

Making Insoluble Polymer Networks Malleable via Olefin Metathesis

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S Supporting Information

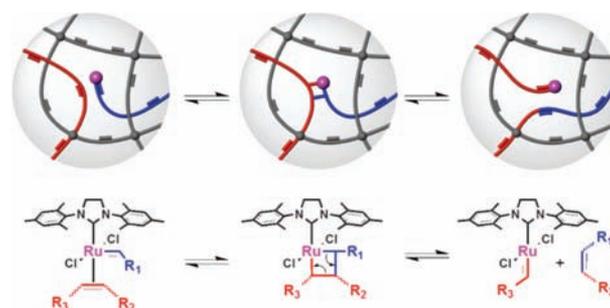
ABSTRACT: Covalently cross-linked polymers have many technological applications for their excellent properties, but they suffer from the lack of processability and adaptive properties. We report a simple, efficient method of generating adaptive cross-linked polymers via olefin metathesis. By introducing a very low level of the Grubbs' second-generation Ru metathesis catalyst, a chemically cross-linked polybutadiene network becomes malleable at room temperature while retaining its insolubility. The stress relaxation capability increases with increasing level of catalyst loading. In sharp contrast, catalyst-free control samples with identical network topology and cross-linking density do not show any adaptive properties. This chemistry should offer a possibility to combine the dimensional stability and solvent resistance of cross-linked polymers and the processability/adaptability of thermoplastics.

Covalently cross-linked polymers have many technological applications because of their excellent mechanical strength, thermal stability and solvent/environmental resistance.¹ However, one major drawback of permanently cross-linked polymers is their lack of processability because they are insoluble and infusible,² in contrast to thermoplastic polymers which can be processed repetitively. To combine the advantages of these two categories of polymers, recently, a growing effort has been devoted to introducing chemical dynamics into polymers.^{3–20}

Toward this goal, a number of elegant approaches^{3–5} have been reported by employing dynamic covalent bond networks.⁶ For example, a reversible Diels–Alder reaction was used to prepare thermally remendable polymer networks, in which an increase of temperature simultaneously shifts the equilibrium toward depolymerization and accelerates the bond breaking/reforming rate, both factors contributing to the fluidity and processability of the network but detrimental to the integrity and performance of the polymer.^{7–10} In another system, a phototriggered radical addition and fragmentation reaction was employed to introduce photoinduced plasticity in cross-linked polymers.¹¹ However, this and other dynamic covalent systems involving radical species^{12–18} cannot avoid the inherent radical termination reactions, limiting their ultimate reversibility. Recently, the concept of glass transition by topology freezing has been introduced, and it was shown that materials having this ability could behave like elastomers or thermosets at room temperature and become malleable at high temperature while keeping their insolubility.^{20,21} This concept relies on exchange

reactions that keep constant the number of cross-links and average functionality. It was initially demonstrated in an epoxy-based network through a catalytic transesterification reaction. Extending this concept to other polymers and in particular to olefin-containing polymers is both scientifically and technologically challenging. Here, we demonstrate that olefin metathesis provides a tool to induce very efficient exchange reactions and produce materials that are both insoluble and malleable at room temperature while using extremely low catalyst loadings (Scheme 1).

Scheme 1. Concept of Using Olefin Metathesis To Make Cross-Linked Polybutadiene Malleable^a



^aRu-catalyzed olefin metathesis reaction covalently rearranges the network topology without changing the number of cross-links, making an insoluble network malleable.

The olefin metathesis reaction is a powerful modern synthetic methodology with numerous applications in organic and polymer synthesis.^{22–24} Olefin-containing polymer networks—such as cross-linked polybutadiene (PBD), polystyrene, and polynorbornenes—are large volume materials with important commercial applications. Introducing olefin metathesis catalysts into such networks would provide a simple, powerful method to access an adaptive while insoluble polymer network. Mechanistically, through a metallocyclobutane intermediate (Scheme 1),^{25,26} the double bonds in the network rapidly exchange via metal-catalyzed olefin metathesis to alter the topology of the network, affording adaptive/dynamic properties; but the number of covalent bonds and cross-links remains constant all the time, maintaining the mechanical integrity and strength for the network. With appropriate catalysts, olefin metathesis reactions are versatile, highly efficient, and can tolerate functional groups. A previous report

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has shown that olefin exchange reaction occurs between linear PBD and unsaturated polyester catalyzed by the first-generation Grubbs' Ru metathesis catalyst.²⁷

