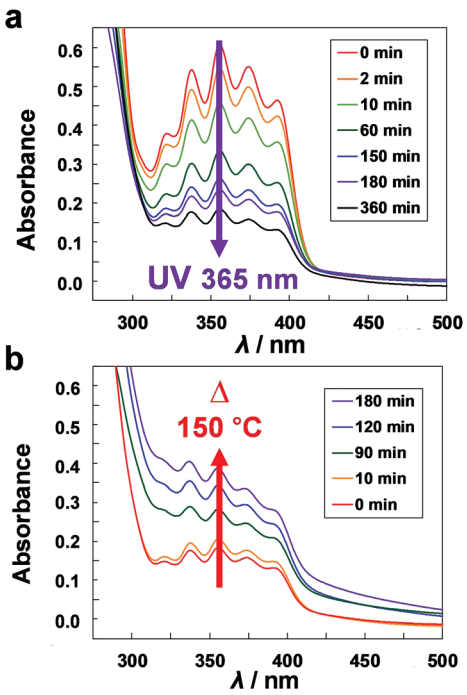

Fig. 2 Variation in the UV-vis spectra for a 1 wt% tetraPEG–Ant solution in $[C_2mim][NTf_2]$ with time (a) under UV light (λ = 365 nm) at room temperature, and (b) upon heating at 150 °C following UV irradiation.

The anthracene modification efficiency was then calculated by ^{1}H NMR, and the efficiency reached 99.5% (Fig. S1, ESI†). Almost the same gel permeation chromatography (GPC) traces of tetraPEG and tetraPEG–Ant indicate that no degradation of polymer chains and dimerisation reaction of anthracene occurred during the reaction (Fig. S2, ESI†).

Due to the good affinity of PEG toward various ILs, tetraPEG–Ant can form solutions in many common ILs. In this study, a well-known imidazolium-based IL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ($[C_2mim][NTf_2]$) was used as a hydrophobic solvent for tetraPEG–Ant. The photo/thermo-responsivities of tetraPEG–Ant in $[C_2mim][NTf_2]$ was investigated *via* UV-vis spectrophotometry. Thus, the UV-vis spectra for the 1 wt% solution of tetraPEG–Ant in $[C_2mim][NTf_2]$ upon UV irradiation at 365 nm are shown in Fig. 2a. As indicated, the absorption peaks at ~365 nm decreased gradually in intensity during UV irradiation, which indicates that in the IL, a [4+4] cycloaddition reaction of the anthracene moieties took place at the polymer terminal. We found that the dimerisation of anthracene was slower than in aqueous systems,[29] which could be attributed to the higher viscosities of ILs compared to water. Similar observations were also made for the [2+2] cycloaddition reaction of coumarin in an IL.[30] In addition, we note that the photodimer of anthracene can be thermally dissociated to regenerate the monomer form.[31] Upon heating at 150 °C, the absorption peaks increased in intensity over time, suggesting that the anthracene monomer was regenerated at the polymer terminal (Fig. 2b). However, a small increase in the spectral baseline was also observed during heating. As UV-vis spectra for pure $[C_2mim][NTf_2]$ under UV irradiation and upon heating did not show any significant change (Fig. S3, ESI†), it is suggested that some irreversible cleavage of anthracene or degradation of the PEG polymer chains took place at high temperatures. Fig. S4 (ESI†) shows changes in the degree of dimerisation calculated from the absorption peak at 365 nm under UV irradiation/heating cycles. Although the slight decrease in the degree of dimerisation in later cycles also implies the presence of irreversible reactions, a moderate reversibility was confirmed for the dimerisation/dissociation of anthracene in ILs.

