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Olefin Metathesis for Effective Polymer Healing via Dynamic Exchange of Strong Carbon−Carbon Double Bonds

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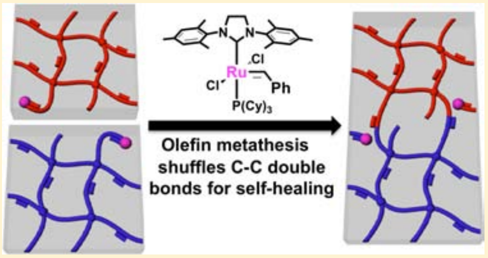
ABSTRACT: In this article, we demonstrate transition-metal-catalyzed olefin metathesis as a simple, effective method for healing polymers via dynamic exchange of strong carbon−carbon double bonds. Upon introducing a very low level of the Grubbs' second-generation Ru metathesis catalyst into cross-linked polybutadiene (PBD) network, the material self-heals effectively at various conditions under moderate pressures. In sharp contrast, catalyst-free control samples with identical network topology and cross-linking density show minimal healing. The healing efficiency of the materials was carefully investigated under different concentrations of the Ru catalyst, compression pressures, and temperatures. It is demonstrated for the first time that a bulk polymer could effectively heal via dynamic covalent bond formation at sub-ambient temperature. The Ru-loaded PBD samples not only heal well with themselves but also with control samples without any catalyst. Furthermore, a completely Ru-free PBD network can heal effectively upon simply applying a very small amount of Ru catalyst only at the fracture surface. The simplicity and effectiveness of this self-healing approach make it potentially applicable to a wide range of olefin-containing polymers.



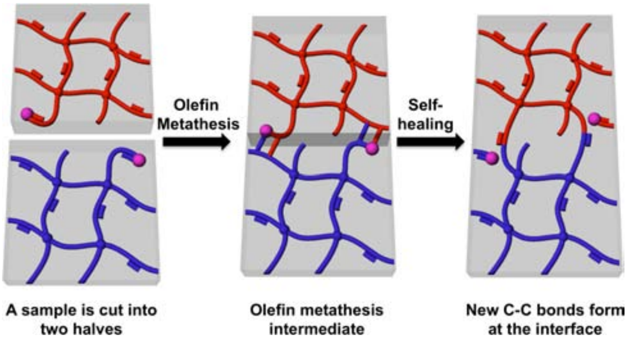
INTRODUCTION

Introducing self-healing capability into materials would greatly improve their safety feature, lifetime, and energy efficiency. A significant amount of effort has been devoted to this field in recent years, and several groups have reported different self-healing polymer designs through the incorporation of encapsulated monomers,[1,2] dynamic non-covalent bonding,[3−12] and reversible[13−25] or irreversible[26,27] covalent bonds into polymers. Recently, dynamic covalent chemistry techniques[28,29]—such as thermal-[13−15] and light-catalyzed cycloaddition,[16,17,30] transesterification,[18,31] radical reactions,[19−21,32] thiol−disulfide exchange,[22] hydrazone formation,[23,24] and siloxane equilibration[25]—have attracted much attention for their applications in self-healing or malleable polymer designs.

Most dynamic covalent bonds used for self-healing applications involve heteroatoms in dynamic exchange reactions.[18,19,22,23,25] In principle, reversible carbon−carbon bond formation should be particularly attractive for such applications because the high stability of C−C bonds may offer the possibility of designing stronger self-healing materials. Among the few examples of dynamic C−C bond-based self-healing polymers, those involving strong C−C bonds, such as reversible Diels−Alder reactions[13] and photochemical cycloaddition reactions,[16,17,30] require substantial inputs of external energy in the form of heat or light to trigger the reversible C−C bond formation. On the other hand, the one using weak dynamic C−C bonds, which can self-heal without providing external energy, only results in relatively weak self-healing polymer gels.[20] In addition, most of those self-healing systems require specially designed monomers or polymers to serve the purpose. It would be highly desirable to develop a simple strategy for effective polymer healing through *dynamic exchange of strong C−C bonds under ambient conditions*.

