Synthesis of Thermally Degradable Epoxy Adhesives

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ABSTRACT: We have developed a new strategy for the synthesis of epoxide-containing polymers where the pendant reactive groups are connected to the main backbone via thermally labile oxonorbornene groups. The polymers were synthesized by radical 1,4-polymerization of the appropriate bicyclic diene monomer. The produced polymers can be crosslinked in the presence of a diamine and de-crosslinked by thermal treatment at 160 °C, which induces retro-Diels–Alder reaction and cleaves pendant groups from the polymer backbone, as confirmed by differential scanning calorimetry. The potential for the utiliza-

tion of this polymer as a thermally removable adhesive was demonstrated by a simple adhesion test. This method provides access to thermally cleavable epoxy networks that can be quickly and irreversibly disintegrated into nonvolatile components upon heating to a specified temperature. © 2013 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2013**, *51*, 4992–4997

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INTRODUCTION Epoxy-based materials possess a combination of many desirable characteristics, such as excellent chemical resistance, electrical insulating properties, superb adhesion and heat resistance, as well as good mechanical properties.^{1,2} As a result, they have found widespread use in a range of applications, including paints and coatings, electrical insulators, fiber-reinforced composites, and structural adhesives. Formulations typically consist of monomers or a short chain prepolymer "resins" containing epoxide groups and a polyamine "hardener." Chemical reaction between amines and epoxide groups leads to the formation of a covalently crosslinked network. The process of curing can be controlled by temperature, choice of resin and hardener compounds, reaction stoichiometry, and the addition of a catalyst. The range of commercially available structural and compositional variants allow for the preparation of cured polymers with controlled mechanical properties, thermal conductivity, and adhesive properties. In general, epoxy adhesives are able to maintain their desirable properties at temperatures up to 300 °C depending on the chemical nature of the epoxy and polyamine components.

Upon curing, epoxy resins form insoluble and infusible crosslinked networks, which are very difficult or impossible to thoroughly remove postapplication without damaging the underlying substrate. Incorporating thermally or chemically degradable linkages into the epoxy resin structure has been a promising approach to circumvent this problem. Such linkages allow for the degradation of the crosslinked polymer network and removal of the adhesive once it has served its function. Continuous efforts to design such materials have resulted in epoxy formulations containing carbamate,³ carbonate,⁴ acetal,⁵ disulfide,^{6–8} and ester⁹ linkages. The breakdown of thermally labile linkages usually requires high temperatures (>200 °C),^{3,4,9} which limits their applications.

Retro-Diels-Alder (retro-DA) reaction is a cycloreversion process, which has also been used for the disintegration of epoxy resins¹⁰⁻¹² and other crosslinked networks.¹³⁻¹⁷ A ubiquitous example of such linkages is based on a reversible maleimide furan coupling¹⁸⁻²⁰ (Scheme 1). For example, Liu et al. reported self-healing polyamide networks using the reversibility of Diels-Alder reaction between polymers bearing maleimide side groups and a furan-containing crosslinking agent.¹⁵ The observed weight loss at 150 °C was attributed to the degradation of crosslinked polymers and volatility of the crosslinking agent. Gandini et al. developed a silicone polymer bearing furan side groups, which can also be crosslinked utilizing Diels-Alder reaction with maleimide at room temperature.^{$\tilde{21}$} The de-crosslinking occurred at 80 °C and the silicone soft segments were preserved during the crosslinking and de-crosslinking processes.

Thermal reversibility of the linkages is certainly appealing for the preparation of recyclable and self-healing

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SCHEME 1 Reversible and irreversible retro-Diels–Alder chemistry.

networks,^{14,16} but it may not be suitable for applications requiring temporary adhesion and removal of the crosslinked materials. The reversible character often results from a Diels–Alder reaction between maleimide and furan groups at low temperatures, and the activation of cycloreversion reaction at high temperatures. The former process is driven by a high reactivity of maleimide as a dienophile, while the latter process is due to a weak aromatic character of furan. By appropriately designing the chemical structure of the Diels–Alder adduct to contain fragments of furan and a poor dienophile (nonactivated olefin), one can produce irreversible cleavage and degradation of polymer networks (Scheme 1).

