An Eco-Friendly Scheme for the Cross-Linked Polybutadiene Elastomer via Thiol–Ene and Diels–Alder Click Chemistry

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ABSTRACT: We reported a novel method of producing the cross-linked polybutadiene elastomer which could be thermally recycled like the plastic materials without the sacrifice of functional utility. The commercial polybutadiene was first attached with furan via thiol–ene reaction, and the cross-linked network was then built via Diels–Alder click reaction between the bismaleimide and attached furan groups from polybutadiene. The obtained polymer had good solvent resistance from ambient temperature to 100 °C. The mechanical properties of modified polybutadiene could be tailored by the amount of attached furan and the ratio of furan to bismaleimide. Furthermore, the dynamic cross-linked polybutadiene had good thermally remolded and self-healing behaviors. By this method, the dynamic cross-linked polybutadiene could be recycled to use in a sustainable way. Concerning all the raw materials were available in large quantities without tedious and multistep synthetic routes, this work demonstrated the high performance recycling solution to the commercial cross-linked polybutadiene, which might be applied in industry in relatively short time.

INTRODUCTION

Nowadays, rubbers have been widely used in various fields, including transport vehicles, sports equipment, building materials, etc. The consumer demands drive the increased production of the rubber materials, and people have produced about 11 million tons of rubber in 2013. However, the discarded or damaged rubber cannot be reprocessed again to produce new rubber products due to its cross-linking structure where all the chains of rubber lose their ability of movement, so that they can only thermally decompose at high temperature. Therefore, it is still difficult to break down the thermodynamically irreversible network of the rubber to produce a valuable recycled material. Consequently, this huge amount of waste rubber material is an environmental problem of great concern. By now, a widely used way to treat this cross-linked rubber is to blend ground discarded rubber with virgin material followed by the cross-linking reaction. However, the discarded or damaged rubber cannot be reprocessed again to produce new rubber products due to its cross-linking structure where all the chains of rubber lose their ability of movement, so that they can only thermally decompose at high temperature. Therefore, it is still difficult to break down the thermodynamically irreversible network of the rubber to produce a valuable recycled material. Consequently, this huge amount of waste rubber material is an environmental problem of great concern. By now, a widely used way to treat this cross-linked rubber is to blend ground discarded rubber with virgin material followed by the cross-linking reaction. But the main disadvantage of this recycling technique is bad adhesion between the crumb and matrix of virgin rubber material due to poor interfacial action. As a result, it is highly desirable to design the reversible dynamic cross-linked rubber with cross-linked structure maintained at operating temperature and unlocked at high temperature to liberate the cross-linked chains of the rubber. In this sustainable way, the cross-linked rubber can be remolded just like plastic materials, and people can reduce the consumption of petroleum-based raw materials and save the nonrenewable resources by recycling the rubber. Today, to design the cross-linked resins in the dynamic way has become a hot research area, and people have designed several kinds of new recyclable cross-linked epoxy and polyurethane materials based on Diels–Alder click reaction in the lab. The Diels–Alder (DA) click reaction can undergo between a conjugated diene and a dienophile resulting in a cyclohexene derivative at room temperature to about 100 °C. In the meantime, the cross-linked DA adducts can undergo a reverse reaction typically at temperatures above 120 °C to produce the raw materials which is known as a retro-Diels–Alder (rDA) reaction. For example, the Sun research group has designed a new kind of polyurethane with maleimide pendant chain extender and the furan cross-linkers; dynamic
cross-linked polyurethane with good mechanical properties was obtained, and it could be recycled at high temperature effectively. However, up to now, few research works have been reported on the commercial available olefin rubber with good recycling ability. Unlike the cross-linked epoxy and polyurethane resins where considerable molecular-selection flexibility can allow great freedom to design dynamic cross-linked network, there are almost no active bonding sites for rubber to attach functional groups for forming dynamic cross-linking network. Only double bonds, which are used as anchor for the cross-linked network, can be selected for chemical modification. Inspired by the chemical reactivity of doubling bonds (ene) toward sulfur derivative (thiol), we modify the chains of rubber through the addition reaction between thiol and vinyl groups, also called thiol–ene click reaction. The highly efficient reaction between C=C and thiol groups under UV irradiation can proceed in mild conditions without the protection of chemical inertness atmosphere. In this paper, we first attached the furan groups onto the chains of olefin elastomer via thiol–ene click reaction, and then the modified rubber was cross-linked to form the network in the presence of bismaleimide. By this way, the cross-linked olefin elastomer has dynamic cross-linked network.

