ACS Macro Letters

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Dynamic Polymer Network System Mediated by Radically Exchangeable Covalent Bond and Carbolong Complex

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Cite This: *ACS Macro Lett.* 2020, 9, 344−349

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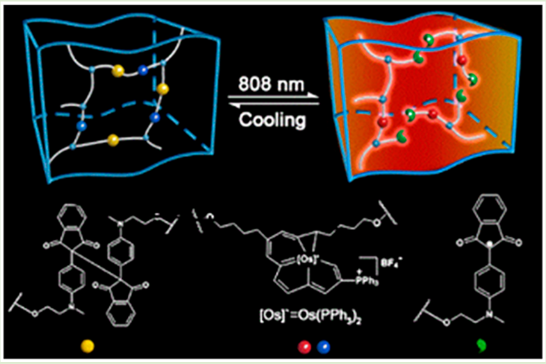
ABSTRACT: It is appealing to develop dynamic polymer systems with multifunctionl properties. Herein, we report a polyurethane elastomer with a dynamic covalent polymer network containing a radically exchangeable 2-arylindane-l,3-dione dimer as thermally sensitive and reversible cross-links. In addition, the carbolong complex, an excellent photothermal agent, is incorporated into the dynamic network backbone. With the irradiation of NIR light, the carbolong complex rapidly generates thermal energy, which subsequently triggers the cleavage of the dynamic covalent bond to generate radicals and activate the polyurethane network. In proof-of-concept experiments, we demonstrate that the utility of a combination of radically exchangeable covalent bond and carbolong moiety brings multiple functional characteristics to the polymer network with a capability of spatiotemporal control, including thermochromism, photochromism, rewritability, malleability, and self-healing. This study holds potentials for exploring more tunable dynamics and improved material properties.



The construction of polymer networks that simultaneously possess topological stability and reprocessability has always been a major challenge in polymer science. In recent years, the rediscovery of dynamic covalent bonds in the role of polymer networks has been found to be an ideal solution to address this challenge.[1−3] The reversible cleavage and generation of dynamic covalent bonds inherently tackles the plastic flow problem of polymer network, making the materials to integrate both the merits of thermosets and thermoplastics. Up to now, series of dynamic covalent systems have been explored in constructing dynamic covalent polymer networks, such as disulfide linkages,[4] Diels−Alder adducts,[5,6] transesterification,[3,7−12] urethane exchange,[13−15] transamidation,[16] imine exchange,[17,18] transalkylation,[19,20] olefin metathesis,[21] boronic ester exchange,[22,23] silyl ether exchange,[24] free radical systems.[25−30]

It is appealing to develop novel dynamic covalent moieties with multiple properties for constructing multifunctional dynamic polymer systems. In addition, the stimuli for triggering the dynamic properties are of great importance. While most dynamic covalent bonds used direct and indirect heating, we are intrigued by photothermal triggering,[31,32] particularly use of near-infrared (NIR) light is preferred,[33] for the benefits of remote spatiotemporal selectivity,[32,34] deep penetration, and low photochemical effect on polymeric materials.

Recently, we have developed a series of novel carbolong complexes, which are metal bridgehead polycyclic frameworks featured with a long carbon chain (≥7C) coordinated to an osmium atom via metal−carbon bonds[35,36] as viable photothermal agents for functional materials.[37−40] We envisage that the excellent photothermal effect of carbolong can be utilized for triggering the thermoresponsiveness of dynamic covalent bonds, which can offer unique opportunities in constructing NIR-responsive dynamic covalent polymer systems.