We have previously reported that polymerization of 2,3dimethylene-7-oxanorbornane produced polymers containing oxanorbornene fragments in the backbone.²² Upon heating to 150 °C, the polymer undergoes cycloreversion to furan containing polymer and ethylene gas. In this contribution, we take advantage of this structural motif for the preparation of thermally removable epoxy adhesives (Scheme 2). The main component in this adhesive is a polyepoxy compound where epoxide groups are linked to the polymer backbone via thermally labile groups. Thermal treatment of the crosslinked network induces retro-DA reaction and cleaves the linkages, which do not reform when the sample is cooled down to room temperature. One of the advantages of using this method is that there are no volatile side products produced during cleavage, which makes the process more ecofriendly and practically useful. Additionally, by incorporating silicon-based linkages into these materials, we have taken advantage of excellent low temperature and optical properties of silicon materials, which extends the range of physical properties of conventional epoxy resin systems enabling their applications in some challenging environments, such as aerospace nanocomposites and optical component mounting.

EXPERIMENTAL

Materials

(3-Glycidoxypropyl)tetramethyldisiloxane was purchased from Gelest, Jeffamine D-400 from Huntsman, while all other chemicals were obtained from Sigma-Aldrich or Acros Organic and used without further purification unless stated otherwise. Dichloromethane was purified by a commercial solvent purification system (Innovative). Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from methanol. *cis*-2,3-Bis(4-methylbenzensulfonate)bicyclo-[2.2.1]hept-5-ene-2,3-dimethanol was synthesized according to literature procedures.²³

Monomer Synthesis

Karstedt's catalyst (0.381 g, 1 mmol) was added to *cis*-2,3bis(4-methylbenzensulfonate)bicyclo-[2.2.1]hept-5-ene-2,3dimethanol (5.15 g, 10 mmol) and (3-glycidoxypropyl)tetramethyldisiloxane (1.94 g, 10 mmol) in 20 mL dichloromethane. The mixture was stirred for 3 days and dichloromethane was evaporated. The obtained oil was used without purification and dissolved in 20 mL DMSO. Potassium *tert*-butoxide (4.48 g, 40 mmol) was added and stirred for overnight. Water was added to the mixture and the product was extracted with pentane. After drying with Na_2SO_4 , pentane was evaporated and the residue was purified by column chromatography using hexanes/ethyl acetate (20:3) as a mobile phase. The product (**1**) was obtained as a colorless liquid (3.2 g, 86% yield).

 $R_{\rm f} = 0.43.$ ¹H NMR (CDCl₃): δ 5.23(s, 1H), 5.09 (s, 1H), 4.97 (s, 1H), 4.84 (s, 2H), 4.75 (s, 1H), 3.74 (m, 1H), 3.40–3.50 (m, 3H), 3.18 (m, 1H), 2.82 (m, 1H), 2.64 (m, 1H), 1.76 (m, 2H), 1.62 (m, 2H), 1.06 (m, 1H), 0.56 (m, 2H), 0.02–0.21 (m, 12H). ¹³C NMR (CDCl₃): δ 150.54, 148.57, 100.93, 98.05, 81.51, 81.38, 74.29, 71.43, 50.87, 44.34, 31.34, 31.38, 30.86, 23.43, 14.15, 1.23, 1.01, 0.25.

Synthesis of Prepolymer 3

A mixture of AIBN (10 mg, 0.061 mmol), *n*-butanthiol (40 mg, 0.444 mmol), and **1** (300 mg, 0.815 mmol) was heated to 65 °C for 72 h. GPC (light scattering): $M_n = 1.6$ kg/mol, $M_w/M_n = 1.60$.



SCHEME 2 Synthesis and thermal decomposition of the new epoxy adhesive. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



SCHEME 3 Direct incorporation of a thermally labile group into the polymer backbone. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Specimen Preparation and Adhesion Test

Before application of adhesive materials, the adhered surfaces were prepared by cleaning the aluminum plate surfaces with methyl ethyl ketone followed by abrading with silicon carbide paper (76-mm grain size). After surface treatment, aluminum pieces (100 \times 25 \times 1.4 mm) were assembled into single lap shear joints with 12.5 mm of overlap length. The applied contact pressure was maintained by a 2 lb plate, which allowed obtaining probes with the same uniform adhesive thickness.

Measurements

GPC analysis was carried out on Viscotek's GPCMax with two PolyPore columns (Polymer Laboratories, Varian) and TDA302 Tetradetector Array system, which contained refractive index, UV, viscosity, low (7°), and right angle light scattering detector modules. Tetrahydrofuran was used as a mobile phase at 30 °C. The system was calibrated with 10 polystyrene standards from 1.2×10^6 to 500 g/mol. NMR measurements were performed on a Varian Inova-500 (500 MHz) spectrometer by using CDCl₃ as a solvent. Thermal gravimetric analysis was performed on a Perkin Elmer TGA7 under nitrogen flow at 10 °C/min heating rate. Differential scanning calorimetry (DSC) was conducted on a TA Instruments Q200 system with an RCS-90 cooling device.