The primary novelties for this paper include (1) expanding the thermally reversible cross-linked structure based on the DA-reaction into the commonly used elastomer materials, (2) the cross-linked elastomer could be easily remolded to produce new products, and (3) properties of the cross-linked network could be tailored by adjusting the grafting ratio of furan groups (RF) and the ratio of furan to maleimide (RFM). Therefore, the comprehensive properties can be designed with great freedom to meet the various requirements in application, overcoming the shortcoming that improving the environmental suitability of materials comes with a sacrifice in material other properties.

### EXPERIMENTAL SECTION

**Materials.** Toluene was purchased from Sinopharm Chemical Reagent Co., Ltd. Bismaleimide was purchased from TCI Chemical CO., Ltd. Polybutadiene (PB) (Mn ~ 200 000) was purchased from Sigma-Aldrich. Furfuryl mercaptan was purchased from J&K Scientific Ltd. All the reagents were used as received.

**Chemical Modification of Polybutadiene with Furfuryl Mercaptan (PB-Fu).** Polybutadiene, furfuryl mercaptan, and the photoinitiator I907 were dissolved in toluene. The addition of furan groups was changed according to the double bond content of PB chain. Take the sample PB-10Fu for example; the addition of furfuryl mercaptan was
where RFM was varied and RF was fixed at 1:1; the other was the PB-3F system where RFM was varied and RF was fixed at 30%. The recipes for different samples are shown in Table S2. (It was proved with elemental analysis that the branch ratio of the furan groups was almost the same as the addition of furfuryl mercaptan as shown in Table S3.)

Preparation of the Films. Bismaleimide was added into the PB-Fu solution. After homogeneous mixing, the solution was cast onto glass plates and dried in an air oven at 100 °C. Then the solution was irradiated with UV light for 12 h and magnetically stirred at room temperature. Modified PB with different grafting molar ratio of furan were obtained including 10%, 12%, 14%, 16%, 18%, 20%, and 30%. The recipes for different samples are shown in Table S2. (It was proved with elemental analysis that the branch ratio of the furan groups was almost the same as the addition of furfuryl mercaptan as shown in Table S3.)

Figure 1. Gel fraction and the swelling ratio of the PB-FM (A) and PB-3F (B) series.

In this paper, a typical example of olefin-based rubber, the butadiene elastomer (PB), was selected for investigation. The general modification and cross-linking reaction are shown in Scheme 1. We first attached the furan group onto the chains of the butadiene based rubber via thiol–ene reaction, and then the furan-modified PB (PB-Fu) was further cross-linked with bismaleimide based on the DA reaction on the solution method.

Structure Analysis of Furan Modified PB by NMR and FTIR. The structure of the furan functional PB was first characterized by 1H NMR. As shown in Figure S1A, the peaks at δ = 6.34, 6.28, and 7.35 ppm were assigned to the protons a, b, and c of the furan ring separately. The peak at δ = 3.68 was the signal of the proton connecting to the carbon atom between furan ring and sulfur. The signal between 5.30 and 5.50 belonged to the proton connecting to the carbon atom between furan ring and sulfur. The signal between 5.30 and 5.50 belonged to the proton connecting to the carbon atom between furan ring and sulfur.

RESULTS AND DISCUSSION

In this paper, a typical example of olefin-based rubber, the butadiene elastomer (PB), was selected for investigation. The general modification and cross-linking reaction are shown in Scheme 1. We first attached the furan group onto the chains of the butadiene based rubber via thiol–ene reaction, and then the furan-modified PB (PB-Fu) was further cross-linked with bismaleimide based on the DA reaction on the solution method.
exhibited new characteristic absorption peaks at 1240 and 1148 cm⁻¹, which was closely related to the furan group. Therefore, based on these spectral analyses, it was verified that furan groups have been successfully grafted to the chain of PB via thiol–ene reaction.

