Synthesis and Characterization of a Single-Component Thermally Remendable Polymer Network: Staudinger and Stille Revisited

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ABSTRACT: Two new single-component, highly cross-linked polymeric materials have been developed that are capable of undergoing repeated cycles of mending. On the basis of the thermally reversible Diels−Alder (r-DA) cycloaddition reaction, these materials are comprised of a dicyclopentadiene core which acts as both diene and dienophile in the r-DA reaction. Polymer specimens have been prepared from two monomeric units, monomers 400 and 401, and the thermal and mechanical properties of these materials have been studied via differential scanning calorimetry, dynamic mechanical analysis, and three-point bending, compression, and fracture tests. After fracture, these hard, colorless, transparent materials are capable of thermal mending at 120 °C, effectively healing cracks formed in the specimen.

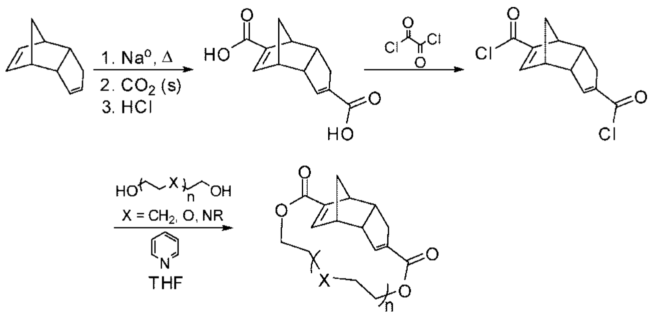
Introduction

In the field of structural materials, highly cross-linked polymeric solids are desirable due to their superior mechanical strength, durability, and solvent resistance.[1,2] In addition to these attributes, however, there also exist drawbacks: these materials experience a loss of recyclability and are usually brittle and rigid. Upon exposure to constant external stress, these systems experience thermal and mechanical fatigue that result in the formation of microcracks. When left untreated, these cracks propagate and enlarge through the sample, resulting in catastrophic failure.[3,4]

There is a requirement, therefore, to address the problem of microcrack formation and propagation before total failure of the system occurs. This has led to the recent development of remendable and self-healing polymer systems. Unique solutions to this problem have been described, including the incorporation of both a healing agent and catalyst into the polymer matrix[5−8] as well as the utilization of the thermally reversible Diels−Alder (r-DA) cycloaddition reaction and of the photoreversible [2 + 2] cycloaddition reaction.[9−13] More recent publications have illustrated the employment of reversible noncovalent interactions, such as hydrogen bonding and metal−ligand coordination, to achieve healing.[14,15]

Each of these approaches offers the potential to extend the lifetime and reliability of highly cross-linked polymers. To date, all of the systems described incorporate more than one component to achieve mending. The addition of multiple components to a monolith brings about a host of potential issues: homogeneous dispersion of components in the sample, uniformity of mechanical strength before and after healing, and phase segregation of the different elements, all of which require a more complicated synthetic procedure. In addition, regarding systems that incorporate microencapsulated healing agents, once the healing agent is released and employed, it is not possible to reheal in the event of additional crack formation.

Scheme 1. General Dicyclopentadiene-Based Monomer Synthesis



To allow for repeat mending cycles, it is advantageous to employ materials that incorporate the re-formation of chemical bonds, such as the r-DA reaction. The energy required to break the DA adducts is much lower than the energy required to break the remaining covalent bonds in the molecule. This allows for rebonding of the intermonomer linkages after crack formation.[10] In this work, we present a novel single-component system that utilizes the r-DA reaction to achieve multiple cycles of mending, thus eliminating problems associated with multicomponent systems. These materials are hard, colorless, and transparent at room temperature and can be custom-tailored to fit a range of desired working temperatures.

The polymerization/cross-linking reported here is based on a combination of discoveries dating back to the "father of polymer science", Hermann Staudinger, and one of the exponents of polymer synthesis in the United States, John Stille. In 1926, Staudinger described a poly(cyclopentadiene) that results from the dienophilicity of the norbornene double bond of dicyclopentadiene.[16] Years later, in 1961, Stille reported on the polymerization of bis(cyclopentadiene)alkanes.[17] Stille and Plummer were puzzled by the inexplicable loss of solubility of their polymers on standing. They assumed that it was due to oxidative cross-linking and tried, without success, to inhibit the process. It apparently did not occur to these authors that the norbornene double bond of their polymers could act as a cross-linking site, a factor that served as inspiration for the present work. In the end, in the results described within, cross-linking

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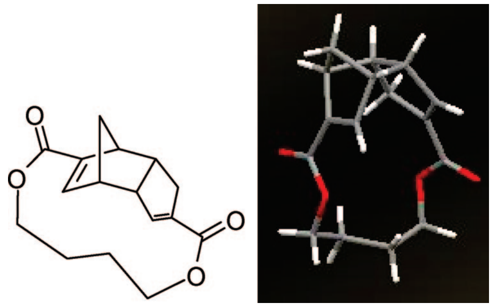
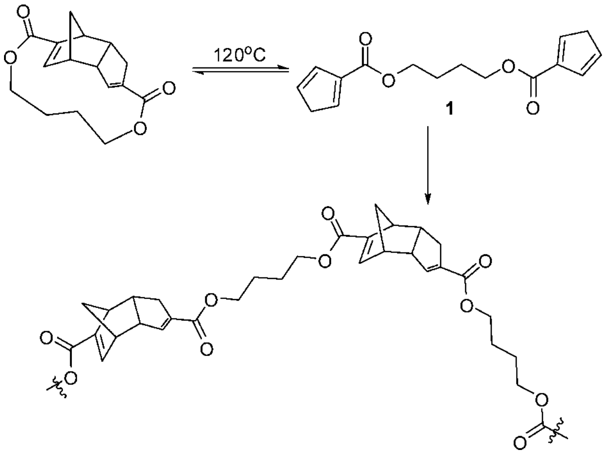


Figure 1. Monomer 400 representation and molecular unit of the X-ray crystal structure.