RESULTS AND DISCUSSION

Synthetic Strategy

The synthetic strategy is based on a unique prepolymer where reactive epoxide groups are linked to the backbone via thermally labile oxanorbornene linkages. Owing to the requirement of having a nonactivated olefin fragment as a part of the oxanorbornene unit, such structures cannot be prepared by a direct Diels-Alder reaction. Therefore, we utilized radical 1,4-addition polymerization of a bicyclic diene^{22,24} to install oxanorbornene units in the polymer backbone in situ (Scheme 3). The polymerization was conducted in the presence of a chain transfer agent to produce low molecular weight oligomers to be used as an epoxy prepolymer with a low glass transition temperature ($T_g = -40$ °C). Crosslinking can be achieved by mixing the prepolymer with a polyamine at 80 °C. The formed network can be disintegrated by heating to 160 °C to initiate the retro Diels-Alder process. The network degradation process does not release volatile compounds, and the products of degradation are not reactive enough at room temperature to reform the network, thus allowing convenient dismounting and removal of the adhesive.

Monomer Synthesis

Based on the concept shown in Scheme 3, we targeted the synthesis of a monomer containing a polymerizable diene group and epoxide pendant units linked together via the oxanorbornane skeleton. The monomer was synthesized in a sequence of five steps, as shown in Scheme 4. Diels-Alder reaction between furan and maleic anhydride produced the bicylic skeleton in high yield. The anhydride group was then converted to a diol by LiAlH₄ mediated reduction, and subsequently esterified by reacting with *p*-toluenesulfonyl chloride produce cis-2,3-bis(4-methylbenzensulfonate)bicycloto [2.2.1]hept-5-ene-2,3-dimethanol. Hydrosilation of the double bond was then carried out to introduce epoxy groups using a commercially available silane and Karstedt catalyst in high yield. The diene monomer 1 was obtained by elimination of p-toluenesulfonic acid in the presence of potassium t-butoxide. It should be noted that the obtained monomer was a mixture of endo- and exo- isomers.

Prepolymer Synthesis

Monomer 1 can be polymerized under free radical polymerization conditions, and high molecular weight (\sim 30 kg/mol) polymers can be obtained by using AIBN as the initiator. But for the application as an adhesive, short oligomers are preferred due to their moderate viscosities and relatively high reactivities. Thus, we conducted prepolymer synthesis by radical polymerization of monomer 1 in the presence of nbutanethiol as a radical chain transfer agent (Scheme 5). The obtained oligomer **2** had $M_{\rm p} = 1600$ g/mol (GPC with polystyrene standards), corresponding to an average of 4.5 epoxide groups per chain. From ¹H NMR analysis, comparing peak areas under signals "n" and "t" in Figure 1 the average number of epoxide groups per chain can be estimated to be 3.5. The dispersity index of 1.6 obtained from GPC suggests that there is a relatively broad distribution of chain lengths, as expected. However, for the purposes of this work, any polymer chain with at least two epoxide groups will



SCHEME 4 Synthesis of the epoxy-containing bicyclic diene monomer.



SCHEME 5 Covalent attachment and thermally activated detachment of substituents.

contribute to crosslinking. As we reported previously, the polymerization of similar bicyclic dienes proceeds predominantly through 1,4-addition, which is necessary in this case for the formation of oxanorbornene linkages.^{22,24} The comparison of ¹H NMR spectra of the monomer and the produced oligomer [Fig. 1(a,b)] confirmed the disappearance of olefinic proton signals at 4.8–5.3 ppm. The remaining resonances in the 4.6–5.0 ppm region of the oligomer spectrum can be attributed to the bridgehead protons (complicated by contributions from 1,4- and 4,1-additions) and to the remaining olefinic protons as a result of 1,2-addition (~20%).

Prepolymer Reactivity

The reactivity of the prepared oligomers was first evaluated by utilizing *n*-hexylamine as a model compound (Scheme 5). Even though each primary amine can potentially react with two epoxide groups, the second reaction is much slower than the first. Therefore, by using equimolar amounts of the amine and the epoxide groups in the polymer, we targeted the preparation of soluble oligomers suitable for NMR analysis (Fig. 1). First, neat n-hexylamine was allowed to react with oligomer **2** at 80 $^{\circ}$ C, which resulted in the quantitative ring opening of the epoxide groups. After the reaction, characteristic epoxide proton signals at 3.15, 2.85, and 2.65 ppm completely disappeared from the ¹H NMR spectrum [Fig. 1(c)], while new resonances were observed at 3.50 and 2.60 ppm, corresponding to the methylene and methine protons of the ring-opened epoxide groups, and at 1.40 and 1.00 ppm, corresponding to the *n*-hexyl protons of the amine. The regiochemistry of the amine addition could not be distinguished from the NMR spectrum. Subsequently, the aminefunctionalized polymer was thermally treated at 160 °C to induce retro-Diels-Alder reaction of the oxanorbornene groups in the polymer backbone. In the ¹H NMR spectrum of the thermally treated polymer [Fig. 1(d)], we observed new vinyl group signals at 5.70-6.20 ppm and furan proton resonances at 7.15 ppm, formed as a result of cycloreversion. These studies have confirmed that the prepolymer 2 can be used for attachment of substituents via the epoxide group and thermal detachment of the substituents via retro-Diels-Alder reaction.