**Solubility Behavior for the Cross-Linked Elastomer.**
Since the linear and cross-linked structures were quite different in their solubility, change in solubility of the furan modified PB elastomer in toluene could be used as the first direct evidence to prove that the modified polybutadiene was actually cross-linked via DA reaction between bismaleimide and furan groups to form tridimensional polymer networks. As shown in Scheme 1, it was observed that the furan-modified PB showed good solubility in toluene. However, after reacting with bismaleimide, the PB could only swell in the toluene. Such comparison proved that the PB rubber was successfully cross-linked with the presence of bismaleimide. Meanwhile, the cross-linking degree of PB rubber could be investigated by its gel fraction and swelling ratio. As shown in Figure 1A for the PB-FM system, it was observed that the gel fraction and swelling degree were 77.3% and 3.38, respectively, as RF was about 10% (PB-FM-10). With increasing RF up to 20% (PB-FM-20), the gel fraction for the cross-linked PB rubber was increased to 99.6% and its swelling ratio was decreased to 2.30. For the PB-3F system, it was also found that increasing RFM could increase the gel fraction and decrease the swelling ratio. The results from the analysis of solubility showed that the cross-linking degree for PB elastomer was easily adjusted by changing RF and RFM, which was convenient for us to investigate mechanical properties of the cross-linked PB rubber by tailoring the amount of grafted furan and bismaleimide.

**Analysis of Morphology for the Cross-Linked PB Elastomer.** AFM could easily detect the hard and soft phases based on their different hardness. Commonly, cantilever oscillation acting on hard surface lost energy and generated smaller phase contrast. Hence, the hard phase was the brighter region reflecting in the phase image. On the contrary, the soft domain was reflected as the dark region. In this system, the cross-linking domains based on the DA reaction between bismaleimide and furan were hard phase. Therefore, the brighter domains correspond to the cross-linking domains (FM phase), and the darker domains correspond to the part of polybutadiene (PB phase). In order to understand the effects of RF and RFM on microstructural morphology, AFM phase images were taken on these two systems. As shown in Figure 2 for the PB-FM system, only bright spherical particle domains attributed to the hard phase (the cross-linking domains) were observed, and the hard domains protruded from the PB phase. The diameter of particle was about 30–50 nm for PB-10FM. With increasing RF content, the size of particles was gradually decreased, and the boundary of particles become obscure with more homogeneous morphology obtained.

The morphology of the PB-3F system is shown in Figure 3. As the RFM was below 40%, only soft phase almost covered the whole surface without obvious phase separation; with further increasing RFM, the hard phase gradually protruded from the soft phase and phase separation structure was obtained.

**Mechanical Properties for the Cross-Linked PB.** Figures 4A and 4D show the tensile stress versus strain curves at room temperature for these two series, and the derived mechanical data are summarized in Tables S7 and S8. As shown in Figure 4A for PB-FM, it was found that increasing grafting RF from 10% to 30% could increase the modulus and decrease the ultimate strain for the cross-linked PB. For example, as RF was increased from 10% to 30%, the modulus was increased from 14.0 to 48.4 MPa, while the ultimate strain was decreased from 80.6% to 44.8% with breaking stress shifting around 4.60 MPa. The main reason for this phenomenon was that increasing RF would lead to increasing cross-linking degree, which finally resulted in increase in the strength and modulus and decrease in strain. For the PB-3F system, a very interesting phenomenon would be observed, which was quite different from PB-FM. As RFM was 10% (PB-3F-10M), the breaking stress and modulus were 1.92 and 2.0 MPa, which were quite lower than those for PB-FM. However, its ultimate strain was 342.5%, much higher than that for PB-FM. With further increasing RFM up to 60% (PB-3F-80M), the breaking stress and modulus for were respectively increased to 5.53 and 45.2 MPa and the ultimate strain was decreased to 44.6%, and these data were quite similar to those for PB-FM-20. Therefore, difference in the mechanical behaviors between PB-FM and PB-3F was decreased with enhancement RFM, which was closely related to their phase structure. For PB-FM, as shown in the results from AFM, the soft PB and hard cross-linking domains were observed, indicating that phase separation was found for PB-FM. Therefore, the sample showed the characteristic “strong” elastomer with high modulus and low ultimate strain (<100%) due to the appearance of the hard domains. However, for the PB-3F system, as RFM was below 60%, only soft PB domains were observed in AFM, which finally resulted in “soft” elastomer with low modulus and high ultimate strain. As RFM was up to 60%, AFM phases showed that phase separation occurred with the appearance of hard cross-linking domains.

![Figure 2. AFM phase images of different samples including (A) PB-FM-10, (B) PB-FM-12, (C) PB-FM-14, (D) PB-FM-16, (E) PB-FM-18, and (F) PB-FM-20.](image-url)

![Figure 3. AFM phase images of different samples including (A) PB-3F-10M, (B) PB-3F-20M, (C) PB-3F-30M, (D) PB-3F-40M, (E) PB-3F-60M, (F) PB-3F-80M, and (G) PB-3F-100M.](image-url)
Therefore, the modulus increased greatly, as accompanied by decreased ultimate strain (<100%). As a result, PB-3F had gradually changed from the “soft” to “strong” elastomer. Based on the above analysis, it was found that the cross-linked PB showed elastomeric character with tunable mechanical properties by changing two parameters in great freedom.