Scheme 2. Polymer Formation from Monomer 400



occurred through the dienophilic electron-poor cyclopentene (conjugated with the ester) double bond.

Results and Discussion

Monomer Synthesis. Building on the implementation of our previous Diels–Alder-based thermally remendable polymer materials, a new system was developed that incorporates a single compound, cyclopentadiene, as both diene and dienophile. Using inexpensive, readily available dicyclopentadiene as the core functional unit, a wide variety of monomers can be developed with the fabrication of a single-component remendable polymer material in mind. Synthesized from the reaction of dicyclopentadiene dicarboxylic acid (Thiele's acid) with oxalyl chloride, followed by subsequent bislactonization with a variable diol unit, the mechanical properties of the resulting polymeric materials can be adjusted to suit specific applications (Scheme 1).

The naming system implemented for these monomers denotes the number of carbon, nitrogen, and oxygen atoms present in the diol unit incorporated in the last step of monomer formation. For example, the original monomer to be developed was synthesized with 1,4-butanediol; this diol contains four carbon atoms, and no nitrogen or oxygen atoms, and was therefore given the name monomer 400 (Figure 1).

The basis for the remendability of this "premonomer" lies in the thermally reversible Diels–Alder cycloaddition. Upon heating to 120 °C, the dicyclopentadiene moiety undergoes the retro-DA reaction to expose two reactive cyclopentadienes. Note that this approach to α,ω-bis(cyclopentadiene) monomers (**1**, Scheme 2) is considerably more efficient than alkylation of cyclopentadienide.[18,19] These units form a DA adduct with other nearby molecules, thus creating the polymer backbone (Scheme 2).

In addition to forming the poly-DA dimer adduct, it is also possible for the backbone dicyclopentadiene units to undergo a second DA reaction with another exposed cyclopentadiene group, leading to trimer formation. This trimer allows for covalent cross-linking of the polymer chains, leading to formation of a network (Figure 2).

The DA dimer adduct contains two distinct C=C bonds that could act as dienophile in the cross-linking reaction: the norbornene bond and the cyclopentene bond. While it is the more reactive norbornene double bond that acts as dienophile for the formation of the unsubstituted cyclopentadiene trimer,[20] we have found that it is the less hindered cyclopentene double bond that acts as dienophile in the formation of the carboxy-substituted trimer (Figure 3).

Polymerization. In order to make a polymer specimen, the crystalline monomer was ground to a fine powder and transferred to either a Teflon mold or a glass vial for bar or cylindrical specimens, respectively. The samples were then heated to 150 °C under vacuum to remove any bubbles that evolved upon melting of the monomer. The samples were heated for ≈10 h, followed by slow cooling to room temperature. Rapid cooling of the samples to room temperature resulted in crack formation; subsequent heating to 150 °C, followed by slow cooling to room temperature, resulted in a healed specimen.

Because of the low solubility of monomer 400, a new monomer (monomer 401) was designed. In the bislactonization step of the synthesis, diethylene glycol was used instead of 1,4-butanediol, yielding a compound with four carbon atoms, no nitrogen atoms, and one oxygen atom in the diol unit (Figure 4). The motivation behind the synthesis of the new monomer was to form a tougher material that would also be easier to process. This was to be accomplished by extending the length of the tethering chain with an ether linkage, while at the same time increasing the rotational freedom through the insertion of an oxygen atom in lieu of a bulkier methylene group. Polymer specimens were fabricated from this new monomer following the same procedure previously described, with the exception of using a cure temperature of 120 °C.

Polymer Characterization. Differential scanning calorimetry (DSC) was performed on monomers 400 and 401, with melting endotherms at 124.5 and 109 °C, respectively. In addition, monomer 400 showed an exotherm at 129.4 °C that can be attributed to polymerization. Polymer specimens of both 400 and 401 were then fabricated for use in three-point flexural tests and compression tests. Dynamic mechanical analysis was performed for each polymer, yielding the storage modulus, loss modulus, and tan δ (Figures 5 and 6). The glass transition temperatures (T_g) were determined from the peaks of the loss modulus curves, according to ASTM D4065.[22] The values of T_g were 138 and 89 °C for polymers 400 and 401, respectively.