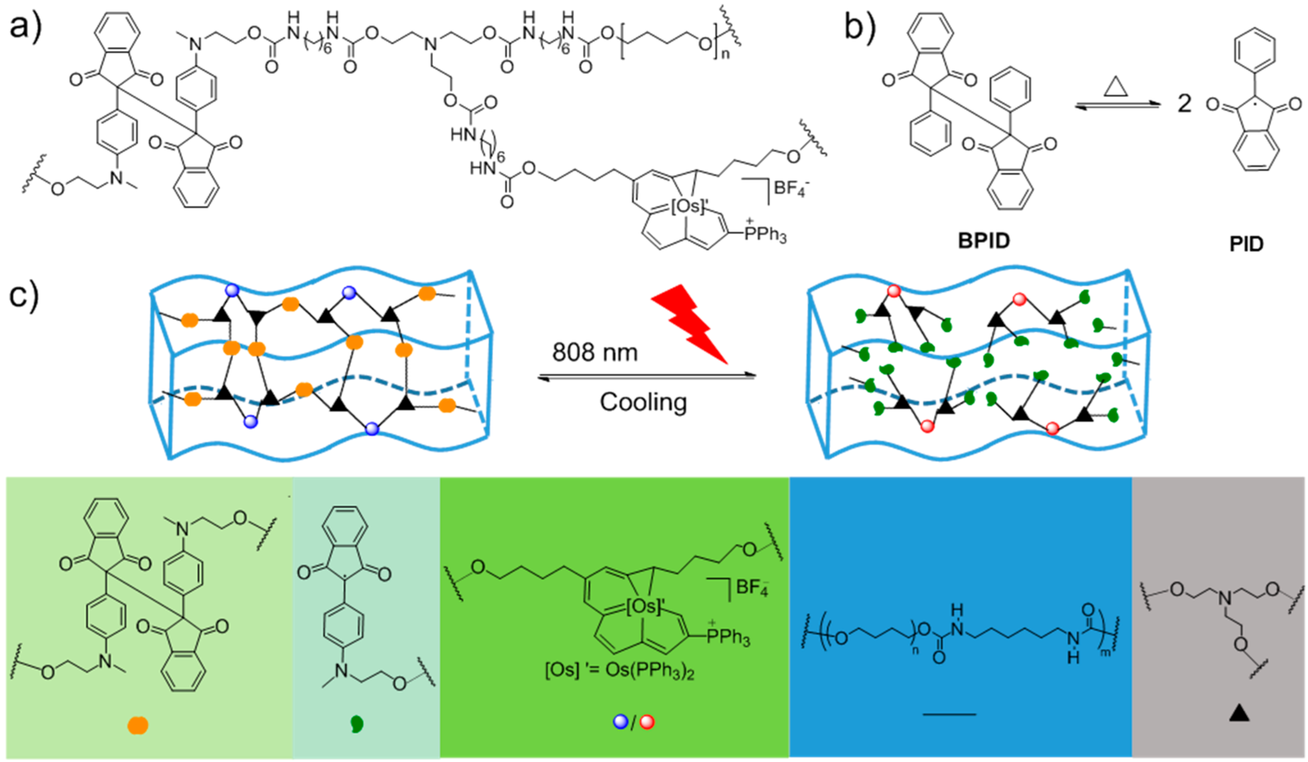
Herein, we report the first dynamic covalent polymer network, which carries dynamic covalent moieties and carbolong complexes in the backbone (Scheme 1a). A dynamic covalent moiety, 2,2′-bis(2-phenylindan-l,3-dione) (BPID), which can be thermally activated into two stable 2-phenylindan-l,3-dione-yl radicals, has been employed in this work (Scheme 1b). With the irradiation of NIR light, the carbolong complex rapidly generates thermal energy that heats up the polymer matrix and consequently triggers the cleavage of the BPID moiety to generate radicals, inducing the segment reshuffling and rearrangement in the polymer network (Scheme 1c). The combination of these two functional moieties brings multiple characteristics to the polymer network, including thermochromism, photochromism, rewrit-

Received: January 15, 2020
Accepted: February 18, 2020

ACS Publications

https://dx.doi.org/10.1021/acsmacrolett.0c00035

Scheme 1. (a) Schematic Structure of Dynamic Polyurethane Network (PUN); (b) Reversible Cleavage and Generation of BPID; (c) Schematic Illustration of the Dynamic Property of PUN Triggered by 808 nm NIR Light



ability, malleability, and self-healing. Importantly, these properties can be manipulated in a spatiotemporal controlled manner.

We began by designing 2,2′-bis[2-(4′′-(2-hydroxyethyl)(methyl)aminophenyl)indan-l,3-dione] (BPID-OH), the hydroxyl-functionalized BPID, which can be readily incorporated into polymer backbones. The newly designed BPID-OH compound was synthesized in two steps and 40% yield from commercially available materials (Scheme S1). The synthesis of hydroxyl functionalized carbolong complex compound 556-OH was accomplished according to the published procedure (Scheme S2).[40] The polyurethane network (PUN) was synthesized via a two-step condensation polymerization (Schemes 1a and S3).

