A Simple Pathway toward Quantitative Modification of Polybutadiene: A New Approach to Thermoreversible Cross-Linking Rubber Comprising Supramolecular Hydrogen-Bonding Networks

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ABSTRACT: A commercial polybutadiene (PB) was modified by a simple three-step polymer analogous reaction (epoxidation, oxirane ring-opening, and sulfonyl isocyanate addition), and the degree of modification is quantitatively controlled by epoxidation reaction. Because of the introduction of sulfonyl urethane groups ($-O-CO-NH-SO_2-$) which is prone to self-complementary thermoreversible supramolecular hydrogen-bonding (HB) networks, the PB was modified from a rubbery material to a thermoplastic elastomer. The modified rubbers were characterized by using ^{1}H NMR, FTIR, DSC, and dynamic mechanical analyses. FTIR spectra showed a shift of S═O stretching to lower frequency with increasing degree of modification as a result of the formation of HB complexes. DSC analysis showed that the crystalline melting was suppressed, and the glass transition was elevated to higher temperatures. From the dynamic mechanical analysis it revealed much clearer the crystallization suppression and the glass transition shifts. The changes in thermal and mechanical properties were attributed to the formation of HB supramolecular networks in the modified polybutadienes.

Introduction

Chemical modifications of rubberlike material, especially natural rubber (NR), have been a useful pathway to new polymeric materials for many years. The first commercially available modified NR was produced 50 years ago (hydrochlorinated, chlorinated, and cyclized rubbers). Because of the high reactivity of double bonds, an organic compound carrying functional groups can be easily grafted onto an olefin by reactions such as electrophilic, nucleophilic, and radical addition reactions. The reactivity, however, is often less in a polymer compared with a low molecular weight olefin, which is not surprising since a double bond in a macromolecule is less accessible than a structurally similar double bond in a small olefin. The steric barriers to reactions on polymers may become quite marked when attempts are made to carry a reaction to completion, which on the other hand could mean the reactions are not quantitatively satisfactory.[1−3]

Among all the well-known chemical modifications of polydiene materials, epoxidation reaction has been the most promising and advantageous method[4−8] since the epoxidized polydienes can be prepared with performic acid at moderate temperature in solution, which makes mass industrial production possible. Moreover, the oxirane ring on the epoxidized polydiene backbone is of great interest because numbers of chemical reactions can be employed for further modifications: for instance, carboxylic acids,[9−12] amines,[13−16] phosphoric acid derivatives,[17,18] and alcohols[19,20] were respectively investigated for synthesis of drug release, vulcanized, antioxidant, photo-cross-linkable, and flame-resistant materials. However, because of the low degree of secondary modification, the mentioned reactions should be conducted at higher temperatures and are always not satisfactory in terms of conversion.

Alternatives to functionalize polydiene are via thermal ene reaction of 4-phenyl-1,2,4-triazoline-3,5-dione derivatives[21−23] and sulfenyl halide[24,25] addition onto the double bonds. Though these two reactions are straightforward (one-step modification) and quantitative at the laboratory scale, the applicability for mass industrial production is limited. There are mainly two reasons for that: First, the chemicals needed for the modification are not available commercially. Second, the synthetic route for the modifying chemicals are tedious, and moreover, it requires highly toxic reagents such as phosgene[24] or nitrogen dioxide.[21]

Despite the fact that hydrogen bonding has been extensively studied in supramolecular systems as a mean of polymer formation or modification between small molecules or oligomers via a self-complementary process,[26−29] very few studies of polymer modification systems using hydrogen bonding between (i) the side groups of polymers[30−34] or (ii) the side group of a polymer and a small molecule were investigated. Meijer reported that supramolecular interaction between (i) the styrene−maleimide alternating copolymer and melamine or (ii) the copolymer of styrene and 2,4-diamino-6-vinyl-1,3,5-triazine is capable of enhancing compatibility between each other.[35] Nevertheless, the chemistry employed in the above work on supramolecular systems was not applicable to industrial applications. Recently, D. Chino et al. applied the ene reaction of maleic anhydride to modifying natural rubber in order to synthesize thermoreversible cross-linking rubber using hydrogen-bonding network.[36] The main drawback of this ene reaction between maleic anhydride and rubber is that the grafting efficiency depends strongly on several factors, for instance reaction time and temperature, molecular weight, and microstructure of the rubber.[37]