Compression tests were performed on both polymer specimens, with the results given in Table 1. The results of consecutive cycles of compression and healing of a polymer 400 specimen are shown in Figure 7, illustrating that the compression modulus does not change after repeated healing. The average calculated compression modulus values were 1.51 and 1.78 GPa for polymers 400 and 401, respectively; the average calculated compressive strength was 95.8 and 98.0 MPa for polymers 400 and 401, respectively. These results indicate, contrary to expectation, that polymer 400 is not as stiff or as strong as polymer 401 (modulus 400 ca. 1.51 GPa, modulus 401 ca. 1.78 GPa; also see Figure 9). Neither of these materials, however, is quite as strong as the furan–maleimide DA polymer previously reported by our group, which had a compression modulus of 3.1 GPa and a compressive strength of 121 MPa.[9]

In addition to the ability of these materials to maintain their initial compression modulus after multiple cycles of testing, the compressed samples that underwent a healing treatment also showed remarkable shape recovery. After undergoing the

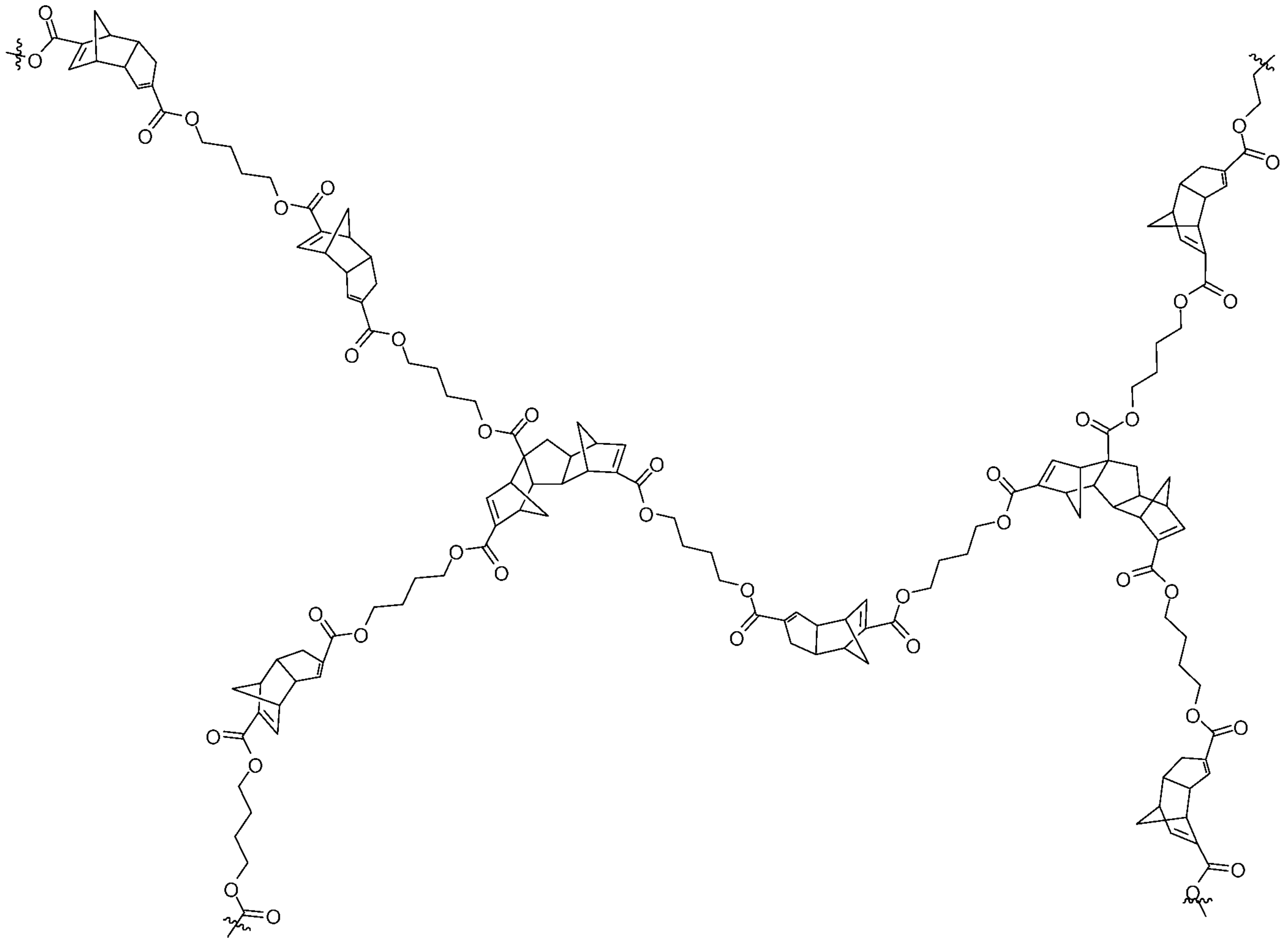


Figure 2. Schematic representation of a segment of polymer network demonstrating cross-linking ability via trimer formation.

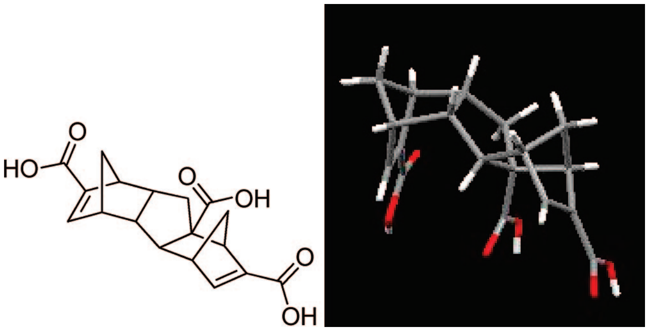


Figure 3. Thiele's acid trimer representation and molecular unit of the X-ray crystal structure.[21]

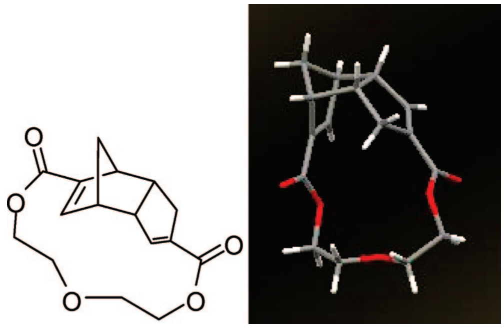


Figure 4. Monomer 401 representation and molecular unit of the X-ray crystal structure.

compression test, a polymer 400 specimen was visibly deformed (Figure 8a.) This specimen was then subjected to healing treatment of 120 °C for 12 h in an argon atmosphere, resulting in full shape recovery to initial specimen dimensions (Figure 8b).