The dynamic property of BPID was first studied by a simple heating−cooling cycle of BPID-OH solution in DMF. As shown in Figure 1a, the color of the BPID-OH solution gradually changed from light yellow to yellow green when the temperature was raised from 20 to 100 °C and recovered to the initial light yellow when cooling down to 20 °C (Figure 1a). The UV−vis spectra of the BPID-OH solution (Figure S8) were observed to changed accordingly during the heating process. The observed green color and change in absorption when heating up suggests the cleavage of C−C bond in BPID and the generation of PID radicals,[41] while the return of yellow color when cooling down indicates the coupling of radical molecular fragments and regeneration of the BPID moieties. The generation of radicals was then further confirmed by electron spin resonance (ESR) spectroscopy measurements. As is clearly shown in ESR spectra (Figure 1b), distinct ESR signals originated from radicals with calculated *g* value of 2.0068 were observed during the heating process, in contrast to the sample at around room temperature. Moreover, the ESR signals were significantly strengthened as the temperature was increased over 90 °C, indicating a faster generation of radicals at higher temperatures. The temperature dependence is in accordance with the mechanism of radical generation.[42] The study also indicated that the PID radical can be well maintained for about 1 h in high temperature solution (Figure

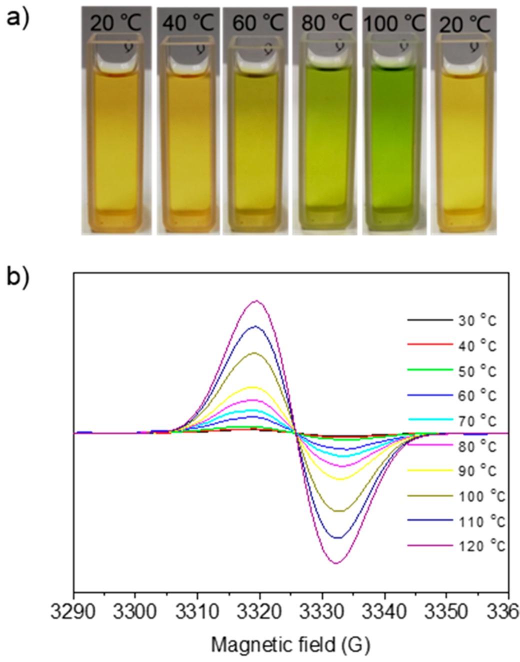


Figure 1. (a) Color change of BPID-OH in DMF solution (3.4 × 10^{-3} M) at various temperatures. (b) ESR spectra of BPID-OH in DMF solution at various temperatures.

S7). Meanwhile, it is worth noting that changes of color and UV−vis spectra were also observed when mixing the BPID-OH with 556-OH in DMF, suggesting good compatibility of the PID radicals with carbolong complex (Figures S9 and S10 in SI).

We then studied the dynamic property of PUN by swelling and thermochromism experiments. A piece of sample (6 mm × 6 mm) was swollen in DMF to an enlarged gel with a 600% increase in mass (Figure S11a) at 25 °C after 6 h, and remained almost unchanged (9 mm × 9 mm) in the next 6 h soaking (Figure S11b). The sample can be continuously swollen when further soaked at higher temperatures and completely dissolved into a homogeneous solution at 120 °C for 10 h. This phenomenon indicates that the PUN is a true covalent polymer network at room temperature but more close to a thermoplastic polymer at high temperature. This behavior can be ascribed to the dynamic bond breaking and exchange of BPID moieties at elevated temperatures, leading to a complete rupture of the cross-linked network. Furthermore, a wafer-like polymer sheet was heated in an oven from 20 to 100 °C. As shown in Figure S12, color change into more greenish started to show up when heating up to around 60 °C and turned deeper as the temperature was further increased, indicating that the thermally induced dissociation of the BPID moieties became more prominent at elevated temperatures. As expected, the sample returned to the original color after cooling down, which is akin to the phenomenon of BPID-OH solution. This reversible color changes during heating−cooling cycle indicates the homolysis and regeneration of C−C bond in the BPID moiety on the polymer network, which corresponds to a reversible deconstruction and recovery of polyurethane cross-linked network.