Dynamic mechanical analysis was further applied in tensile mode in order to measure the thermomechanical properties of cross-linked PB based on these two systems. Figure 4 shows storage modulus and dissipation factor (tan δ) as a function of temperature for several samples, and their characteristic data are summarized in Table S9. As shown in Figure 4, the storage modulus of two cross-linked blends were increased with increasing RF and RFM, which was in agreement with the results from the tensile stress tests. For PB-FM system (Figure 4C), two glass transition temperatures (Tg) were found. One was located at low temperature of ∼−85 °C, which was related with the soft domains from PB chain, and the other was located

Figure 4. Stress–strain curves, storage modulus, and tan δ of PB-FM series (A, B, C) and PB-3F series (D, E, F) composites.

Figure 5. (A) Temperature-dependent rheological behavior of the sample PB-FM-20. (B) FTIR spectra of the sample PB-FM-20 at room temperature (I), upon heating to 150 °C for 5 min (II), and after cooling to room temperature (III). (C) Photos of the sample stretched at different temperatures.
at high temperature around 85 °C, which was associated with the hard domains from the DA cross-linked structure. Such phase separation structure was responsible for the strong cross-linked PB (Figure 2). For PB-3F blends, the sample only possessed one $T_g$ transition at low temperature of $\sim 90$ °C as RFM was less than 60%, indicating that only one soft phase was obtained for the cross-linked PB rubber (Figure 3). However, further increasing bismaleimide content led to the appearance of the second $T_g$ at higher temperature at $\sim 90$ °C. Such results demonstrated that phase separation happened, and the hard phase related to the bismaleimide cross-linked structure was formed at higher ratio of furan to bismaleimide (>60%), which is in agreement with the observation from AFM measurements. The appearance of phase separation with increasing RFM could be used as explanation for the transition from “soft” to “strong” elastomer for PB-3F blends with increasing RFM from 10 to 100%. Therefore, we could easily design the cross-linked PB rubber by changing the furan grafting ratio and ratio of furan to bismaleimide to meet the corresponding requirements for different application.

**Remolding Ability and Thermal Recyclability of the Materials.** The thermal recyclability was first demonstrated by the variation of solubility under different temperature. Figure S3 shows the behavior of solubility as the temperature was set from 30 to 130 °C for the sample of PB-FM-20 using dichlorobenzene as solvent. It was found that the cross-linked PB could only swell in dichlorobenzene with good solvent resistance, even at high temperature of 130 °C. As the temperature was further increased up to 160 °C (shown in Figure 6E), the cross-linked PB could gradually dissolve into dichlorobenzene to form a clear and transparent solution. This phenomena indicated that the disconnection of DA linkage due to rDA reaction happened on the temperature range between 130 and 160 °C, which could finally lead to dissolution of the modified PB rubber. As the solution was cooled down to room temperature, the sample changed to a homogeneous and transparent gel which could be dissolved again at high temperature, proving that the cross-linked PB rubber had a thermal reversible dynamic cross-linked network. DSC was further carried out on the cross-linked sample to verify the temperature range for the rDA reaction. As demonstrated in Figure S4, the single exothermic peak related to the rDA reaction was observed for all the PB-FM blends, and the reaction starts at 125–130 °C with the peak temperature located at 180–190 °C, which was in agreement with the results from dissolution tests.

For more detailed analysis of the thermally reversible DA reaction in the network, temperature-dependent rheology experiments were performed. As shown in Figure 5A, three periods was observed for storage modulus ($G'$) and loss modulus ($G''$). In the first period as the temperature ranged from 80 to 120 °C, there was plateau for these two moduli with $G'$ higher than $G''$, indicating that the cross-linked elastomer was in the high elastic state. In the second period, $G'$ and $G''$ decreased rapidly as the temperature was increased from 120 to 130 °C, which was attributed to the breakage of the network due to retro-DA reaction. In the third period, $G'$ and $G''$ formed the second plateau when the temperature was up to 130 °C and $G'$ was still higher than $G''$, which meant that the de-cross-linked elastomer was still in the elastic state instead of in the flow state, which was difficult to maintain their integrity during the heating process. Such good integrity could be applied in stress relaxation for the cross-linked PB elastomer. For example, as shown in Figure 5C when the film was stretched at 60 °C (lower than the temperature for the rDA reaction) and then cooled down, the film could return to original length upon heating to 60 °C, showing good shape memory due to the stress produced in the network at high temperature. However, when the same operation was done at 130 °C (above the temperature for the rDA reaction), the film could not return to original length since the rDA reaction enabled the stress relaxation in the network and the sample lost the function of shape memory.