Three-point bending tests were conducted on the polymer specimens, with the results given in Table 2 and shown in Figure 9. The data show that polymer 401 is stronger, stiffer, and more brittle than polymer 400. Polymer 401 shows a steep linear curve before fracture, with a calculated elastic modulus E of 3.26 GPa and a maximum deflection of 7 mm. In contrast, polymer 400 shows a lower modulus ($E = 2.63$ GPa), and the elastic stage is followed by a region of extensive plastic deformation before fracture. Though not as strong as polymer 401, polymer 400 is tougher and more ductile.

Fracture tests were performed on polymer 400 and 401 specimens, followed by subsequent healing treatments of 120 °C for 20 h in an argon atmosphere and then repeated testing. The results from these experiments are given in Table 3, including the fracture strength for each cycle as well as the recovered strength between healing cycles. The recovered strength between cycles for polymer 400 ranges from 40 to 60%, with an average recovered strength of 46%. Polymer 401, however, showed a much lower average recovered strength of 23%. The data from one of the polymer 400 samples are shown in detail in Figure 10, illustrating the consistency of strength recovered between healing and testing cycles.

A typical example of the results of the healing treatment on a fractured polymer specimen is shown in Figures 11 and 12. The healed specimen shows a faint scar that can easily be

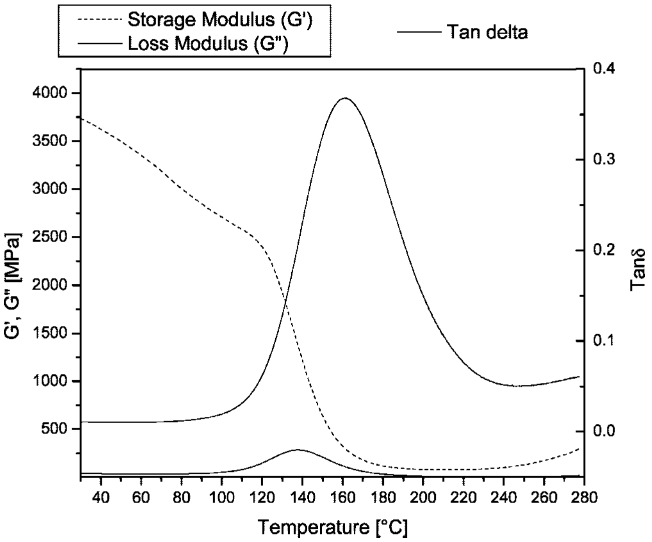


Figure 5. Dynamic mechanical analysis of polymer 400.

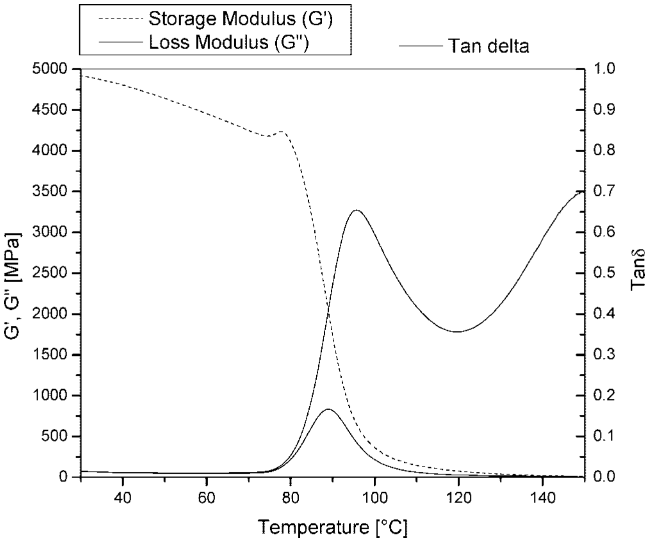


Figure 6. Dynamic mechanical analysis of polymer 401.

Table 1. Compression Data for Polymers 400 and 401

	sample	compression modulus [MPa]	compression strength [MPa]
polymer 400	cycle 1 (virgin sample)	1560 ± 218	85 ± 25
	cycle 2 (after healing)	1570 ± 211	95 ± 18
	cycle 3 (after healing)	1412 ± 214	107 ± 19
polymer 401	cycle 1 (virgin sample)	1759 ± 126	99 ± 10
	cycle 2 (after healing)	1802 ± 267	97 ± 5

removed by polishing the surface of the sample (Figures 12b,c). We believe the scar is due to a phenomenon akin to surface tension based on SEM examination of the bulk after healing, which indicates near-perfect bond formation (disappearance of the crack without the presence of a "ghost" scar).

Though polymer 401 was designed to be tougher and stronger than polymer 400 due to the additional oxygen in the tether, it turned out to be *more brittle* and hence more difficult to remend. One possible explanation for this observation is that the degree of cross-linking in this case is higher because in the early stages of the polymerization/cross-linking the growing macromolecules have more degrees of freedom due to the more flexible linker and hence higher probability for cross-linking.