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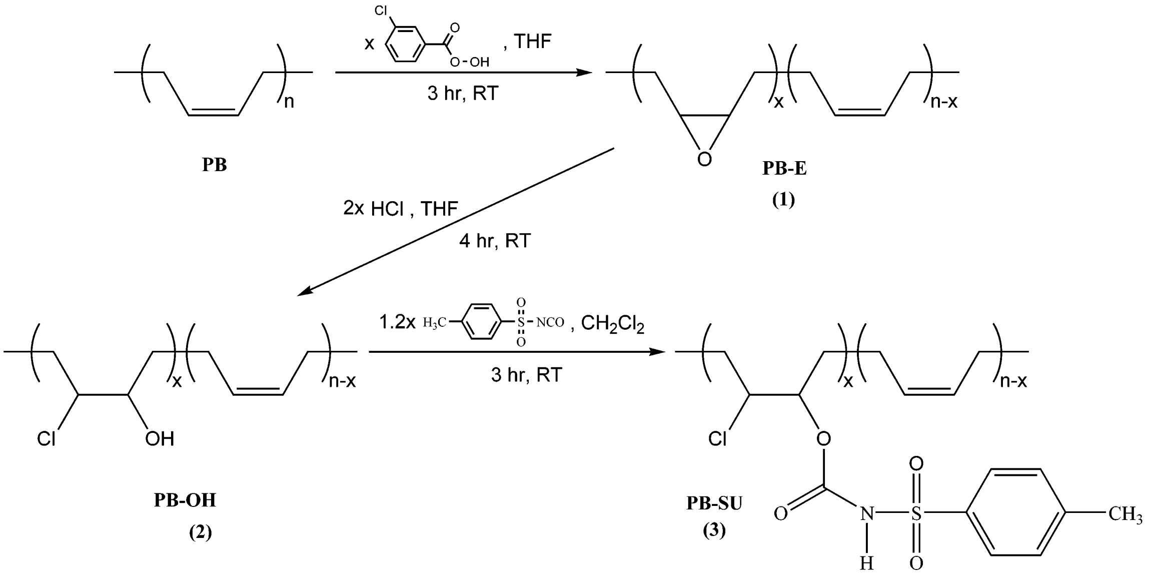
Scheme 1. Three-Step Pathway toward Quantitative Modification of Polybutadiene



Therefore, such a procedure is not always a satisfactory way to modifying rubber. Here we present a new, economical, and simple three-step polymer analogous reaction based on epoxidation reaction (Scheme 1) to quantitatively modify polydiene polymers. This results in a thermoreversible cross-linked supramolecular network which is formed in the rubber matrix. Moreover, simply by controlling the degree of modification, one is able to design rubber materials which meet special requirements for different sorts of rubbery products.

Experimental Section

Materials. Technical grade polybutadiene, Bayer Buna CB 10, with 96% *cis*-1,4 units and Mooney viscosity = 47 (ML1+4 at 100 °C) (GPC data with PS standards: $M_w = 576\,000$, DPI = 2.6), was received from Deutsches Institut für Kautschuktechnologie e.V. (DIK, Germany). According to the supplier, this material has a fairly wide molecular weight distribution and a medium degree of long-chain branching. *m*-Chloroperbenzoic acid (MCPBA, 70%, Fluka), hydrochloric acid (32 wt % HCl, Merck), and *p*-toluenesulfonyl isocyanate (PTSI, 96%, Aldrich) were used as received. Tetrahydrofuran (THF) and dichloromethane (analytical grade) were purchased from Merck and were used without any further purification.

Synthesis of PB-E (1) (Epoxidation). The epoxidation reaction was performed and modified according to the literature procedure,[38,39] and here PB with 5 mol % degree of modification is highlighted as a typical example. In a 1 L one-neck round-bottom flask equipped with magnetic stirrer, 16.2 g of CB 10 (0.3 mol of C=C) was first dissolved in 600 mL of THF (typical concentration for various degrees of modification). A solution of 3.69 g of MCPBA (0.015 mol) in 50 mL of THF was then added dropwise at room temperature into the polymer solution at such a rate that the MCPBA solution was added completely after 1 h. The reaction mixture was then further stirred for another 2 h, and 2 mL of reaction solution was taken out for ^{1}H NMR before the ring-opening reaction. The degree of modification was calculated using the ^{1}H NMR technique as described in the literature.[40]