In our initial study, we chose the second-generation Grubbs' Ru metathesis catalyst for its stability, high activity at ambient temperature, and good functional group tolerance.²⁶ A cross-linked PBD network based on commercially available linear PBD ($M_w = 200\text{--}300$ kDa, with 99% of cis-1,4-addition) was prepared by radical-induced cross-linking. Specifically, treating PBD with 1% benzoyl peroxide (BPO) (relative to the molarity of olefin) at 100 °C for 15 h yields permanently cross-linked rubbery polymers that were swellaible but insoluble in organic solvents. After removing any soluble species through extensive swelling/washing, the samples were then swollen in dichloromethane (DCM) solutions of the Grubbs' Ru catalyst at low temperature to incorporate 0.0050%, 0.0075%, and 0.010% of the catalyst (relative to the molarity of olefin), respectively, into the PBD network. During the equilibration at ambient temperature, metathesis between the alkylidene on the original Ru catalyst and double bonds on PBD should covalently load Ru catalyst onto the polymer network. The samples were dried under vacuum and subjected to swelling and various mechanical tests. For control studies, after testing each sample, the catalyst incorporated into the network was quenched by swelling the sample in excess vinyl ether. As reported in literature, vinyl ether should efficiently cleave Ru catalyst from polymer chain ends through cross metathesis to deactivate the Ru species.^{28,29} This provides catalyst-free but otherwise identical polymer networks for direct comparative studies.

According to previous studies,³⁰ the radical cross-linking condition employed in this study resulted in a lightly cross-linked network. This is consistent with the observation that the Young's modulus for the PBD network is lower than the value estimated from the plateau modulus of ideally cross-linked PBD.³¹ Nevertheless, all the samples are insoluble networks as demonstrated by an equilibrium swelling experiment in *n*-heptane. Minimal weight loss was observed for the catalyst-loaded samples after swelling in *n*-heptane. Upon loading the cross-linked PBD with Ru catalyst, cross metathesis with olefins on the network will initially cleave some double bonds to attach the Ru catalyst on chain ends, decreasing the effective cross-linking density. Because of relatively light cross-linking, it is inaccurate to calculate the cross-linking density using the Flory and Rehner treatment.³² Instead, we compare directly the equilibrium-swelling ratio, which is defined as the equilibrium volume ratio of the solvent swollen sample to the initial dry sample. As expected, the swelling ratios are increasing consistently with the increase of catalyst loading (Table 1). Accordingly, the Young's modulus of the samples decreases with the increase of catalyst loading. Because of the low cross-linking density of the samples, relatively low catalyst loading resulted in significant increase in swelling ratio and decrease in modulus. Notably, the static mechanical properties (modulus) for the samples with and without Ru catalyst are almost identical within experimental errors of the measurements, confirming that treatment with vinyl ether did not cause additional cross-linking. Therefore, the controls are otherwise identical polymer networks for direct comparative studies.

To reveal the adaptive properties of the Ru-loaded PBD samples, both the Ru-loaded samples and controls were subjected to various mechanical testing. First, the time-dependent strain profiles of the samples with and without Ru catalyst were compared (Figure 1). Upon applying a constant

Table 1. Swelling Ratio, Relaxation Time, and Young's Modulus

catalyst (mol %)	swelling ratio ^a	τ (min) ^b	E (MPa) ^c	
			samples	controls
0	2.13 ± 0.05	N.A.	1.76 ± 0.02	1.75 ± 0.02
0.0050	2.50 ± 0.06	50.6 ± 4.2	1.37 ± 0.02	1.34 ± 0.02
0.0075	2.63 ± 0.07	21.8 ± 1.2	1.17 ± 0.02	1.13 ± 0.02
0.010	2.86 ± 0.08	9.6 ± 0.4	0.94 ± 0.01	0.91 ± 0.01

^aSwelling experiments were conducted in *n*-heptane, 25 °C.

^bRelaxation time (τ) is calculated from time-dependent strain profiles.

^cYoung's modulus (E) was obtained from DMA at strain rate of 10 mm/min, 25 °C.