At polymer concentrations above the chain overlap concentration, photo-induced gelation of tetraPEG–Ant in ILs is expected through the photodimerisation of anthracene at the polymer terminal, which acts as a chemical cross-linking point. Thus, Fig. S5 (ESI†) shows photographic images before and after UV irradiation of the tetraPEG–Ant solutions in $[C_2mim][NTf_2]$ at different polymer concentrations. Indeed, photoinduced gelation was confirmed at polymer concentrations >7 wt%. The required concentration for gelation was higher than those required for tetraPEG hydrogels and ion gels formed through A–B type cross-coupling reactions.[32,33] This could be accounted for by considering intramolecular dimerisation and the lower reaction rate of dimerisation (~60%). Nevertheless, the prepared tetraPEG–Ant formed mechanically stable ion gels at lower concentrations than previously reported photohealable ion gels that had been prepared through the physical association of triblock copolymers.[19] Subsequently, the rheological changes caused by the photodimerisation and thermal dissociation of the dimers during UV irradiation and heating were investigated by oscillatory shear measurements. Fig. 3 shows the variation in the storage (G') and loss (G'') moduli with time upon sequential cycles of UV irradiation and heating at 150 °C. Initially, a 10 wt% solution of tetraPEG–Ant in $[C_2mim][NTf_2]$ was irradiated by UV light at 365 nm, which resulted in sharp increases in G' and G''. In addition, the crossover of G' and G'',

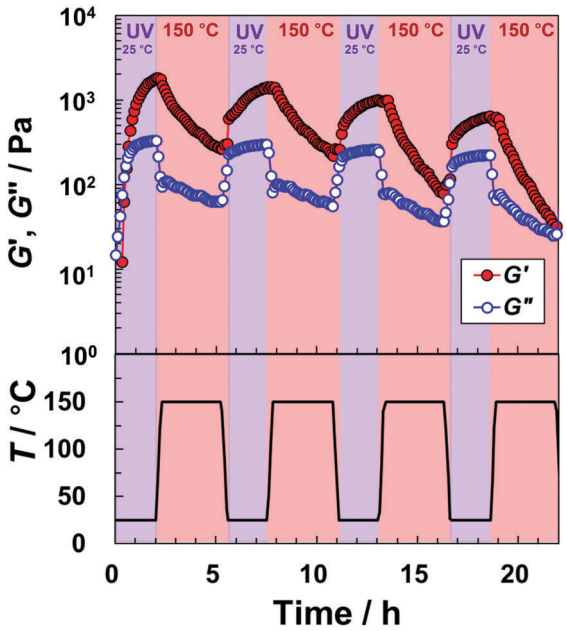

Fig. 3 Variation in G' and G'' for a 10 wt% solution of tetraPEG–Ant in [C_2mim][NTf_2] as a function of time under alternating UV irradiation at 365 nm (2 h) and heating at 150 °C (3 h) at a frequency = 1 Hz and strain amplitude = 1%.

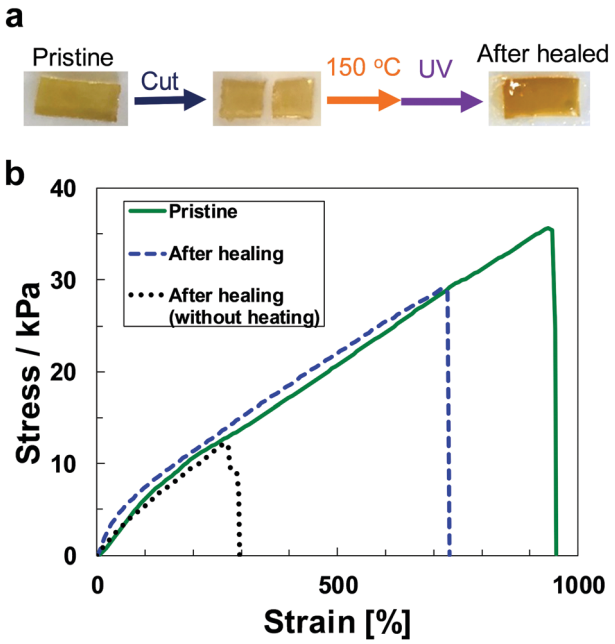

Fig. 4 (a) Photographic images of the pristine (left), cut (centre), and healed (right) 10 wt% tetraPEG–Ant ion gels. The cut ion gel pieces were re-contacted and healed by heating at 150 °C for 10 h and by UV irradiation overnight under an argon atmosphere. (b) Stress–strain curves for the pristine ion gel (green solid line), the healed ion gel by heating and UV irradiation (blue dashed line) and the healed ion gel only by UV irradiation (black dotted line).