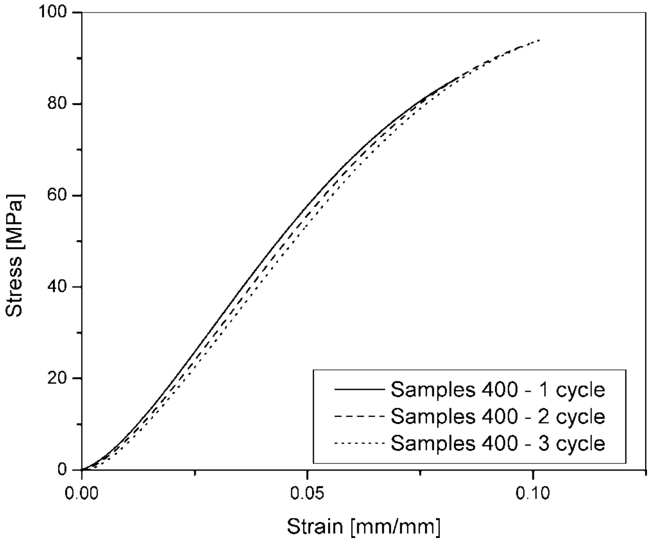


Figure 7. Compression data for polymer 400 after consecutive cycles of compression and healing.

Conclusion

A new single-component remendable polymer system has been developed which utilizes the dicyclopentadiene moiety as both diene and dieneophile in the thermally reversible Diels–Alder cycloaddition reaction. Indeed, the Staudinger cross-linking of the dienophilic DA dimer adduct double bond of the growing polymer chains is key to the strength of the materials. It appears to have caused polymer 401 to be more brittle than its more rigid analogue, polymer 400.

Further mechanical analysis of these materials is currently underway as well as the synthesis and fabrication of new monomers and polymers. In addition, we are investigating alternative postdamage repair strategies for these materials and their composites. This new system holds promise for the creation of highly cross-linked materials with tunable mechanical properties that are capable of undergoing repeated cycles of mending, thus increasing their functional lifetimes.

Experimental Section

All reagents were purchased from Sigma-Aldrich, Fisher Scientific, or Acros Organics and used without further purification. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker Avance 500 MHz nuclear magnetic resonance spectrometer. High-resolution mass spectra were obtained on a Micromass QTOF2 quadrupole/time-of-flight tandem mass spectrometer. Elemental analyses were obtained on a Control Equipment Corp. CEC 440HA organic elemental analyzer. Crystal structures were obtained on a Bruker Smart 1000K single crystal X-ray diffractometer.

The thermal data were obtained on a TA Instruments Q10 thermogravimetric analyzer and a TA Instruments Q50 differential scanning calorimeter. The glass transition of the samples was determined as the temperature corresponding to the maxiumum in the tan δ curve. The thermomechanical response of the cured resins was determined using a dynamic mechanical analyzer (TA Instruments, Newark, DE). Beam samples were cut to 3 mm × 5.5 mm × 60 mm and clamped in the frame using dual cantilever mode. For analysis, samples were heated from 25 to 280 °C at a rate of 10 °C/min, and cyclic load was applied at a frequency of 10 Hz.

Mechanical tests were carried out at room temperature using a universal testing machine (Instron model 4467). The flexural tangent elastic modulus and strength were determined in accordance with standard methods (ASTM D970M) using a loading rate of 1.7 mm/min. The compressive yield behavior was determined using cylindrical specimens, with an aspect ratio of three. Specimens were machined from samples molded in glass tubes. Care was taken to

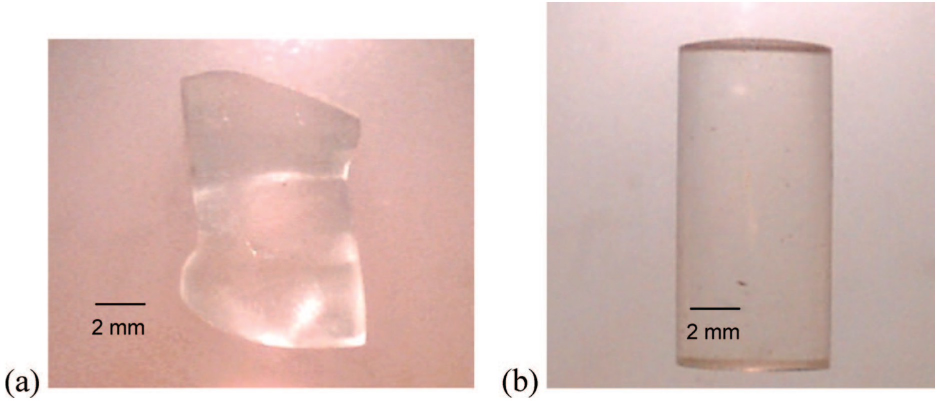


Figure 8. Polymer 400 (a) after compression testing and (b) after healing, identical shape to the pretest state.