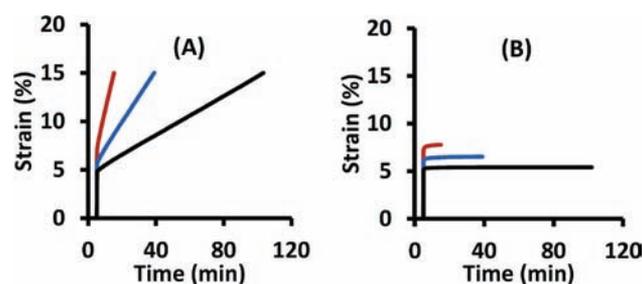


Figure 1. Strain profiles of the controls and real samples loaded with various levels of the Ru catalyst (black line, 0.0050 mol %; blue line, 0.0075 mol %; red line, 0.010 mol %). (A) for samples with catalyst, 1 N of force was applied from $t = 5$ min until the strain reached 15%. (B) for controls, 1 N of force was applied from $t = 5$ min for the same time as the corresponding samples with catalyst.

force (1 N), the Ru-loaded samples continuously reshape, with their strains increasing linearly with time (Figure 1A). Furthermore, the higher the catalyst loading for the sample, the more dramatic the strain–time dependence is. In sharp contrast, compared at the same external force (1 N) and same time scale, the strains are constant with time for all the control samples, which have identical structures and cross-linking densities to their corresponding Ru-loaded samples except without the catalyst (Figure 1B). This comparison clearly demonstrates that the Ru catalyst is responsible for the adaptability of the network. It should be stressed that the samples are insoluble networks; therefore, the observed malleability cannot be simply attributed to viscous flow of polymer chains. Otherwise, we should expect to see similar behavior in the Ru-free control samples. As illustrated in Scheme 1, the Ru catalyzes rapid exchange between the double bonds to alter the cross-linking topology, allowing the network to constantly reshape to relax the stresses.³³ At higher catalyst loading, the rates of bond shuffling via olefin metathesis are higher, and fewer exchanges are needed to alter the network topology due to a lower cross-linking density. Both factors contribute to the more pronounced strain dependence on time as observed. The variation in the degree of strain for samples with different catalyst loading is due to the difference in cross-linking density of the networks. As explained previously, higher catalyst loading results in lower cross-linking density and thus higher degree of strain at constant force. The relaxation times were then calculated from the following equations:

$$\eta = \sigma / \dot{\epsilon}, \quad \tau = \eta / E$$

where η is the viscosity (Pa·s), σ is the stress applied (Pa), $\dot{\epsilon}$ is the equivalent plastic strain rate (s^{-1}), E is the Young's modulus

(Pa), and τ is the relaxation time (s) (Table 1). The strong dependence of the stress relaxation time on Ru loading can be explained by the fact that (1) more covalent exchange occurs at higher catalyst loading because more catalyst is present, and (2) more catalyst brings the system closer to the gelation threshold and less exchanges are needed to relax stress.

Next, we tested the reversibility of deformation-shape recovery for samples upon applying and removing external forces. Classical cross-linked rubbers deform upon applying external force and recover to their original shapes after removal of forces. However, for our Ru-loaded samples, the double bonds in the PBD backbone should constantly exchange via Ru catalyzed olefin metathesis reaction, allowing the network to constantly rearrange the network topology to adapt to the applied forces. When the stress was released, the covalently rearranged network topology would not allow the sample to return to its original shape. This irreversibility has been clearly shown in our cyclic strain/recovery experiments (Figure 2). For

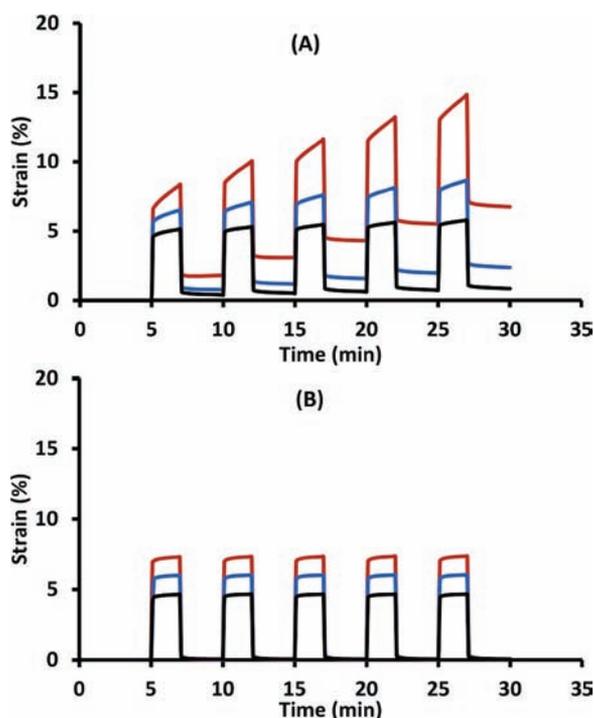


Figure 2. Cyclic strain/recovery profiles of the controls and real samples loaded with various levels of the Ru catalyst (black line, 0.0050 mol %; blue line, 0.0075 mol %; red line, 0.010 mol %). The force was alternated between 1 N for 2 min and 0 N for 3 min from $t = 5$ min to $t = 30$ min. (A) Samples with catalyst; (B) controls.