Synthesis of Hydrochlorinated PB, PB-OH (2) (Ring-Opening). A solution of 3.42 g of hydrochloric acid (0.03 mol of HCl) in 50 mL of THF was first prepared and transferred into a 100 mL dropping funnel; it was then added dropwise at room temperature into the epoxidized PB solution prepared previously. After the addition of HCl solution, the reaction mixture was further stirred for another 3 h in order to complete the ring-opening reaction. Afterward, the polymer was isolated by precipitation into 400 mL of methanol and then dried at 50 °C under vacuum for 2 days. The yield of the hydrochlorinated PB was 99%, and the extent of oxirane ring-opening was verified by ^{1}H NMR.

Table 1. PBs of Various Degrees of Hydrochlorination

sample ID	deg of hydroxylation (mol %) (based on C=C unit)	MCPBA (g)	HCl (g)	yield (%)[a]
PB-OH-1	1	0.74	0.68	99
PB-OH-2	2	1.48	1.37	99
PB-OH-5	5	3.69	3.42	99
PB-OH-10	10	7.39	6.84	98
PB-OH-20	20	14.78	13.68	95

[a] Yield is calculated for 16.2 g of PB by $(w/[54 + x(17 + 35.5)])/(16.2/54) \times 100\%$, where w is product weight in grams and x is the degree of modification in mol %.

Table 2. PBs of Various Degrees of Modification

sample ID	deg of modification (mol %) (based on $[\mathrm{OH}]/[\mathrm{C{=}C}]_0$)	PTSI (g)[a]	yield (%)[b]
PB-SU-1	1	0.23	98
PB-SU-2	2	0.44	98
PB-SU-5	5	1.09	98
PB-SU-10	10	1.66	95
PB-SU-20	20	3.82	90

[a] The amount of PTSI required is calculated based on mole of −OH in 5.0 g of PB−OH. −OH mol = $5.0x/[54 + x(17 + 35.5)]$, where x is the degree of modification in mol %. [b] Yield is calculated by $\{w/[54 + x(17 + 35.5 + 197)]\}/\{5.0/[54 + x(17 + 35.5)]\} \times 100\%$, where w is product weight in gram and x is the degree of modification in mol %.

Synthesis of PB-SU (3) (Sulfonyl Isocyanate Addition). In a 200 mL one-neck round-bottom flask, equipped with magnetic stirrer, 5.0 g of 5 mol % hydrochlorinated PB **(2)** (4.42×10^{-3} mol of −OH) was first dissolved in 100 mL of CH_2Cl_2. 1.09 g of PTSI (5.30×10^{-3} mol) was then added at one dose into the solution, and the system was stirred at room temperature for 3 h. After the reaction, the final product was isolated by precipitation into 100 mL of methanol and then dried at 50 °C under vacuum for 2 days. The yield of the isolated product was 98%, and the extent of reaction was verified by ^{1}H NMR. PBs of other degrees of modification were also prepared according to the above recipe, and the details are summarized in Tables 1 and 2. ^{1}H NMR spectra of different sulfonylurethane contents are given in the Supporting Information.

Characterization. ^{1}H NMR spectra were recorded on a Bruker 250 MHz spectrometer using $CDCl_3$ as a solvent; the signals were normalized by unifying the methylene protons