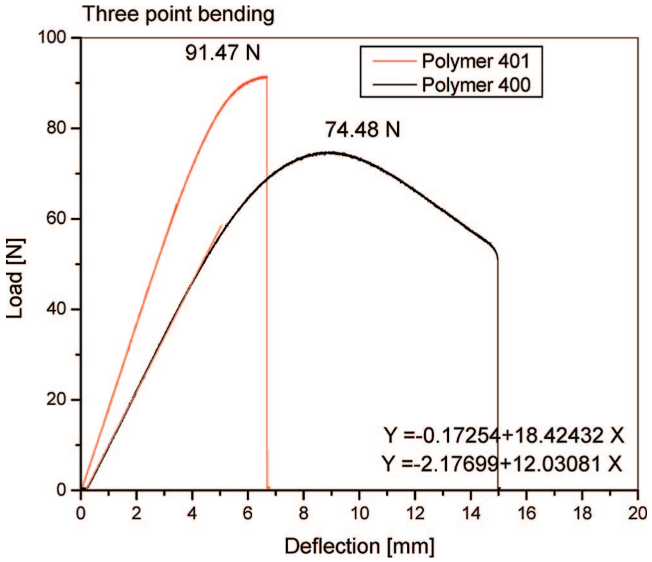


Figure 9. Results of three-point bending test on polymers 400 and 401.

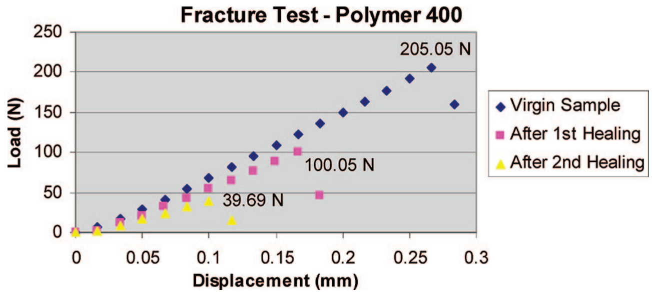


Figure 10. Load vs displacement for polymer 400, sample 2.

Table 2. Flexural Data for Polymers 400 and 401

sample	elastic modulus [GPa]	flexure strength [N]
polymer 400	2.63	74.48
polymer 401	3.26	91.47

Table 3. Fracture Mending Efficiency for Polymers 400 and 401

sample			fracture strength [N]	recovered strength [%]
polymer 400	1	virgin sample	201	
		after 1st healing	103	51.2
		after 2nd healing	48	46.6
	2	virgin sample	205	
		after 1st healing	100	48.8
		after 2nd healing	40	40
		after 3rd healing	17	42.5
	3	virgin sample	750	
		after 1st healing	150	20
	4	virgin sample	390	
		after 1st healing	232	59.5
		after 2nd healing	135	58.2
polymer 401	1	virgin sample	400	
		after 1st healing	123	30.7
	2	virgin sample	150	
		after 1st healing	21.8	14.5

obtain smooth and parallel faces. Uniaxial compression tests were performed at a loading rate of 0.5 mm/min following ASTM 695. Fracture toughness was determined using a single edge notched (SEN) type specimen (6.4 mm × 12.7 mm × 60 mm). Tests were performed according to ASTM D5045-93. After making a notch at the center of the sample with a reciprocating saw, a sharp crack of length *a* was initiated by tapping a fresh razor blade into the notch tip at room temperature. Samples were loaded in a three-point bending fixture at a crosshead speed of 10 mm/min.

Thiele's Acid Synthesis. Instead of a known, more intricate synthetic procedure,[23] the reaction conditions were modified to eliminate the need for precracking of dicyclopentadiene as well as the use of additional solvent, and the work-up was optimized to reduce exposure of the highly reactive sodium cyclopentadienide to oxygen. The reaction itself **must** be carried out under O_2-scrubbed (Ridox column) ultrahigh-purity Ar. Freshly cut sodium (10 g, 0.434 mol) was added to an excess (~500 mL) of dicyclopentadiene at room temperature. Upon heating, the solution turned blue at ~35 °C; before the sodium was completely molten the solution slowly discolored. The mixture was heated for 6 h at 160 °C, resulting in the evolution of hydrogen gas and the precipitation of a white solid. Once the alkali metal was consumed, the hydrogen evolution ceased; to ensure a quantitative conversion, heating was continued for an additional 30 min. The reaction mixture was filtered, taking care to minimize exposure of the solid cake to air by performing the filtration under a flow and blanket of ultrahigh-purity argon that had been passed through an oxygen-scavenging Ridox column. Upon the slightest exposure to oxygen, the white solid immediately turns brown, causing very substantial losses in yield. The unreacted dicyclopentadiene was recycled.

The white solid filter cake was washed with three 50 mL portions of *n*-pentane and then quickly transferred to a large recrystallizing dish containing an anhydrous THF/dry ice (~1 kg) slurry. Additional dry ice was added until the sodium cyclopentadienide was completely consumed. The resulting material was dissolved in water and extracted with three 100 mL portions of $CHCl_3$. The aqueous layer was then acidified with concentrated HCl; the precipitate was vacuum filtered, washed with 500 mL of water, and air-dried overnight. The resulting crude diacid was recrystallized from methanol to yield 92% (44.05 g, based on Na,) of Thiele's acid. ^{1}H NMR (d-DMSO, 500 MHz): δ 1.37 (d, 1H), 1.54 (d, 1H), 1.88 (m, 1H), 2.31 (m, 1H), 2.91 (m, 1H), 3.11 (d, 1H), 3.18 (d, 1H),