all Ru-loaded samples, irreversible strain recovery is clearly observed (Figure 2A), with the sample having higher Ru loading exhibiting more pronounced irreversibility. In contrast, in the absence of the Ru catalyst, all the control samples returned to their original length after the stress was released (Figure 2B). On the basis of the data in Figure 2A, we calculated the moduli of the samples in each loading step from each respective stress and strain. It is worth noting that the modulus did not change during the cyclic test for the Ru-loaded samples, consistent with our premise that the cross-linking density of the samples did not change during olefin-metathesis (see Supporting Information, Table S3).

Furthermore, stress relaxation experiments were performed by deforming the samples to certain strains and then monitoring their relaxation of the resulted stresses. Whereas the stresses were mostly retained for the control samples during the experimental time (Figure 3B), the Ru-loaded samples

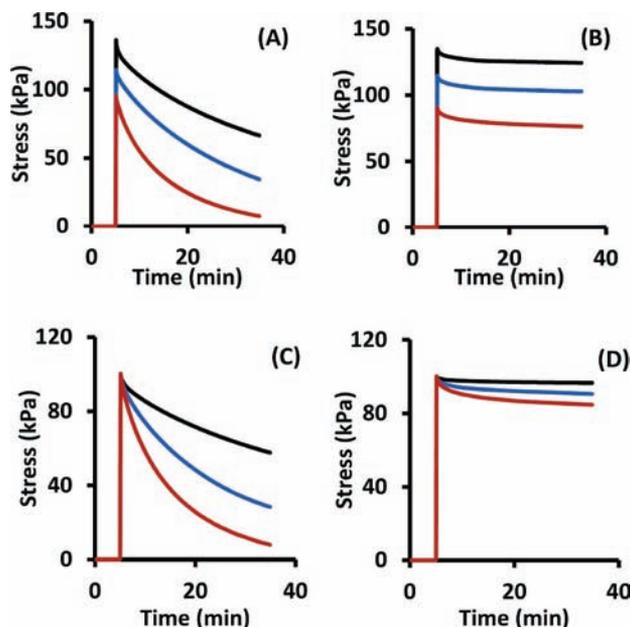


Figure 3. Stress relaxation profiles of the controls and real samples loaded with various levels of the Ru catalyst (black line, 0.0050 mol %; blue line, 0.0075 mol %; red line, 0.010 mol %). (A,C) samples with catalyst; (B,D) controls. (A,B) constant strain; (C,D) constant initial stress. The strain or stress was applied at $t = 5$ min and the relaxation was conducted for 30 min.

undergo substantial stress relaxation with time (Figure 3A). The relaxation is exponential and gives relaxation times comparable to the values measured in a creep experiment (Table 1). Because the network structure and cross-linking density remain constant during the process, the stress relaxation must be attributed to chemical effects; that is, the double bond exchanges via metathesis. To demonstrate more clearly the impact of catalyst loading, stress relaxation experiments were also conducted at constant initial stress (Figure 3C,D). At a constant initial stress of 100 kPa, both the rate and degree of stress relaxation of Ru-loaded samples increase with increasing catalyst load, consistent with other observations discussed previously. On the contrary, all the control samples exhibit relatively small stress relaxation under identical conditions (Figure 3D). Owing to relatively light cross-linking in the network, residual stress relaxation with time was observed in control samples due to defects in the network, and more stress relaxation was seen for the control with more defects.

In summary, we report here a simple, efficient method of generating malleable, insoluble polymer networks via olefin metathesis. By introducing very low levels of the Grubb's second-generation Ru metathesis catalyst, a chemically cross-linked insoluble PBD network exhibits adaptive behavior without compromising its mechanical properties. A variety of mechanical tests, including time-dependent strain profile, cyclic strain recovery, and stress relaxation, have clearly demonstrated the adaptive and dynamic properties for the Ru-loaded PBD samples. In sharp contrast, catalyst-free control samples having

identical network structure and cross-linking density do not show malleability. The dramatic different behavior for the otherwise identical, insoluble PBD networks with and without the Ru catalyst suggests that the malleability of the Ru-loaded samples must arise from Ru-catalyzed olefin metathesis reactions. Such materials may combine the mechanical strength of cross-linked polymers and the processability/adaptability of noncross-linked polymers to produce malleable, insoluble networks. Given the simplicity, efficiency, and abundance of olefin-containing polymers, this method may find broad applications in designing responsive materials. The possibility of deactivating the catalyst offers a powerful method to restore permanent elastomeric properties after processing.