The dynamic bond also endows the polymer network stress relaxation and creep behavior of typical dynamic network. At relatively low temperatures, the stress declined dramatically at the beginning and reached a plateau (Figure 2a). Such a stress relaxation behavior is analogue to the conventional cross-linked polymers, indicating that PUN is close to a thermoset polymer at relatively low temperature (<50 °C). While heating up to 60 °C and higher temperatures, the stress relaxed more and more quickly to zero, consistent with the faster dissociation of BPID moieties and consequent reshuffling of polymer segments to form less stretched networks at elevated temperatures. This relaxation results agree well with the swelling and thermochromism behaviors. The activation energy of the relaxation was calculated to be 63.31 kJ/mol, comparable to the reported value.[14,43] For the creep tests, as shown in Figure 2b, the stress led to higher strains and larger permanent deformations after removing the stress when temperature was increased. Meanwhile, in DMA analysis (Figure S14), the elasticity modulus and storage modulus decreased simultaneously as the temperature increased over room temperature. These results again are consistent with the faster dissociation of dynamic covalent BPID bonds at elevated temperatures and indicates excellent plasticity and malleability of the PUN at high temperatures.

When irradiated with NIR light (808 nm, 0.5 W cm^{-2}), the surface temperature of PUN at the laser spot increased rapidly and reached a steady state of around 80 °C (Figure S15) as a consequence of the photothermal property of carbolong complex. On account of the photothermal effect, the plasticity and malleability of PUN can be achieved using NIR irradiation. As can be seen from Figure 3, with the help of NIR irradiation, a certain pattern can be easily stamped onto the surface of the PUN specimen and remained after removing the light source. Stretching a piece of NIR-irradiated PUN specimen can also lead to permanent deformation (Figures S16 and S17 and videos 1 and 2 in SI). Thanks to the dynamic covalent BPID bond, the PUN combines the merits both of thermoset and thermoplastic polymers, that is, the topological stability and processability, which are normally incompatible in a single polymer system.

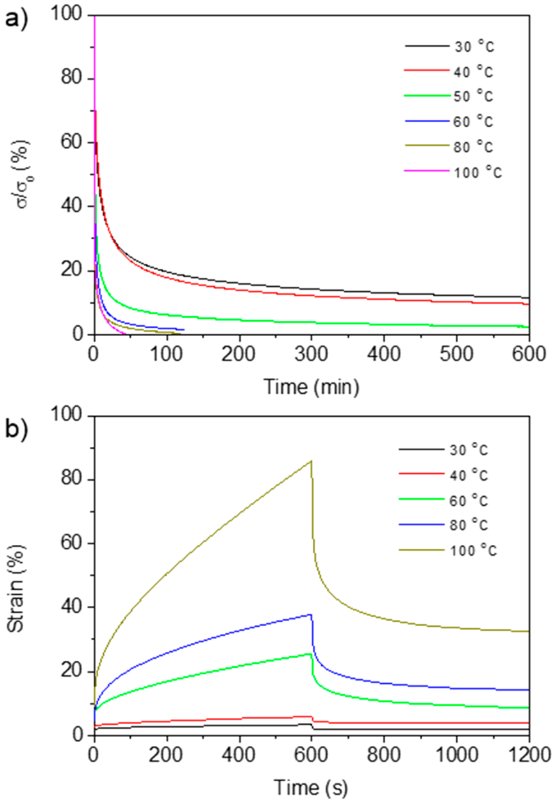


Figure 2. (a) Stress relaxation behavior of PUN at different temperatures. (b) Creep behaviors of PUN at different temperatures.

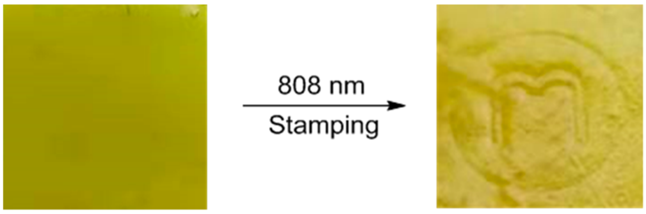


Figure 3. Pattern stamped on the surface of PUN with the help of NIR light.