Polymer Network

We next explored the formation of thermally cleavable networks by using prepolymer **2** as an epoxy "resin" and a polydiamine (Jeffamine D-400, $T_{\rm g} < -75$ °C) as a "hardener." As there are multiple reactive epoxide groups on each prepolymer chain and potentially four reactive sites on Jeffamine D-



FIGURE 1 ¹H NMR spectra of (A) monomer **1**, (B) prepolymer **2**, (C) amine-functionalized prepolymer **3**, and (D) thermally treated prepolymer **4**.

400, the reaction between the two should produce a crosslinked network. Both components have low glass transition temperatures and therefore flow easily at ambient conditions. The reaction between the two components at 80 °C overnight produces an insoluble material. Upon heating to 160 °C, the network disintegrates to produce mostly soluble by-products. Thermogravimetric analysis of the crosslinked network confirmed that there were no volatile by-products forming at 160 °C, as evidenced by no weight loss observed at temperatures as high as 200 °C. The degradation of the polymer network could also be observed by DSC (Fig. 2). In the first heating scan, the polymer network exhibited a glass transition temperature of -40 °C followed up by an endothermic peak at 160 $^{\circ}$ C. The latter was attributed to the retro-DA reaction, which proceeds with the release of ring strain and the formation of aromatic furan moieties. The sample was then cooled down and reheated to evaluate the reversibility of the DA reaction. In the second heating scan, glass transition temperature observed for the thermally cleaved polymer decreased by about 10 °C, consistent with increased segmental mobility in the cleaved sample. Concurrently, there was no evidence of other thermal transitions, indicating that the cycloreversion process was complete and irreversible. Importantly, since there was no weight loss observed by TGA upon heating to 200 °C, we conclude that the network disintegrates into smaller nonvolatile oligomeric fragments. As a control experiment, we analyzed a commercial epoxy glue without any degradable linkages. In this case, DSC only showed a glass transition temperature of 90 °C and the sample was thermally stable up to 200 °C. These results further indicate that the endothermic transition at 160 °C observed in our sample is a result of a retro-DA reaction that leads to network degradation.

The formation and degradation of the polymer network was further evaluated in a form of adhesive holding two aluminum plates together. The plates were treated with a mixture of oligomer **2** and Jeffamine D-400, and held together at 80 °C to promote adhesion. Upon curing, the adhesion between the two plates was strong enough to support up to 2 kg weight (Fig. 3). After thermal treatment at 160 °C for 5 s, the two pieces were easily separated without any force and the surface can be easily cleaned with acetone. For comparison, we tried the same experiment using commercial epoxy glue. In this case, there is



FIGURE 2 DSC (A) and TGA (B) analysis of the crosslinked network.



FIGURE 3 Adhesion demonstration: pieces held together by a cured mixture of oligomer **2** and diamine (left, middle), and adhesion failure after thermal treatment at 160 °C for 5 s (right). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

almost no difference in terms of adhesion before and after thermal treatment. The pieces cannot be easily separated and the surface cannot be cleaned without scratching. Further experiments evaluating adhesion strength and rheological properties of these degradable polymeric networks are underway.

CONCLUSIONS

A new bicyclic diene with an epoxide group substituent has been synthesized and polymerized by free radical polymerizations with *n*-butylthiol as a radical transfer agent. Pendant epoxide groups can be used for the attachment of functional groups to the polymer, while bicyclic groups in the backbone allow thermal detachment of substituents. The obtained oligomers were crosslinked with a diamine to produce polymeric networks where chains are connected through thermally labile oxonorbornene linkages. Heating the sample to a specified temperature promotes retro-DA reaction with concurrent network degradation. The thermally labile linkages were specifically designed to irreversibly disintegrate at temperatures below 200 °C, where no formation of other volatile products is observed. Preliminary testing showed that such materials can be used as thermally removable adhesives. We are exploring applications of such adhesives in temporary component mounting and protective coatings.

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