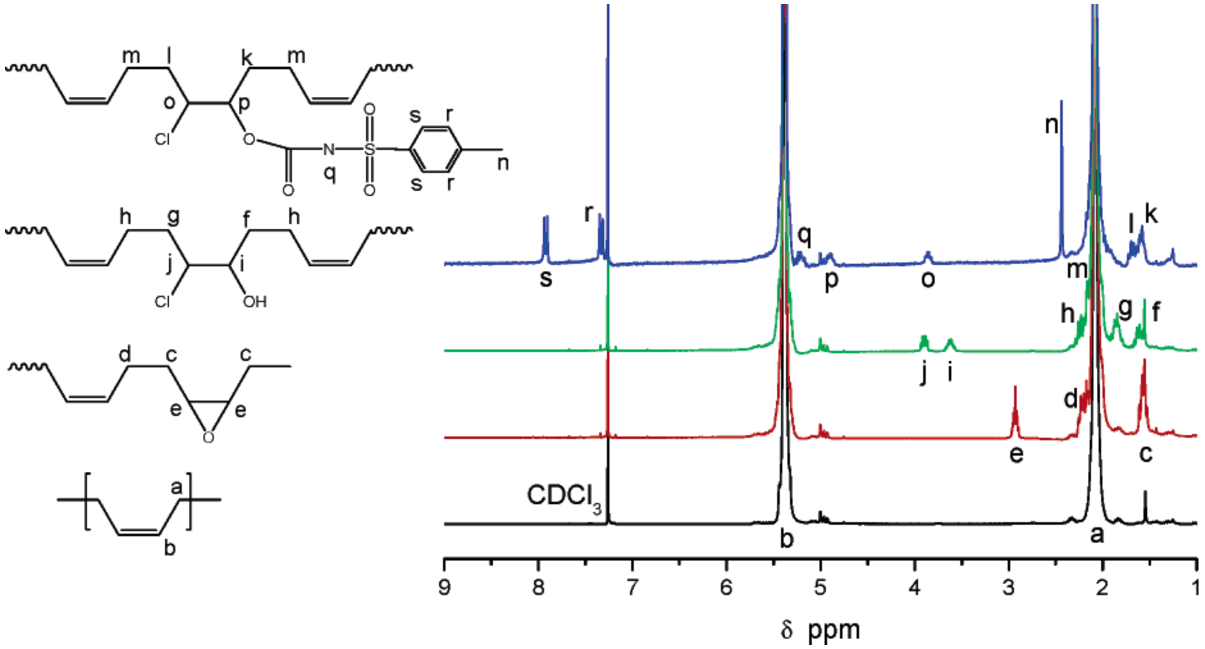


Figure 1. ^{1}H NMR spectra of PB with 5 mol % degree of modification (NMR spectra of other degree of modification are given in the Supporting Information).

at 2.08 ppm. FTIR spectra were recorded at room temperature using a Bruker FTIR EQUINOX 55/S spectrometer at a resolution of 4 cm^{-1}. The samples for FTIR analysis were first dissolved in CH_2Cl_2 (10 mg of PB in 1 mL of CH_2Cl_2) and prepared by solution-casting onto a KBr plate, and the absorption signals were normalized by unifying the asymmetric methylene stretching absorption at 2941 cm^{-1}. DSC experiments were run on a Perkin-Elmer Pyris 1, with a scanning rate of 40 °C/min between −120 and 60 °C, and the transition temperatures were taken from the second heating curves. The crystalline melting (T_m) and crystallization (T_c) temperatures were taken at the peak values (local extrema), and the glass transition (T_g) temperatures were taken at the midpoint ($^1/_2\Delta C_p$) of the curves. All transition temperatures were taken without extrapolating to zero scanning rate. Dynamic mechanical measurements were performed using an Advanced Rheometrics Expansion System (ARES) from TA, and dynamic shear moduli were recorded employing the "dynamic temperature ramp test" program (scanning from 80 to −100 °C at a rate of −2 °C/min) with 8 mm parallel-plate geometry. Sample films of 8 mm diameter were prepared by compression-molding. (A 25 mg sample was first heated and molded under pressure at 80 °C for 10 min in an 8 mm diameter mold, and the buttonlike specimen was taken out after the mold was cooled to room temperature.) All tests were performed at an oscillating frequency of 1 Hz, and dynamic strain-sweep tests were done before the temperature ramp tests in order to ensure that all the measurements were perfomred within the linear viscoelastic regime.

Results and Discussion

The epoxidation reaction of polybutadiene by using *m*-chloroperbenzoic acid showed excellent efficiency and was in agreement with literature data;[20] i.e., the reaction was quantitative. The extents of the subsequent reactions were verified using ^{1}H NMR by monitoring the proton signals on the oxirane ring and the one adjacent to the hydroxyl group. As shown in Figure 1, from the vicissitudes of proton signals the oxirane ring was successfully cleaved, and PTSI was added with excellent efficiency. However, as a result of the increasing hydrophilicity, which is in favor of the solubility of modified PBs in methanol, the yields of the isolated products were decreased with increasing sulfonylurethane content (Table 2).