An intriguing application of such a dynamic polymer system is photo triggered self-healing materials. To this end, rectangle samples (20 mm (L) × 2 mm (W) × 0.6−0.8 mm (T)) with a 0.4 mm deep and 4 mm long cut on the surface were irradiated by NIR light for healing. Compared to the legible cut at first, the polymer matrix beside the crack started to coalesce and narrowed down the crack gradually during irradiation. After 30 min, the cut was almost unobservable, putatively complete healing was achieved (Figure 4a), consistent with healing using direct heating (Figure S18). In contrast, no photothermal effect (Figure S19) and no healing (Figure S20) were observed for a control PUN sample (Scheme S4) without carbolong

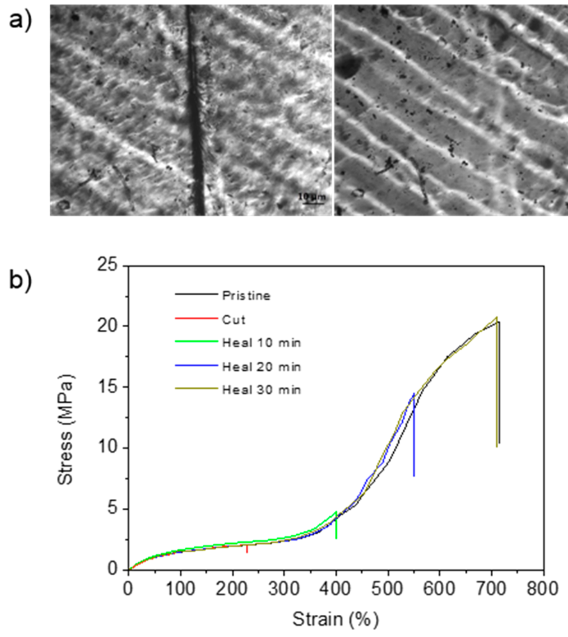


Figure 4. (a) Microscopic images of PUN specimen with a cutting crack and the diminish crack after photothermal healing. (b) Mechanical property study of PUN specimens with different NIR healing times.

complex irradiated with NIR light. The efficiency of healing was also evaluated by tensile tests. Dog-bone specimens with a cutting notch (0.4 mm wide, 0.4 mm deep) were tested before and after NIR healing for various irradiation times. Representative stress−strain curves of the cut, healed and the pristine samples are displayed in Figures 4b and S21−S25, and the detailed mechanical data are summarized in Figure S26 and Table S1 in the Supporting Information. As can be clearly seen, for NIR-irradiated samples, the longer healing time, the higher mechanical strength regained. A 30 min healing guaranteed almost full recovery of the mechanical property.

Taking advantage of the photothermal property of carbolong moiety and the thermochromism of the dynamic covalent BPID bond, the PUN can be used as an ideal NIR rewritable material. As a demonstration, we irradiated the PUN sheet by NIR through a photomask with "X" shape hole (Figure 5a). After NIR irradiation for about 10 min, the exposed region turned to green, whereas the unexposed region retained the original color (Figure 5b). The green "X" pattern was then easily "erased" when the sheet was cooled down to room temperature.

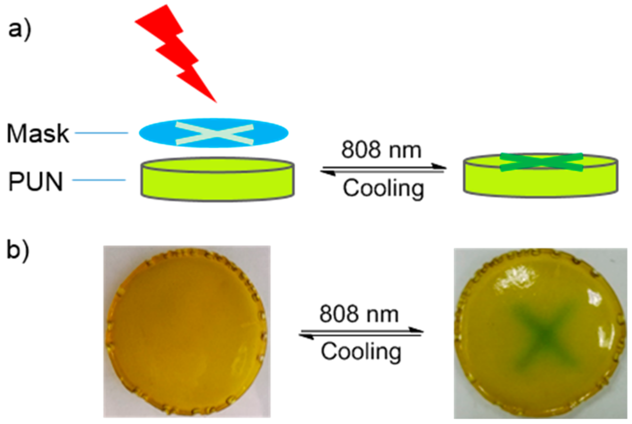


Figure 5. (a) Schematic illustration of the PUN that was irradiated by NIR light under the shielding of a mask. (b) Rewritable "X" pattern on the surface of PUN manipulated by NIR light.