Toward this goal, herein we report a simple, efficient self-healing polymer design employing transition-metal-catalyzed olefin metathesis for reversible C−C double bond exchange (Scheme 1). Olefin metathesis reaction is attractive for this purpose because it is highly efficient for shuffling strong C−C

Scheme 1. Olefin Metathesis for Effective Polymer Healing via Dynamic Exchange of Strong Carbon−Carbon Double Bonds[a]



[a] Ru-catalyzed olefin metathesis at fracture interfaces results in formation of new C−C double bonds between the two surfaces, affording covalent healing of the fractured polymer (the polymer chains are color coded to indicate that they come from two separate pieces).

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double bonds under ambient conditions.[33,34] In the current study, we have shown that by introducing a very low level of the Grubb's second-generation Ru metathesis catalyst into a readily available polybutadiene (PBD) network, the material can heal efficiently under mild conditions. With moderate pressure, this material can effectively heal in the air, at ambient or even sub-ambient temperature. Given the efficiency and versatility of olefin metathesis as well as the abundance of olefin-containing polymers, we envision that this could be a powerful approach for self-healing material design.

■ RESULTS AND DISCUSSION

We recently reported the use of olefin metathesis for generating adaptive, malleable polymer networks.[35] Introduction of low levels of the Grubbs' second-generation Ru metathesis catalyst into cross-linked PBD network makes it malleable at room temperature while retaining its insolubility. The malleability arises from Ru-catalyzed olefin metathesis reaction, which covalently shuffles C−C double bonds in bulk network and rearranges network topology in response to external force. We reasoned that the same mechanism can be employed to reversibly form C−C double bonds at fracture interfaces, which should result in strong covalent self-healing without the need of heat or light.

To test our hypothesis, into a cross-linked PBD network (cross-linking density ~3.6×10^{-4} mol/cm^3), we loaded the second-generation Grubbs' Ru metathesis catalyst at 0.0050, 0.0075, and 0.010 mol% (relative to the molarity of olefin), respectively. For self-healing tests, a sample was first cut with a razor blade into two separate parts and the cut faces were pressed together. Then the sample was let to heal in a Teflon mold under different conditions. Under moderate compressions (10−30 kPa), two completely cut samples could heal effectively at room temperature or even under cooling condition. In the following, we describe our detailed self-healing studies of this system under various conditions (different catalyst loading, compression pressure, temperature, etc.).

Effects of Ru Catalyst Loading on Healing Efficiency. First, we investigated the self-healing efficiency of PBD network loaded with different amounts of the Ru catalyst (Figure 1). All cut samples were healed in mold at room temperature under 20 kPa of compression. At 0.010 and 0.0075 mol% Ru catalyst loading, the cut samples self-healed completely and recovered their original mechanical properties after 1 and 3 h healing, respectively (Figure 1A,B). The quantitative healing was also evidenced by the observation that, during the tensile tests, the healed samples finally broke statistically at different positions instead of just at the healing interface. At the lowest catalyst loading (0.0050 mol%), the sample healed at a slower rate, but still recovered 95% of the ultimate tensile strength after 6 h of healing (Figure 1C). As expected, higher catalyst loading accelerates the self-healing process because more Ru catalyst should speed up olefin metathesis reaction at the healing interface. For all three samples, self-healing occurred faster in the beginning and then gradually leveled off (Figure 1D). Presumably, initial olefin metathesis reaction at the healing interface would contribute more effectively to new bonds formation between the two cut surfaces. With an increasing number of bonds forming between the healing surfaces, olefin metathesis reactions in later stage would contribute less to new bonds formation between the interfaces. As will be discussed later (Figure 5B), the catalyst-free control PBD network only shows minimal healing capability (*vide infra*).