In addition, FTIR spectroscopy was observed to analyze the reversibility of the cross-linking via the thermal reversible reaction between PB-Fu and bismaleimide in the solid state. The samples were subjected to the following designed temperature: $\text{DA(room temperature)→rDA(150 °C)→DA(room temperature)}$ (Figure 5B). The obvious change in this process was the intensity of the absorption peak at 1184 and 1148 cm$^{-1}$. Once the sample was heated to 150 °C and kept for 3 min, it was observed that intensity of the peak at 1184 cm$^{-1}$ (II of Figure 5B) decreased, but the intensity of the peak at 1148 cm$^{-1}$ increased. The peak at 1184 cm$^{-1}$ could be ascribed to the debonding of the DA adduct ($\text{C=O−C}$) via the retro-DA, while the peak at 1148 cm$^{-1}$ was the absorption peaks of furan rings. After slow cooling from 150 to 25 °C, III in Figure 2B showed that the intensities at 1184 and 1148 cm$^{-1}$ recovered to its original state. This phenomenon attributed to the regeneration of the DA adduct ($\text{C=O−C}$) and consumption of the furan during the cooling process due to the DA reaction. Three cycles of rDA and DA reactions were observed, and similar results were obtained. Therefore, it was concluded that PB-Fu could be de-cross-linked and re-cross-linked with bismaleimide repeatedly even in the solid state. Therefore, the cross-linked PB rubber could be recycled to produce new sample via hot compression molding at an elevated temperature. As shown in Figure 6A, pieces of broken samples were reprocessed under a pressure of 10 MPa for 5 min at 160 °C and a solid polymer film was re-formed again. Then the remolded film was cut into pieces, and recycling process was repeated two times. Figure 6D shows the mechanical properties...
of the remodeled elastomer exhibited almost the same mechanical properties even through three generations of recycling. Therefore, the cross-linked PB elastomer could be repossessed like plastics materials. In addition, the self-healing property of PB-FM was investigated by observing the evolution of a crack created by a surgical blade. The film with crack was put on a heating stage, and the temperature was increased at a rate of 10 °C/min to induce the consequent healing process. Photographs were taken at different temperatures during the heating process. As shown in Figure 6B, the crack on PB-FM began to decrease at about 90 °C and disappeared completely after the temperature reached 150 °C, indicating that the cross-linked PB rubber could be self-healed under high temperature. It could be concluded that the self-healing property was attributed to the DA and rDA reaction between furan groups on polybutadiene chains and bismaleimide as shown in Scheme 1. At high temperature, rDA reaction liberates the polymer chain from the network. Meanwhile, the new formed DA bonds connected the polymer chains together. Therefore, the rDA and DA reaction were responsible for healing the cross-linked rubber.

### CONCLUSION

We prepared the thermally reversible cross-linked polybutadiene elastomer based on Diels–Alder reaction (DA). In this way, PB could be thermally recycled like plastic materials to prolong its service life and solve its unrecyclable problem. The commercial available PB elastomer was first attached with furan via thiol–ene click reaction and then cross-linked with bismaleimide via DA. Based on this method, the thermally reversible cross-linked network was established for PB elastomer with good solvent resistance at ambient temperature. The obtained PB elastomer also could have tunable mechanical properties by adjusting the cross-linking degree. For example, for the PB-3F-M system, the cross-linked PB shows low tensile strength of 1.92 MPa with high strain at break of 342.5% in relative low cross-linking degree as RFM was 10%. With increasing cross-linking degree, the tensile strength was gradually increased up to 5.59 MPa with reduced strain at break to 44.8% as RFM was 100%. More importantly, the new cross-linked elastomer possessed good recyclability and could be thermally remolded to produce new sample without obvious negative effects on its mechanical properties. All in all, this work demonstrated good eco-friendly recycling solution to the commercial cross-linked PB elastomer.

### ASSOCIATED CONTENT

1. **Supporting Information**
   Figures S1–S3 and Tables S1–S10. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.5b00389.

2. **AUTHOR INFORMATION**

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   **Notes**
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### REFERENCES