In conclusion, we have developed a novel dynamic covalent polymer network by introducing radically exchangeable covalent BPID bond and metallo-organic complex with excellent photothermal effect into the polymer backbone. The dynamic covalent BPID bond was shown to be thermally responsive with coloration that is reversible, because the colored free radicals reformed the BPID upon cooling. Swelling results reflected both covalent and dynamic characteristics of the BPID in the polymer network. Relaxation tests confirmed the dynamic covalent characteristics of the elastomer, and the creep tests indicated excellent plasticity and malleability of the PUN at high temperatures, which are suitable for material reprocessing. The dynamic nature of the BPID also led to thermochromism of the polymer, which could be triggered by direct heating and photothermal heating by using the carbolong agents. The NIR triggered dissociation and consequent thermochromism made the elastomer useful for remote patterning and rewriting. The as-prepared elastomers exhibited high elongation and excellent toughness (>700% and >400 MJ m^{-3}, respectively). Finally, the material was found to be fully healable. The marriage of dynamic covalent BPID bond and carbolong complex endows the polymer network excellent dynamic properties, featured by thermochromism, photochromism, NIR rewritability, malleability, and self-healing. We believe that this line of research will offer a general strategy for a wide range of versatile dynamic covalent polymer systems toward smart properties with great tunability.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmacrolett.0c00035.

Video 1(MP4)

Video 2 (MP4)

Experimental and characterization details (PDF)

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https://pubs.acs.org/10.1021/acsmacrolett.0c00035

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Funding

We are thankful for the financial support from the National Natural Science Foundation of China (Nos. U1705254, 21472155, 21490573, 21774106).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Haibo Zhao is acknowledged for the help of carbolong complex synthesis and instructive discussion. Guping Hu (School of Chemistry, Sun Yat-Sen University) is acknowledged for the help of electron spin resonance (ESR) spectroscopy measurements.

■ REFERENCES

(1) Zou, W.; Dong, J.; Luo, Y.; Zhao, Q.; Xie, T. Dynamic Covalent Polymer Networks: from Old Chemistry to Modern Day Innovations. *Adv. Mater.* **2017**, *29*, 1606100.

(2) Denissen, W.; Winne, J. M.; DuPrez, F. E. Vitrimers: Permanent Organic Networks with Glass-Like Fluidity. *Chem. Sci.* **2016**, *7*, 30−38.

(3) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-Like Malleable Materials from Permanent Organic Networks. *Science* **2011**, *334*, 965.

(4) Amamoto, Y.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. Self-healing of Covalently Cross-Linked Polymers by Reshuffling Thiuram Disulfide Moieties in Air under Visible Light. *Adv. Mater.* **2012**, *24*, 3975−3980.

(5) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A Thermally Re-mendable Cross-Linked Polymeric Material. *Science* **2002**, *295*, 1698.

(6) Zhang, G.; Zhao, Q.; Yang, L.; Zou, W.; Xi, X.; Xie, T. Exploring Dynamic Equilibrium of Diels-Alder Reaction for Solid State Plasticity in Remoldable Shape Memory Polymer Network. *ACS Macro Lett.* **2016**, *5*, 805−808.

(7) Pei, Z.; Yang, Y.; Chen, Q.; Wei, Y.; Ji, Y. Regional Shape Control of Strategically Assembled Multishape Memory Vitrimers. *Adv. Mater.* **2016**, *28*, 156−160.

(8) Brutman, J. P.; Delgado, P. A.; Hillmyer, M. A. Regional Shape Control of Strategically Assembled Multishape Memory Vitrimers. *ACS Macro Lett.* **2014**, *3*, 607−610.

(9) Pei, Z.; Yang, Y.; Chen, Q.; Terentjev, E. M.; Wei, Y.; Ji, Y. Mouldable Liquid-crystalline Elastomer Actuators with Exchangeable Covalent Bonds. *Nat. Mater.* **2014**, *13*, 36−41.

(10) Yang, Y.; Pei, Z.; Li, Z.; Wei, Y.; Ji, Y. Making and Remaking Dynamic 3D Structures by Shining Light on Flat Liquid Crystalline Vitrimer Films without a Mold. *J. Am. Chem. Soc.* **2016**, *138*, 2118−2121.

(11) Capelot, M.; Unterlass, M. M.; Tournilhac, F.; Leibler, L. Catalytic Control of the Vitrimer Glass Transition. *ACS Macro Lett.* **2012**, *1*, 789−792.

(12) Snyder, R. L.; Fortman, D. J.; De Hoe, G. X.; Hillmyer, M. A.; Dichtel, W. R. Reprocessable Acid-Degradable Polycarbonate Vitrimers. *Macromolecules* **2018**, *51*, 389−397.

(13) Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Reprocessable Acid-Degradable Polycarbonate Vitrimers. *Angew. Chem., Int. Ed.* **2016**, *55*, 11421−11425.