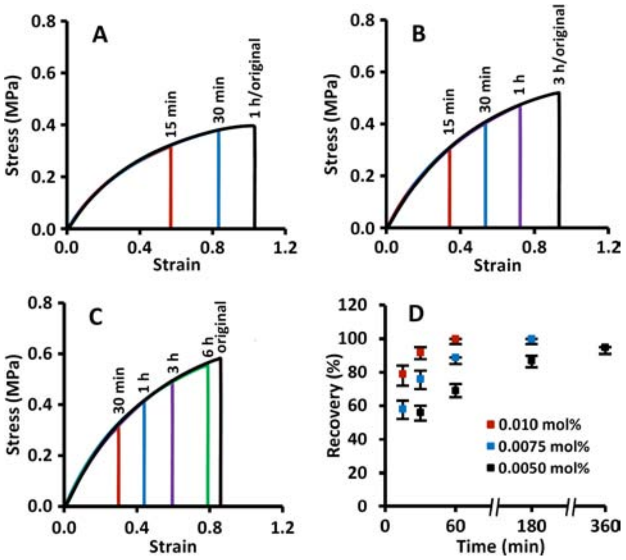

Figure 1. Self-healing data of cross-linked PBD with Ru catalyst loading of 0.010 (A), 0.0075 (B), and 0.0050 mol% (C), healed at 20 kPa pressure and room temperature (22 °C). Tensile tests were conducted after different healing times. Colored vertical lines indicate elongation at break for the given healing times. The last vertical line in black always represents the strain at break for the original sample. For samples with complete healing, the final healing curves superimpose with the stress−strain curves of the original samples, which are labeled as "# h (final healing time)/original". (D) Percentage recovery of tensile stress with time for PBD network with different catalyst loading at the healing conditions specified above.

Effects of Pressure on Healing Efficiency. Next, we investigated the effect of compression pressure on self-healing efficiency of the materials. Thus, we applied 10, 20, and 30 kPa of compression pressure, respectively, to two freshly cut specimens with 0.0075 mol% of Ru catalyst loading and let the sample heal at room temperature. As shown in Figure 2, a moderate pressure is necessary for the healing and the sample heals more efficiently at higher compression pressure. For example, the strain at break recovered to respective 45, 78, and 90% of the original sample after 1 h of healing under compression pressure of 10, 20, and 30 kPa, respectively (Figure 2). A couple of factors should be noted here. First, as a covalent 3D network, the cross-linked PBD chains have limited long-range translational mobility at the fracture interface to facilitate the healing process. Second, as a very nonpolar polymer for PBD, there are no strong molecular interactions to spontaneously attract the two cut surfaces together. Third, our healing experiments were conducted at room temperature or under cooling conditions, without inputting any external energy in heat or light. Given the microscopic roughness of the cut surfaces and the three factors discussed above, a moderate pressure is necessary to bring the two cut surfaces into molecular contact so that olefin cross metathesis between the two surfaces can occur. Higher compression pressure (Figure 2A) would bring more polymer chains from the two cut surfaces into molecular contact, hence more efficient metathesis between the two surfaces and faster healing.

Effects of Temperature on Healing Efficiency. To find out if such self-healing materials would be generally applicable at ambient conditions, we then investigated the temperature

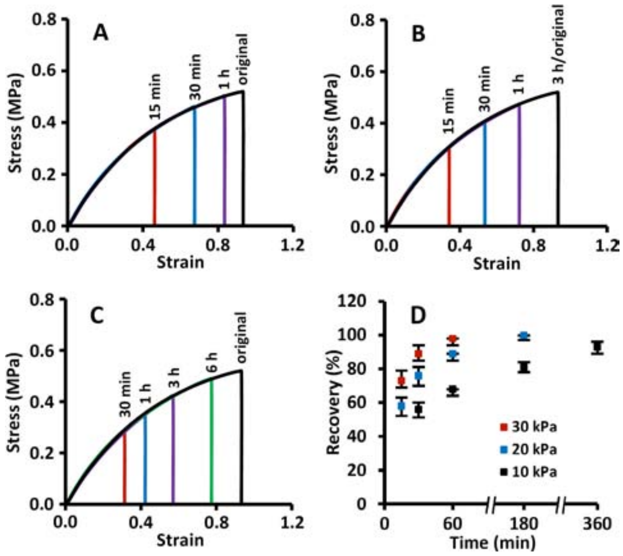

Figure 2. Self-healing data of cross-linked PBD with 0.0075 mol% Ru catalyst loading at different compression pressure, (A) 30, (B) 20, and (C) 10 kPa, at room temperature (22 °C). All labels and format follow the same as Figure 1. (D) Percentage recovery of tensile stress with time for the same samples at different compression pressure at room temperature.

dependence of their self-healing behavior. First, the temperature dependence of the Ru catalyst activity was studied via bulk stress relaxation experiments,[35] which shows that the relaxation time of the materials decreases with increasing temperature (Figure 3A). Quantitative correlation of viscosity–temperature data follows a simple Arrhenius law[36] with activation energy of 25.8 kcal/mol, a value agreeing well with literature reported value (23.0 ± 0.4 kcal/mol) for olefin metathesis reaction using the same catalyst.[37] Based on this activation energy value, the olefin metathesis reaction is estimated to accelerate by ~5 times for every increase of 10 °C.