FTIR spectra of modified PBs are shown in Figure 2. Typical N−H, C=O, and S=O stretching vibrations from the sulfonylurethane group (−O−CO−NH−SO_2−) were observed at 3245, 1751, 1362 (asymmetric), and 1163 cm^{-1} (symmetric). Their intensities were significantly increased with increasing degree of modification. Since the sulfonylurethane groups present in the polymer matrix are capable of forming a supramolecular hydrogen-bonding network, it is possible to verify the hydrogen-bonding formation by keeping eyes on the variation of specific absorption bands, such as the C=O and S=O stretching modes, for example. It was found that the C=O vibration band was split into two peaks: one (stronger, free C=O) was at 1751 cm^{-1}, and the other (weaker, HB-bonded C=O) showed up as a shoulder at 1718 cm^{-1}. Nevertheless, since the C=O absorption was too strong, it is difficult to tell whether the formation of HB network was enhanced with increasing sulfonylurethane content alone by the relative intensity of these two peaks. On the contrary, note that the asymmetric S=O stretching band of sulfonyl urethane did tell the story about how HB network was effected by increasing degree of modification: with increasing sulfonylurethane content, the asymmetric stretching band vanished at 1362 cm^{-1} and was shifted to 1349 cm^{-1}. This observation, as it was, did not contradict the known fact that the hydrogen-bonding strength of C=O···H−N is higher than that of S=O···H−N. A possible reason could be that the IR molar absorptivity of C=O and asymmetric S=O stretching of a sulfonyl urethane are much higher than that of symmetric S=O stretching (Figure 2); thus, the relative absorption band vicissitudes of the former were less significant. Taking into account the high flexibility of the PB matrix and together with the FTIR analysis, we propose that there could be three different kinds of HB complexes, A, B, and C, as shown in Figure 3, formed in the PB matrix.

Several interesting behaviors were observed in the DSC analysis of both the unmodified and the modified

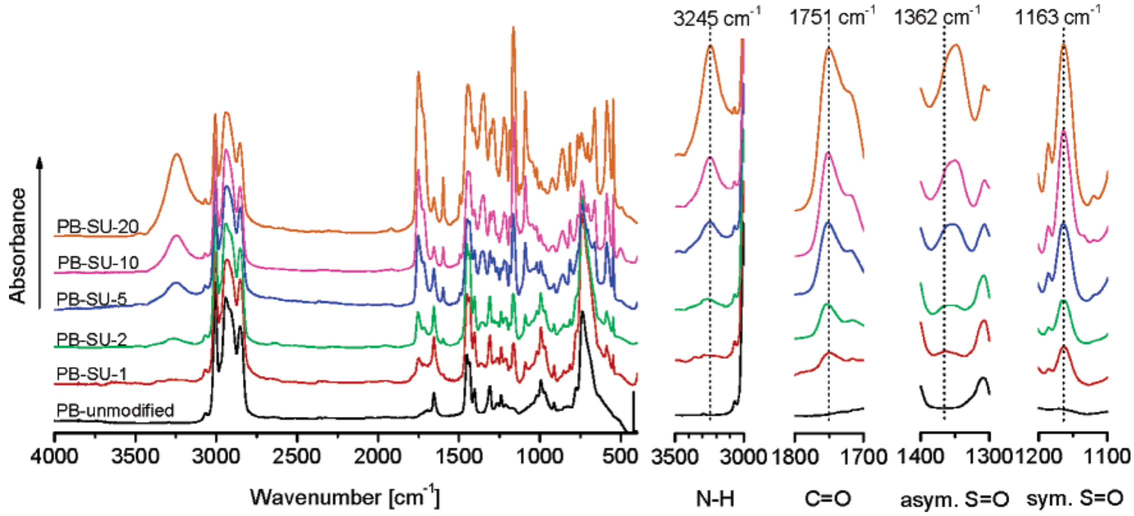


Figure 2. FTIR spectra of PBs with various degrees of modification.