which is indicative of the sol–gel transition, was observed within 1 h. After 2 h irradiation, G' was >2 kPa, which was comparable to that of our previously reported physically crosslinked photo-healable ion gel with a polymer concentration of 20 wt%,[19] indicating that a mechanically stable ion gel had been formed through photodimerisation of the terminal anthracene groups as chemical cross-linking points. After subsequent heating of the sample to 150 °C in the absence of light, G' and G'' gradually decreased over time. Thermogravimetric analysis (TGA) indicated that the ion gel was thermally stable at 150 °C for >10 h (Fig. S6, ESI†), and so the decreases in G' and G'' upon heating were likely due to a reduction in the number of chemical cross-linking points due to the dissociation of anthracene dimers at high temperatures. The observed variations in G' and G'' upon UV irradiation and heating were confirmed over four cycles; however, the gradual decrease in G' as the number of cycles increased was again indicative of the occurrence of irreversible reactions during cycling.

Finally, the photohealing ability of the tetraPEG–Ant ion gel was investigated. For this purpose, an ion gel sheet was prepared by irradiating the 10 wt% tetraPEG–Ant/[C_2mim][NTf_2] solution with UV light in a rectangular mould. The resulting tetraPEG–Ant ion gel sheet was then cut into two pieces using a sharp blade. As the mechanochemical cycloreversion of anthracene photodimers has been previously reported at crack surfaces through fluorescent sensing,[34,35] the weak bonds present in the anthracene photodimer were expected to be cleaved preferentially in the ion gel network. However, when the cut surfaces of the two ion gels were brought back into contact with one another and irradiated with UV light, healing of the cut segments was very incomplete. This implies that a sufficient amount of anthracene monomer is required to promote the bimolecular reaction of the chain end anthracene units at the surface. In addition, we note that thermal annealing at high temperatures has been previously employed to dissociate dimerised terminal anthracene moieties.[36,37] In this case, when the ion gel segments were brought into contact and thermally treated at 150 °C, healing of the cut surfaces was indeed observed by UV light irradiation (Fig. 4a).

The mechanical properties of the pristine and healed tetraPEG–Ant ion gel sheets were then investigated by tensile tests (Fig. 4b). As indicated, the pristine tetraPEG–Ant ion gel exhibited excellent stretchability, and the elongation at break reached 950%. Although the A–A type coupling reaction inevitably includes self-reaction, which does not contribute to the network elasticity, the high stretchability of the tetraPEG–Ant ion gel indicates that the terminal chemical cross-linking of branched polymer chains *via* photodimerisation can withstand significantly higher strains than ion gels formed by physical associations (*e.g.*, triblock copolymer-based gels).[19] We also found that the ion gel sheet healed by thermal treatment and UV irradiation could be elongated over 700%, thereby indicating that it recovered good mechanical strength. Upon comparison of the fracture energies of the pristine and healed ion gels, the healing efficiency was calculated to be 66%. This implies that a sufficient quantity of anthracene photodimers acting as chemical cross-linking points were reformed through the photohealing process. Furthermore, the stress–strain curve shapes were similar for the pristine and healed ion gels, suggesting that the bulk polymer network was not altered significantly by heating or UV irradiation. On the other hand,

healing efficiency of the ion gel only by UV irradiation without heating was very poor, 11%.

In summary, we demonstrated for the first time the photohealing of ion gels through the photodimerisation of anthracene as dynamic covalent bonds. More specifically, anthracene-terminated tetra-arm PEG (tetraPEG–Ant) was synthesised by modification of the terminal hydroxy groups of tetraPEG using anthracene isocyanate. The desired ion gels were successfully prepared by UV light irradiation of the tetraPEG–Ant solutions in ILs due to the formation of anthracene photodimers as chemical cross-linking points. In addition, repeated increases and decreases in the G' and G'' values of the ion gel were observed upon heating and UV irradiation cycling, thereby indicating that the anthracene photodimer can be quasi-reversibly cleaved and reformed. Indeed, a cut ion gel sheet was successfully healed with a good healing efficiency through sequential heating and UV irradiation. The reversibility of the dimerisation/dissociation cycles of anthracene was, however, not sufficient, and so further improvements are desirable to improve the healing efficiencies of ion gels based on photodimerisation chemistry. We expect that these results will be of importance in terms of the application of such nonvolatile soft materials in flexible sensors, actuators, and coatings.

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Conflicts of interest

There are no conflicts to declare.

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