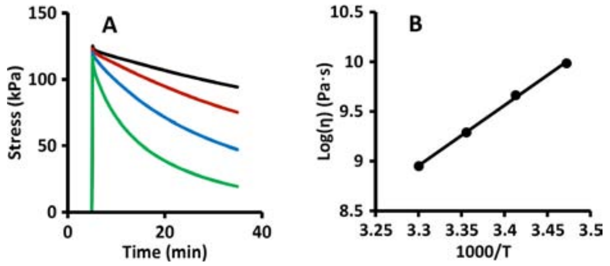

Figure 3. (A) Stress relaxation profiles of the PBD network loaded with 0.0075 mol% Ru catalyst at different temperatures (black line, 15 °C; red line, 20 °C; blue line, 25 °C; green line, 30 °C). 10% of strain was applied at $t = 5$ min and the relaxation was conducted for 30 min. (B) The temperature dependence of zero-shear viscosity.

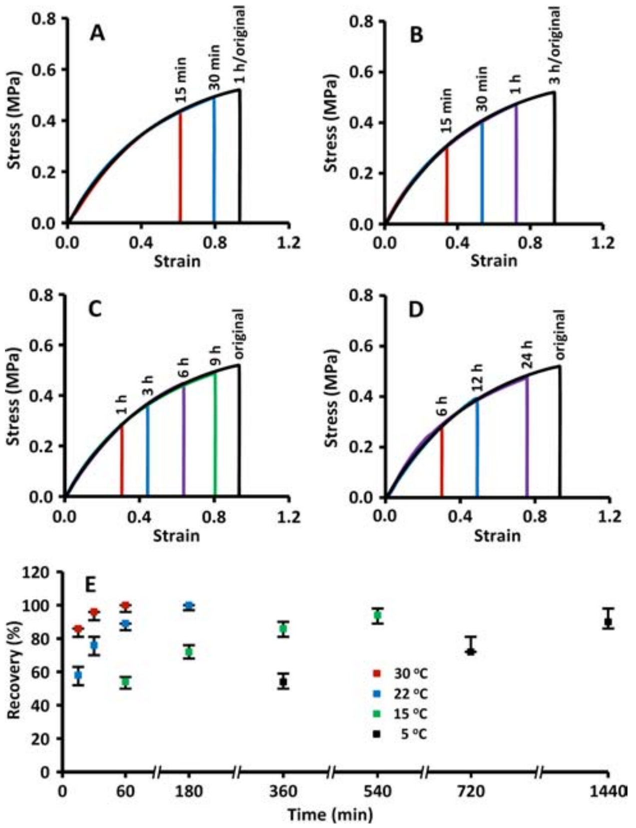

Figure 4. Self-healing data of PBD network with 0.0075 mol% Ru catalyst loading. Two freshly cut surfaces were pressed together at 20 kPa and let heal at 30 (A), 22 (room temperature) (B), 15 (C), and 5 °C (D). Tensile tests were conducted after different healing times. All labels and format follow the same as Figure 1. (E) Percentage recovery of tensile stress with time for the same samples healed at different temperatures.

We then carried out self-healing tests on a PBD sample at four different temperatures: 5, 15, 22 (room temperature), and 30 °C. At constant catalyst loading (0.0075 mol%) and compression pressure (20 kPa), the sample healed faster at higher temperature (Figure 4). For example, while it takes 3 h to fully heal the sample at room temperature (Figure 4B), a slight heat (30 °C) enabled the sample to completely heal after only 1 h (Figure 4A). This can be attributed to the accelerated olefin metathesis reaction at higher temperature as discussed previously (Figure 3). Capitalizing the high healing efficiency of this system, we further tested healing at cooling condition. While cooling decreases the catalyst activity and slows down the healing process, the sample could still recover ~94% and ~90% of tensile strength at 15 °C after 9 h (Figure 4C) and 5 °C after 24 h (Figure 4D), respectively. To our knowledge, this is the first example of a dynamic covalent polymer that can self-heal efficiently at sub-ambient temperature. The quantitative comparison of temperature-dependence for self-healing efficiency for this sample is shown in Figure 4E.