(14) Fortman, D. J.; Brutman, J. P.; Cramer, C. J.; Hillmyer, M. A.; Dichtel, W. R. Mechanically Activated Catalyst-Free Polyhydroxyurethane Vitrimers. *J. Am. Chem. Soc.* **2015**, *137*, 14019−14022.

(15) Ying, H.; Zhang, Y.; Cheng, J. Dynamic Urea Bond for the Design of Reversible and Self-healing Polymers. *Nat. Commun.* **2014**, *5*, 3218.

(16) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Vinylogous Urethane Vitrimers. *Adv. Funct. Mater.* **2015**, *25*, 2451−2457.

(17) Taynton, P.; Yu, K.; Shoemaker, R. K.; Jin, Y.; Qi, H. J.; Zhang, W. Heat- or Water-Driven Malleability in a Highly Recyclable Covalent Network Polymer. *Adv. Mater.* **2014**, *26*, 3938−3942.

(18) Deng, G.; Tang, C.; Li, F.; Jiang, H.; Chen, Y. Covalent Cross-Linked Polymer Gels with Reversible Sol-Gel Transition and Self-healing Properties. *Macromolecules* **2010**, *43*, 1191−1194.

(19) Obadia, M. M.; Mudraboyina, B. P.; Serghei, A.; Montarnal, D.; Drockenmuller, E. Reprocessing and Recycling of Highly Cross-linked Ion-Conducting Networks through Transalkylation Exchanges of C−N Bonds. *J. Am. Chem. Soc.* **2015**, *137*, 6078−6083.

(20) Hendriks, B.; Waelkens, J.; Winne, J. M.; Du Prez, F. E. Poly(thioether) Vitrimers via Transalkylation of Trialkylsulfonium Salts. *ACS Macro Lett.* **2017**, *6*, 930−934.

(21) Lu, Y.; Tournilhac, F.; Leibler, L.; Guan, Z. Making Insoluble Polymer Networks Malleable via Olefin Metathesis. *J. Am. Chem. Soc.* **2012**, *134*, 8424−8427.

(22) Lai, J.; Mei, J.; Jia, X.; Li, C.; You, X.; Bao, Z. A Stiff and Healable Polymer Based on Dynamic-Covalent Boroxine Bonds. *Adv. Mater.* **2016**, *28*, 8277−8282.

(23) Ogden, W. A.; Guan, Z. Recyclable, Strong, and Highly Malleable Thermosets Based on Boroxine Networks. *J. Am. Chem. Soc.* **2018**, *140*, 6217−6220.

(24) Nishimura, Y.; Chung, J.; Muradyan, H.; Guan, Z. Silyl Ether as a Robust and Thermally Stable Dynamic Covalent Motif for Malleable Polymer Design. *J. Am. Chem. Soc.* **2017**, *139*, 14881−14884.

(25) Zhang, Z. P.; Rong, M. Z.; Zhang, M. Q. Mechanically Robust, Self-healable, and Highly Stretchable "Living" Cros-linked Polyurethane Based on a Reversible C-C Bond. *Adv. Funct. Mater.* **2018**, *28*, 1706050.

(26) Imato, K.; Takahara, A.; Otsuka, H. Self-healing of a Cross-Linked Polymer with Dynamic Covalent Linkages at Mild Temperature and Evaluation at Macroscopic and Molecular Levels. *Macromolecules* **2015**, *48*, 5632−5639.

(27) Fan, L. F.; Rong, M. Z.; Zhang, M. Q.; Chen, X. D. Dynamic Reversible Bonds Enable External Stress-Free Two-way Shape Memory Effect of a Polymer Network and the Interrelated Intrinsic Self-healability of Wider Crack and Recyclability. *J. Mater. Chem. A* **2018**, *6*, 16053−16063.

(28) Takahashi, A.; Goseki, R.; Otsuka, H. Thermally Adjustable Dynamic Disulfide Linkages Mediated by Highly AirStable 2,2,6,6-Tetramethylpiperidine-1-sulfanyl (TEMPS) Radicals. *Angew. Chem.* **2017**, *129*, 2048−2053.

(29) Imato, K.; Nishihara, M.; Kanehara, T.; Amamoto, Y.; Takahara, A.; Otsuka, H. Self-healing of Chemical Gels Cross-Linked by Diarylbibenzofuranone-Based Trigger-Free Dynamic Covalent Bonds at Room Temperature. *Angew. Chem., Int. Ed.* **2012**, *51*, 1138−1142.