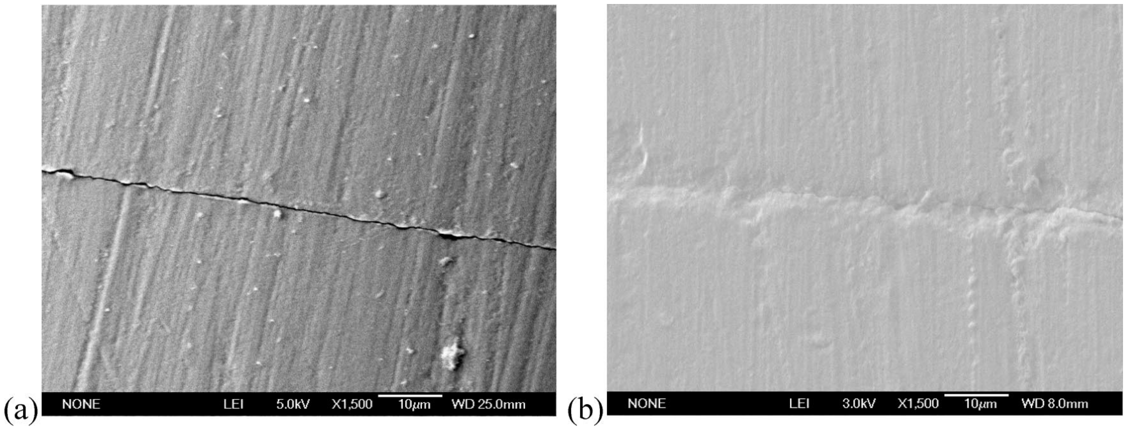


Figure 11. Scanning electron microscopy images of a polymer 401 fracture specimen (a) before and (b) after the healing treatment.

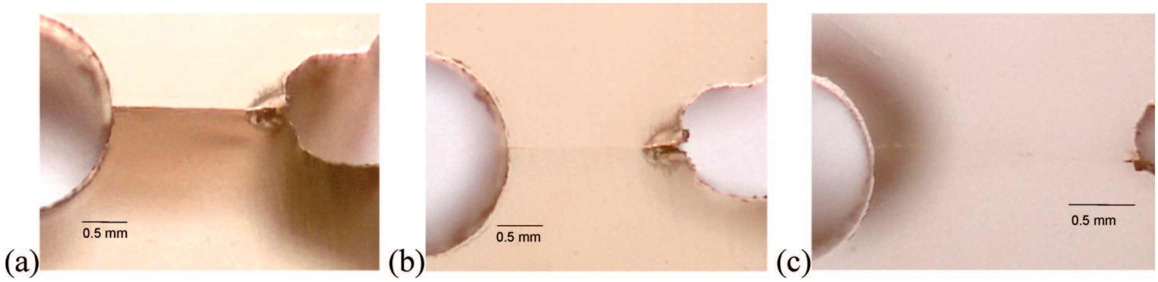


Figure 12. Polymer 400 (a) after fracture, (b) after healing, and (c) after surface polishing.

3.47 (m, 1H), 6.39 (d, 1H), 6.73 (d, 1H), 12.08 ppm (s, 2H). ^{13}C NMR (d-DMSO, 500 MHz): δ 33.14, 40.70, 46.56, 47.29, 50.59, 54.27, 138.63, 139.54, 142.88, 147.24, 166.12, 166.37 ppm. Elemental Analysis Calculated for $C_{12m}H_{12n}O_{4o}$: C, 68.18; H, 5.72. Found: C, 67.69; H, 5.43. HRMS ESI *m*/*z* calculated for $C_{12}H_{12}O_4$ (M + Na): 243.06; found 243.0582.

Thiele's Acid Chloride Synthesis. To an anhydrous Schlenk round-bottom flask was added Thiele's acid (10.0 g) under argon. To this was added ≈500 mL of oxalyl chloride. This reaction mixture was allowed to stir at 55 °C for 36 h. The reaction progress was monitored via CO_2 evolution and was considered complete when evolution ceased, and the reaction mixture had become a transparent light brown color. The oxalyl chloride was recovered via vacuum distillation. It was assumed to be a quantitative reaction, and the product was used without further purification.

Monomer 400 Synthesis. To a 3 L anhydrous round-bottom flask containing pyridine (19.58 mL, 0.243 mol) and dry tetrahydrofuran (300 mL) was added dropwise a solution of Thiele's acid chloride (12.45 g, 0.049 mol) in 500 mL of THF as well as a solution of 1,4-butanediol (4.38 g, 0.049 mol) in 500 mL of THF at approximately equal rates. Once both solutions had been added to the reaction flask, the solution was concentrated. The resulting brown solid was dissolved in 10% aqueous HCl and extracted with CH_2Cl_2 (3×). The organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated. This crude brown viscous oil was purified via flash chromatography using silica gel and 20% Et_2O in CH_2Cl_2 as the eluent, yielding 6.42 g of white crystals (48% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.31 (d, 1H), 1.54 (m, 2H), 1.67−1.82 (m, 2H), 1.84−1.96 (m, 1H), 2.14 (d, 1H), 2.39 (m, 1H), 2.83 (m, 1H), 3.21 (m, 1H), 3.47−3.59 (m, 4H), 4.78 (m, 1H), 4.91 (m, 1H), 6.49 (d, 1H), 6.57 ppm (d, 1H). ^{13}C CP-MAS (300 MHz): δ 26.15, 26.60, 33.43, 39.96, 48.21, 48.85, 55.25, 63.26, 65.77, 137.10, 139.84, 145.11, 148.13, 165.21 ppm. Elemental Analysis: Calculated for $C_{16n}H_{18m}O_{4o}$: C, 70.06%; H, 6.61%. Found: C, 69.46%; H, 6.51%. HRMS ESI *m*/*z* calculated for $C_{16}H_{18}O_4$ (M + Na): 297.10; found 297.097.