High Effectiveness of Self-Healing via Olefin Metathesis. The effectiveness and high healing efficiency of this system was further demonstrated by the following experiment in which a Ru-loaded sample healed with a corresponding control PBD sample with the Ru catalyst removed by treating with vinyl ether.[37,38] We reasoned that with one surface containing the Ru catalyst, olefin metathesis reaction could still occur at the interface, forming new C–C bonds to connect with the other surface containing no Ru catalyst. Indeed, at room temperature and 20 kPa pressure, the Ru-loaded sample healed with the Ru-free samples with time (Figure 5A). After 3 h of healing, the sample recovered ~80% of the maximal strain. This offers a promising new strategy for healing mechanical damages: filling the crack of a normal catalyst-free PBD network with PBD containing a small amount of the Ru catalyst, olefin metathesis between the catalyst-free surface of the fractured sample and the newly added Ru-loaded PBD

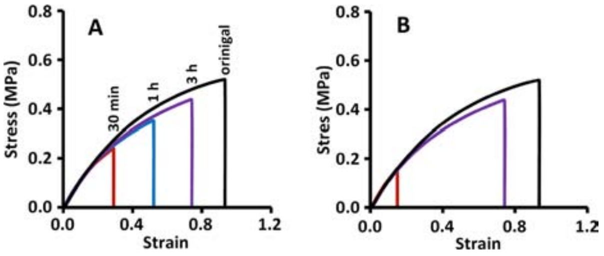

Figure 5. (A) Healing test of 0.0075 mol% Ru-loaded PBD sample and Ru-free control PBD at normal healing condition (compression pressure 20 kPa, 22 °C). (B) Comparison of self-healing profiles of Ru-free control (red), Ru-loaded (0.0075 mol%)/Ru-free control (purple), and Ru-loaded/Ru-loaded (black) samples after 3 h of healing time.

would result in covalent healing of the crack. In sharp contrast, two pieces of freshly cut Ru-free control sample showed only minimal healing capability (Figure 5B, ~15% recovery of the maximal strain). Presumably, the minimal healing of the control sample could be due to diffusion of some long dangling polymer chains across the interface.[39] It should be noted that the cross-linked PBD networks used in this study contain minimal soluble polymers. We quantitatively investigated the fraction of soluble polymers for Ru-loaded PBD networks by repetitive extraction with a good solvent, *n*-heptane. For example, for the most commonly used PBD samples in this study (Ru loading of 0.0075 mol%), we observed 2.7, 1.0, and 0.8% weight loss, respectively, after three cycles of 1-h extractions. Based on this data, we conclude that the contribution of diffusion of soluble polymers to healing should be insignificant, which agrees with the minimal healing observed for the control sample (Figure 5B).

Finally, the high effectiveness of olefin metathesis for self-healing is demonstrated by another experiment. Instead of loading the Ru catalyst to the bulk sample, we applied a small amount of Ru catalyst only to the fracture surfaces of a pristine PBD network containing no Ru catalyst. Since healing occurs at the fracture interfaces, we reasoned that only a small amount of Ru catalyst at the fracture interface is necessary to catalyze the C═C bond metathesis between the two surfaces for healing. In one set of tests, we evenly applied 1.25, 2.5, and 5.0 μg of Ru catalyst, respectively, onto both fracture surfaces (10 mm × 2 mm), which were subsequently pressed together at 20 kPa for healing (Figure 6A). In another set of experiments, the same total amounts of Ru catalyst were applied to only one fracture surface, which was then pressed to a pristine PBD cut surface without any catalyst (Figure 6B). Visually, the colored Ru catalyst resides only at the fracture interface. In both cases, the samples healed very effectively (Figure 6). In sharp contrast, the identical samples without applying any Ru catalyst at fracture interfaces showed very minimal healing (red curves in Figure 6).