(30) Scott, T. F.; Schneider, A. D.; Cook, W. D.; Bowman, C. N. Photoinduced Plasticity in Cross-Linked Polymers. *Science* **2005**, *308*, 1615−1617.

(31) Michal, B. T.; Jaye, C. A.; Spencer, E. J.; Rowan, S. J. Inherently Photohealable and Thermal Shape-Memory Polydisulfide Networks. *ACS Macro Lett.* **2013**, *2*, 694−699.

(32) Kloxin, C. J.; Scott, T. F.; Park, H. Y.; Bowman, C. N. Mechanophotopatterning on a Photoresponsive Elastomer. *Adv. Mater.* **2011**, *23*, 1977−1981.

(33) Du, W.; Jin, Y.; Lai, S.; Shi, L.; Fan, W.; Pan, J. Near-infrared Light Triggered Shape Memory and Self-healable Polyurethane/Functionalized Graphene Oxide Composites Containing Diselenide Bonds. *Polymer* **2018**, *158*, 120−129.

(34) Mu, X.; Sowan, N.; Tumbic, J. A.; Bowman, C. N.; Mather, P. T.; Qi, H. J. Photo-induced Bending in a Light-activated Polymer Laminated Composite. *Soft Matter* **2015**, *11*, 2673−2682.

(35) Zhu, C.; Xia, H. Carbolong Chemistry: A Story of Carbon Chain Ligands and Transition Metals. *Acc. Chem. Res.* **2018**, *51*, 1691−1700.

(36) Zhu, C.; Li, S.; Luo, M.; Zhou, X.; Niu, Y.; Lin, M.; Zhu, J.; Cao, Z.; Lu, X.; Wen, T.; Xie, Z.; Schleyer, P. V. R.; Xia, H. Stabilization of anti-Aromatic and Strained Five-membered Rings with a Transition Metal. *Nat. Chem.* **2013**, *5*, 698−703.

(37) Lu, Z.; Cai, Y.; Wei, Y.; Lin, Q.; Chen, J.; He, X.; Li, S.; Wu, W.; Xia, H. Photothermal Möbius Aromatic Metallapentalenofuran and its NIR-responsive Copolymer. *Polym. Chem.* **2018**, *9*, 2092−2100.

(38) He, X.; He, X.; Li, S.; Zhuo, K.; Qin, W.; Dong, S.; Chen, J.; Ren, L.; Liu, G.; Xia, H. Amphipathic Metal-containing Macromolecules with Photothermal Properties. *Polym. Chem.* **2017**, *8*, 3674−3678.

(39) Zhu, C.; Yang, C.; Wang, Y.; Lin, G.; Yang, Y.; Wang, X.; Zhu, J.; Chen, X.; Lu, X.; Liu, G.; Xia, H. CCCCC Pentadentate Chelates with Planar Möbius Aromaticity and Unique Properties. *Science Adv.* **2016**, *2*, No. e1601031.

(40) Zhang, H.; Zhao, H.; Zhuo, K.; Hua, Y.; Chen, J.; He, X.; Weng, W.; Xia, H. "Carbolong" Polymers with Near Infrared Triggered, Spatially Resolved and Rapid Self-healing Properties. *Polym. Chem.* **2019**, *10*, 386−394.

(41) Aliev, Z. G.; Chekhlov, A. N.; Atovmyan, L. O.; Pisarenko, L. M.; Nikulin, V. I. Crystal and Molecular Structure of 2,2'-Bis[2-(p-Dimethylaminophenyl)Indane-1,3-Dione] Displaying Mechanochromic Properties. *J. Struct. Chem.* **1991**, *31*, 779−783.

(42) Kobashi, T.; Sakamaki, D.; Seki, S. N-Substituted Dicyanomethylphenyl Radicals: Dynamic Covalent Properties and Formation of Stimuli-Responsive Cyclophanes by Self-Assembly. *Angew. Chem., Int. Ed.* **2016**, *55*, 8634−8638.

(43) Pisarenko, L. M.; Nikulin, V. I.; Blagorazumov, M. P.; Neiland, O. Y.; Paulin'sh, L. L. Influence of Onium Substituent in Phthaloyl Ring Parameters of Equilibrium between Dimer and Free 2-(4-Dimethylaminophenyl)-1,3-Indandiones. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1990**, *39*, 1379−1385.