Monomer 401 Synthesis. To a 3 L anhydrous round-bottom flask containing pyridine (27.94 mL, 0.35 mol) and dry THF (500 mL) was added dropwise a solution of Thiele's acid chloride (17.77 g, 0.069 mol) in 600 mL of THF as well as a solution of diethylene glycol (7.36 g, 0.069 mol) in 600 mL of THF at approximately equal rates. Once both solutions had been added to the reaction flask, the solution was concentrated. The resulting brown solid was dissolved in 10% aqueous HCl and extracted with CH_2Cl_2 (3×). The organic phase was dried over anhydrous magnesium sulfate, filtered, and concentrated. This crude brown viscous oil was purified via flash chromatography using silica gel and 20% Et_2O in CH_2Cl_2 as the eluent, yielding 8.73 g of white crystals (43% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.32 (1H, m), 1.57 (1H, m), 2.21 (1H, m), 2.35−2.46 (1H, m), 2.81−2.89 (1H, m), 3.29 (1H, m), 3.43 (1H, m), 3.47−3.08 (2H, m), 3.61−3.67 (2H, m) 3.68−3.70 (2H, m), 3.82−3.89 (1H, m), 4.67−4.73 (1H, m), 4.86−4.94 (1H, m), 6.48 (1H, m), 6.69 ppm (1H, m). ^{13}C NMR (500 MHz, $CDCl_3$): δ 33.34, 40.28, 46.89, 47.63, 48.00, 53.61, 62.26, 62.32, 68.31, 69.80, 136.77, 138.02, 143.95, 147.37, 165.00, 165.21 ppm. Elemental Analysis: Calculated for $C_{16n}H_{18m}O_{5o}$: C, 66.19%; H, 6.26%. Found: C, 66.01%; H, 6.16%. HRMS ESI *m*/*z* calculated for $C_{16}H_{18}O_5$ (M + Na): 313.11; found 313.1104.

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Supporting Information Available: Differential scanning calorimetry, thermogravimetric analysis, crystallographic information files, and additional compression and flexural data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Tsige, M.; Lorenz, C. D.; Stevens, M. J. *Macromolecules* **2004**, *37*, 8466–8472.
(2) Cook, W. D. *J. Appl. Polym. Sci.* **1992**, *42*, 1259–1269.
(3) Sadeghipour, K.; Baran, G.; Zhang, H.; Wu, W. *J. Eng. Mater. Technol.* **2003**, *125*, 97–106.

(4) Hertzberg, R. W.; Nordberg, H.; Manson, J. A. *J. Mater. Sci.* **1970**, *5*, 521–526.

(5) White, S. R.; Sottos, N. R.; Geubelle, J. S.; Moore, J. S.; Kessler, M. R.; Sriram, S. R.; Brown, E. N.; Viswanathan, S. *Nature (London)* **2001**, *409*, 794–797.

(6) Yin, T.; Rong, M. Z.; Zhang, M. Q.; Yang, G. C. *Compos. Sci. Technol.* **2007**, *67*, 201–212.

(7) Cho, S. H.; Andersson, H. M.; White, S. R.; Sottos, N. R.; Braun, P. V. *Adv. Mater.* **2006**, *18*, 997–1000.

(8) Trask, R. S.; Williams, G. J.; Bond, I. P. *J. R. Soc. Interface* **2007**, *4*, 363–371.

(9) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698–1702.

(10) Chen, X.; Wudl, F.; Mal, A. K.; Shen, H.; Nutt, S. R. *Macromolecules* **2003**, *36*, 1802–1807.

(11) Liu, Y. L.; Chen, Y. W. *Macromol. Chem. Phys.* **2007**, *208*, 224–232.

(12) Liu, Y. L.; Hsieh, C. Y. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 905–913.

(13) Chung, C. M.; Roh, Y. S.; Cho, S. Y.; Kim, J. G. *Chem. Mater.* **2004**, *16*, 3982–3984.

(14) Varghese, S.; Lele, A.; Mashelkar, R. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 666–670.

(15) Kersey, F. R.; Loveless, D. M.; Craig, S. L. *J. R. Soc. Interface* **2007**, *4*, 373–380.

(16) Staudinger, H.; Bruson, H. A. *Justus Liebigs Ann. Chem.* **1926**, *447*, 97–110.

(17) Stille, J. K.; Plummer, L. *J. Org. Chem.* **1961**, *26*, 4026–4028.

(18) Hirsch, S S.; Bailey, W. J. *J. Org. Chem.* **1978**, *43*, 4090–4094.

(19) Dehmlow, E. V.; Bollmann, C. *Tetrahedron Lett.* **1991**, *32*, 5773–5776.

(20) Xiong, Z.; Zhentao, M.; Zhang, X. *React. Kinet. Catal. Lett.* **2005**, *85*, 89–97.

(21) Bolanos, E.; Murphy, E. B.; Wudl, F., unpublished results.

(22) Goertzen, W. K.; Kessler, M. R. *Composites, Part B* **2007**, *38*, 1–9.

(23) Marchand, A. P.; Namboothiri, I. N. N.; Lewis, S. B. *Tetrahedron* **1998**, *54*, 12691–12698.

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