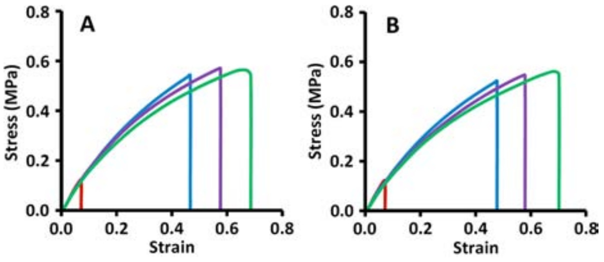

Figure 6. (A) Healing result of pristine PBD samples with 0 (red), 1.25 (blue), 2.5 (purple), and 5.0 μg (green) of Ru catalyst respectively applied onto both fracture surfaces (10 mm × 2 mm). (B) Healing result of pristine PBD samples with 0 (red), 2.5 (blue), 5.0 (purple), and 10.0 μg (green) of Ru catalyst respectively applied onto only one single fracture surface (10 mm × 2 mm). The two cut pieces were pressed together at 20 kPa and let heal at room temperature for 3 h.

Besides further demonstration of the effectiveness of our healing method via olefin metathesis, this last result is significant for a few reasons. First, by applying Ru catalyst only to fracture surfaces, self-healing can be achieved without introducing malleability into the bulk sample. As we demonstrated previously, loading Ru catalyst into a bulk PBD network makes it malleable.[35] While malleability is beneficial for some applications, shape persistence is desirable for some other applications. By applying a very small amount of Ru catalyst only onto the fracture interfaces, this provides an option to achieve effective self-healing while maintaining shape persistence. Indeed, we did not observe any appreciable shape change for samples during these healing tests. Second, this new approach not only reduces the catalyst quantity, but, more importantly, offers a practical method to heal pristine PBD networks without requiring any pre-treatment for the bulk samples.

■ CONCLUSION

In summary, we report here the first example of an olefin metathesis-mediated self-healing polymer based on dynamic exchange of strong covalent C−C double bonds. Due to the high healing effectiveness and efficiency, for the first time a bulk polymer could effectively heal via dynamic covalent bond formation at sub-ambient temperature. Upon introduction of a very low level of the Grubbs' second-generation Ru metathesis catalyst and application of a moderate pressure, a commodity PBD network self-heals effectively in air under various temperatures. We investigated the effect of concentration of catalyst, compression pressure, and temperature on the self-healing efficiency of the material. We also observed that the materials heal not only with themselves but also with control samples without any Ru catalyst. Furthermore, Ru-free PBD samples can be healed effectively by applying a very small amount of Ru catalyst only to the fracture surfaces, which allows self-healing to be achieved without compromising shape persistence. The approach is simple, effective, and potentially applicable to a wide range of olefin-containing polymers such as polyisoprene, butyl rubber, polynorbornene, and other polymers containing double bonds amenable for metathesis. Given the strength of C−C double bonds, this method may offer the possibility of designing strong self-healing polymers.

■ EXPERIMENTAL METHODS

General. All the chemicals were obtained from commercial vendors and used as received without further purification. Polybutadiene (PBD) was purchased from Aldrich with an average M_w of 200−300 kDa, with 99% of *cis*-1,4 addition. Grubbs' second-generation catalyst was obtained from the Materia Inc. as free samples.

Sample Preparation. The Ru-loaded samples and Ru-free control samples were prepared following the same method as reported previously,[35] which is briefly described as follows. First, PBD was dissolved in dichloromethane (DCM) and then 1 mol% (relative to the molarity of double bonds in PBD) of benzyl peroxide was added to the polymer solution. The solvent was then evaporated at room temperature and the residue was molded in Teflon mold and heated at

100 °C under vacuum for 6 h. The specimens (20 mm × 10 mm × 2 mm) were then swelled in DCM and washed thoroughly to remove unreacted BPO and any byproducts. Under cooling condition using an acetonitrile/dry ice bath (−42 °C), the samples were then swelled in DCM solutions containing the Grubbs' second-generation Ru metathesis catalyst for 1 h to incorporate different amount of the Ru catalyst: 0.010, 0.0075, and 0.0050 mol% (relative to the molarity of olefin), respectively. The specimens were then dried under vacuum at room temperature for 2 h and finally subjected to self-healing tests. For control samples, the same Ru-loaded specimens were quenched in vinyl ether at room temperature for 2 h and then washed thoroughly with DCM to remove cleaved catalyst.[37,38] The specimens were then dried under vacuum at room temperature for 2 h and subjected to self-healing tests.