■ ASSOCIATED CONTENT

📄 Supporting Information

All experimental details including sample preparation and characterization. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Ferry, J. *Viscoelastic Properties of Polymers*; Wiley: New York, 1980.
- (2) Billmeyer, F. W. *Textbook of Polymer Science*; 3rd ed.; Wiley: New York, 1984.
- (3) Kloxin, C. J.; Scott, T. F.; Adzima, B. J.; Bowman, C. N. *Macromolecules* **2010**, *43*, 2643–2653.
- (4) Maeda, T.; Otsuka, H.; Takahara, A. *Prog. Polym. Sci.* **2009**, *34*, 581–604.
- (5) Wojtecki, R. J.; Meador, M. A.; Rowan, S. J. *Nat. Mater.* **2011**, *10*, 14–27.
- (6) Rowan, S. J.; Cantrill, S. J.; Cousins, G. R. L.; Sanders, J. K. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2002**, *41*, 898–952.
- (7) Zhang, Y.; Broekhuis, A. A.; Picchioni, F. *Macromolecules* **2009**, *42*, 1906–1912.
- (8) Adzima, B. J.; Aguirre, H. A.; Kloxin, C. J.; Scott, T. F.; Bowman, C. N. *Macromolecules* **2008**, *41*, 9112–9117.
- (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) Reutenauer, P.; Buhler, E.; Boul, P. J.; Candau, S. J.; Lehn, J. M. *Chem—Eur. J.* **2009**, *15*, 1893–1900.
- (11) Scott, T. F.; Schneider, A. D.; Cook, W. D.; Bowman, C. N. *Science* **2005**, *308*, 1615–1617.
- (12) Amamoto, Y.; Kamada, J.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 1660–1663.
- (13) Canadell, J.; Goossens, H.; Klumperman, B. *Macromolecules* **2011**, *44*, 2536–2541.
- (14) Ghosh, B.; Urban, M. W. *Science* **2009**, *323*, 1458–1460.
- (15) Higaki, Y.; Otsuka, H.; Takahara, A. *Macromolecules* **2006**, *39*, 2121–2125.
- (16) Nicolay, R.; Kamada, J.; Van Wassen, A.; Matyjaszewski, K. *Macromolecules* **2010**, *43*, 4355–4361.

- (17) Park, H. Y.; Kloxin, C. J.; Scott, T. F.; Bowman, C. N. *Macromolecules* **2010**, *43*, 10188–10190.
- (18) Yoon, J. A.; Kamada, J.; Koynov, K.; Mohin, J.; Nicolay, R.; Zhang, Y.; Balazs, A. C.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2011**, *45*, 142–149.
- (19) Zheng, P.; McCarthy, T. J. *J. Am. Chem. Soc.* **2012**, *134*, 2024–2027.
- (20) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. *Science* **2011**, *334*, 965–968.
- (21) Capelot, M.; Montarnal, D.; Tournilhac, F.; Leibler, L. *J. Am. Chem. Soc.* **2012**, DOI: 10.1021/ja302894k.
- (22) Grubbs, R. H. *Tetrahedron* **2004**, *60*, 7117–7140.
- (23) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413–4450.
- (24) Schrock, R. R. *J. Mol. Catal. A: Chem.* **2004**, *213*, 21–30.
- (25) Jean-Louis Hérisson, P.; Chauvin, Y. *Die Makromol. Chem.* **1971**, *141*, 161–176.
- (26) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2009**, *110*, 1746–1787.
- (27) Otsuka, H.; Muta, T.; Sakada, M.; Maeda, T.; Takahara, A. *Chem. Commun.* **2009**, 1073–1075.
- (28) Maynard, H. D.; Okada, S. Y.; Grubbs, R. H. *Macromolecules* **2000**, *33*, 6239–6248.
- (29) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543–6554.
- (30) Gent, A. N.; Zhang, L. Q. *J. Polym. Sci., Part B* **2001**, *39*, 811–817.
- (31) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630–2643.
- (32) Sperling, L. H. *Introduction to Physical Polymer Science*, 4th ed.; John Wiley & Sons: Bethlehem, PA, 2006.
- (33) Leibler, L.; Rubinstein, M.; Colby, R. H. *J. Phys. II (France)* **1993**, *3*, 1581–1590.