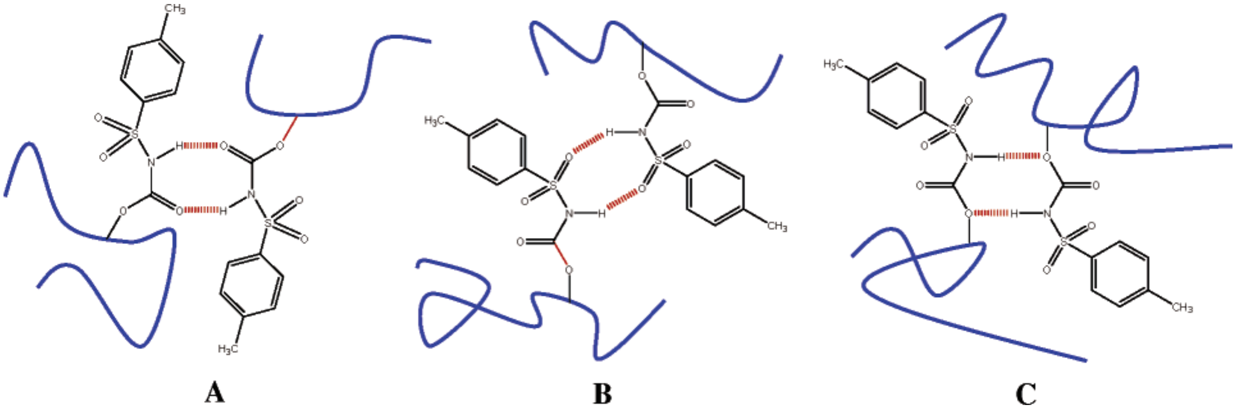


Figure 3. Schematical representation of three possible hydrogen-bonding complexes between two sulfonylurethane groups.

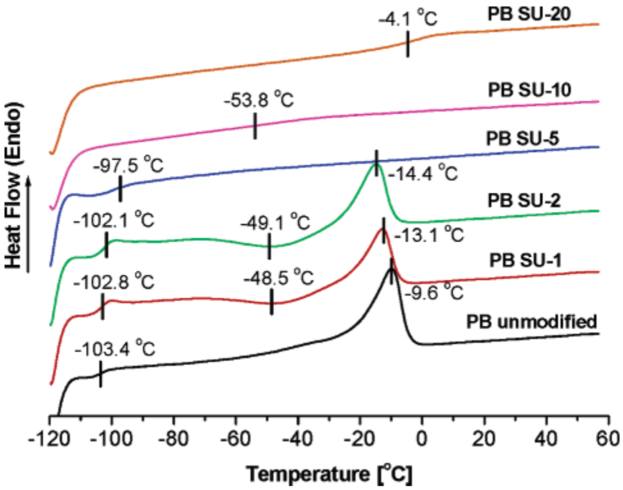


Figure 4. DSC traces of PBs with various degrees of modification (second heating; heating rate 40 °C/min; normalized data).

PBs. First, since the commercial polybutadiene investigated in this study contains basically high *cis*-1,4 units, as shown in Figure 4, it turned out that the unmodified CB 10 had a glass transition at −103.4 °C and a crystalline melting temperature at −9.6 °C. Second, for the PBs with lower degrees of modification, T_m was slightly shifted to lower temperatures, and it was totally suppressed upon a 5 mol % modification. A possible explanation is that the introduction of few side chains disturbed the well-ordered *cis*-1,4 crystalline structure; therefore, the smaller crystals melted at a lower temperature. Third, the glass transition temperatures of the modified PBs were first shifted moderately to higher temperatures up to 5 mol % modification, similar to results described in the literature,[32] which was attributed to a phase separation between the polar groups and the nonpolar polybutadiene. On the other hand, because of the formation of strong hydrogen-bonding network, the glass transition was greatly shifted to higher temperatures with higher degree of modifications (Figure 4). It is important to note that the glass transition temperature was elevated from −103 to −4.1 °C upon a 20 mol % modification. Finally, the most interesting observation was that, with increasing degree of modification up to 2 mol %, crystal formation (T_c) at −49 °C can be observed in the DSC traces. To our knowledge it has never been reported before, and the induced crystallization could result from the nucleating effect of the low sulfonyl urethane group concentration that acted as a heterogeneity in the semicrystalline PB matrix.

Because of the difference in sensitivity to thermal transitions, dynamic mechanical analysis was used as an independent method to probe the thermal behavior of the modified PBs. As shown in Figure 5, for the unmodified polybutadiene, the region where the storage shear modulus (G') fell steeply and the loss shear modulus (G'') soared corresponds to the crystalline melting temperature. However, since CB 10 has a high molecular weight, a fairly wide molecular weight dis-