Mechanical Tests. The tensile mechanical properties of the polymers were measured using an Instron 3365 machine in standard stress/strain experiments. The specimens were extended at 100 mm/min at room temperature. Stress−relaxation experiments (Figure 3) were performed using a TA Instruments DMA Q800 with attached cryo accessory. A constant strain of 10% was applied at $t = 5$ min and then was maintained for 30 min at 15, 20, 25, and 30 °C.

Self-Healing Tests. *A. For self-healing tests of Ru-loaded samples:* a sample loaded with a certain concentration of the Ru catalyst (0.010, 0.0075, or 0.0050 mol%) was first cut with a razor blade and the cut faces were pressed together right after being cut. Then the samples were let to self-heal in a Teflon mold under a certain compression pressure (10, 20, or 30 kPa) and at a certain temperature (5, 15, 22 (room temperature), or 30 °C) in air. After various healing times, the samples were subjected to stress−strain tests at room temperature at 100 mm/min pulling rate.

B. For self-healing tests of a Ru-loaded sample with its corresponding Ru-free control sample: a Ru loaded sample (0.0075 mol% Ru loading) and a Ru-free control sample were first cut with a razor blade. One piece of the Ru-loaded sample and the other piece from its corresponding Ru-free control sample were pressed together right after being cut. Then they were let to self-heal in a Teflon mold at 20 kPa of compression pressure at room temperature (22 °C) in air. After various healing times, the samples were then subjected to stress−strain tests at room temperature at 100 mm/min pulling rate.

C. For self-healing tests of the control samples: the Ru-quenched controls (before quenching, the sample was loaded with 0.0075 mol% of the Ru catalyst) was first cut with a razor blade and the cut faces were pressed together right after being cut. Then they were let to self-heal in a Teflon mold at 20 kPa of compression pressure at room temperature (22 °C) in air for 3 h. The samples were then subjected to stress−strain tests at room temperature at 100 mm/min pulling rate.

D. For self-healing tests of pristine PBD samples with Ru catalyst applied only at the cut surfaces: a pristine PBD sample was first cut with a razor blade. Using a 25 μL micro syringe, a DCM solution of Ru catalyst (0.5 mg/mL) was applied onto both cut faces (2.5, 5.0, or 10 μL each face) or only one cut face (5.0, 10, or 20 μL) and then the cut pieces were let dry under vacuum for 5 min. The cut faces were then pressed together and were let to self-heal in a Teflon mold at 20 kPa of compression pressure at room temperature (22 °C) in air for 3 h. The samples were then subjected to stress−strain tests at room temperature at 100 mm/min pulling rate.

E. For self-healing tests of pristine PBD samples without any Ru catalyst: a pristine PBD sample was first cut with a razor blade. The cut faces were then pressed together right after being cut and were let to self-heal in a Teflon mold at 20 kPa of compression pressure at room temperature (22 °C) in air for 3 h. The samples were then subjected to stress−strain tests at room temperature at 100 mm/min pulling rate.

Quantitation of Soluble Polymers in PBD Networks. The Ru-loaded samples (with 0.010, 0.0075, or 0.0050 mol% Ru) were swollen in *n*-heptane for 1 h and then dried under vacuum for 12 h. The weight loss was calculated from the weights of the initial samples and of the samples after swelling and drying. The same process was repeated three times for each sample. The percentage weight losses for all samples in three cycles of extraction are as follows: 4.8, 1.5, and 1.7% weight loss for the 0.010 mol% Ru-loaded sample, 2.7, 1.0, and 0.8% weight loss for the 0.0075 mol% Ru-loaded sample, and 1.1, 0.3, and 0.4% weight loss for the 0.0050 mol% Ru-loaded sample.

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Notes

The authors declare no competing financial interest.

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