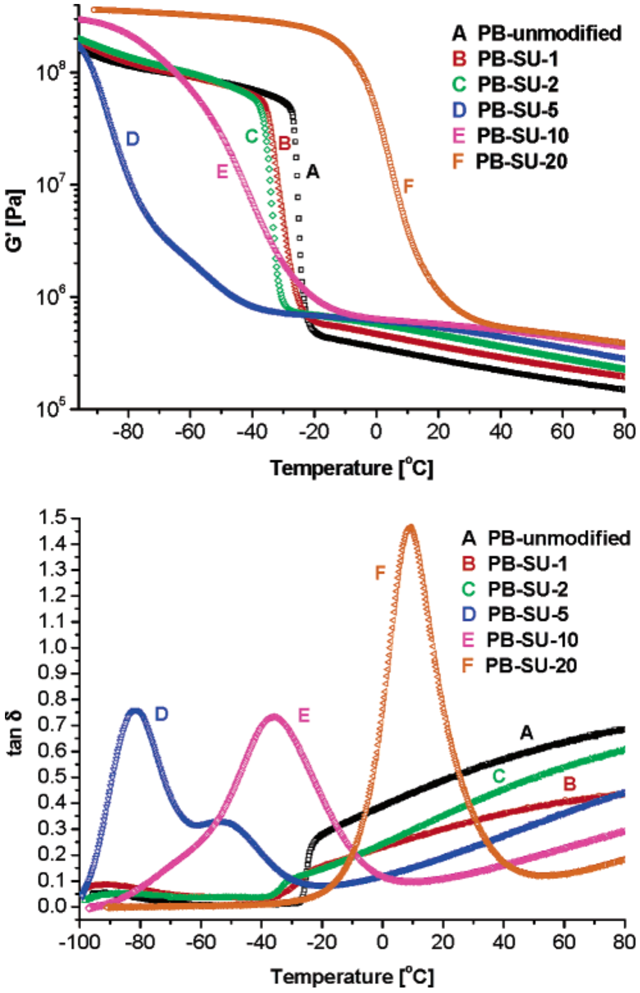


Figure 5. Dynamic mechanical spectra of modified PBs.

tribution, and a medium degree of long-chain branching, the storage modulus was still high enough to sustain a rubbery material even if the surrounding temperature was above T_m (G' still higher than G'', due to the effective constrained entanglements from the long chain branching[41,42]). First, for the modified PBs with lower degree of modification up to 5 mol %, T_m was shifted to lower temperatures and the values of G' below T_m were reduced. This observation was mainly attributed to the suppression of PB crystallization caused by modification. (DSC traces showed that crystalline melting was no longer detectable upon a 5 mol % modification.) Second, despite the fact that modification influenced the PB crystallinity, the thermoreversible hydrogen-bonding network served as a mechanically effective cross-linking; G' increased with higher degree of modification. Finally, the shift of the maximum in tan $\delta(T_g)$ to higher temperature again gives a clear evidence that the introduction of this self-complementary hydrogen-bonding moiety is capable of forming an effective "pseudo"-cross-linking network. The G' of modified PBs at temperature above 0 °C shows an interesting behavior. The data show that G' was increased only slightly with higher degree of modification, which is indeed strange at the first glance. However, this behavior could be due to the long-chain branching nature of CB 10, which implies that the branched chains were "long enough" to form "effective entanglements", and the introduction of hydrogen-bonding networks led only to a small increase of the entanglements (see also the master curve of CB 10 and detailed explanation given in the Supporting Information).

Conclusion

In this paper a commercial polybutadiene rubber, CB 10, was quantitatively modified from 1 to 20 mol % by a three-step polymer analogous reaction. The modified PBs were capable of forming supramolecular hydrogen-bonding networks. The reactions were monitored by ^{1}H NMR, and the formation of hydrogen-bonding complexes was verified by FTIR analysis. DSC analysis showed that crystallinity of the investigated PB was suppressed with a degree of modification >2 mol %, and the glass transition was shifted from −103 to −4.1 °C upon a sample with 20 mol % modification. Dynamic mechanical analysis showed that upon a 5 mol % modification the crystallization was totally supressed, and with higher degree of modification the glass transition was further elevated to higher temperatures. These observations indicate that the introduction of this type of hydrogen-bonding complex led to the formation of effective supramolecular networks. The proposed modification pathway is a simple, economical, and highly effective route for rubber and tire industries to design products of a new generation.

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Supporting Information Available: Figures showing ^{1}H NMR spectra of other degree of modification and master curve of CB 10. This material is available free of charge via the Internet at http://pubs.acs.org.

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