Synthesis and Characterization of Polyhydroxylated Polybutadiene Binding 2,2′-Thiobis(4-methyl-6-*tert*-butylphenol) with Isophorone Diisocyanate

Wenjian Wu, Xingrong Zeng, Hongqiang Li, Xuejun Lai, Zengyang Yan
College of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, People's Republic of China
Correspondence to: X. Zeng (E-mail: psxrzeng@gmail.com)

ABSTRACT: A macromolecular hindered phenol antioxidant, polyhydroxylated polybutadiene containing thioether binding 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) (PHPBT-b-TPH), was synthesized via a two-step nucleophilic addition reaction using isophorone diisocyanate (IPDI) as linkage. First, the —OH groups of PHPBT reacted with secondary —NCO groups of IPDI to form the adduct PHPBT-NCO, then the PHPBT-b-TPH was obtained by one phenolic —OH of 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) (TPH) reacting with the PHPBT-NCO. The PHPBT-b-TPH was characterized by Fourier transform infrared spectroscopy, ^{1}H nuclear magnetic resonance (^{1}H-NMR), ^{13}C-NMR, and thermogravimetric analysis, and its antioxidant activity in natural rubber was studied by an accelerated aging test. Influences of reaction conditions on the two nucleophilic reactions between —OH group and —NCO group were investigated. In addition, catalytic mechanism for the reaction between PHPBT-NCO and TPH was discussed. The results showed that the adduct PHPBT-NCO could be obtained by using dibutyltin dilaurate (DBTDL) as catalyst, and the suitable temperature and DBTDL amount were 35°C and 3 wt %, respectively. However, triethylamine (TEA) was more efficient than DBTDL to catalyze the reaction between PHPBT-NCO and TPH because of steric hindrance effect. In addition, it was found that the thermal stability and antioxidant activity of PHPBT-b-TPH were higher than those of the low molecular weight antioxidant TPH. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40942.

INTRODUCTION

Due to low thermal stability, poor migration resistance and poor extraction resistance, the physical loss of low molecular weight antioxidant was large during polymer processing and long-term service, which severely restricted its applications. In order to overcome the problem, macromolecular antioxidant had attracted much attention in recent years.[1–15] For example, Kim[5–7] synthesized several kinds of polymeric antioxidants by copolymerization or homopolymerization of functional monomers containing hindered phenol. El-Wakil et al.[9–12] studied the grafting of o-aminophenol, 1,2-phenylenediamine,1,5-diaminonaphthalene, and N-(4-aminodiphenyl methane) acrylamide onto natural rubber. Podesva[13,14] synthesized a polymer-bound antioxidant by free radical addition reaction between a hindered phenolic antioxidant with a sulfanyl group and hydroxyl-terminated polybutadiene. The thermal stability and extraction resistance of the obtained macromolecular antioxidants were improved obviously. However, most of the macromolecular antioxidants were synthesized by radical polymerization or grafting. On one hand, antioxidant groups would capture free radicals during synthetic process, thus the radical reaction was not easy to take place. Meanwhile, the anti-oxidative moieties content of obtained macromolecular antioxidant was relatively low due to the consumption of the antioxidant groups, resulting in low anti-oxidative efficiency.[16] On the other hand, the structures of prepared macromolecular antioxidant, such as molecular weight, distribution of anti-oxidative group, were difficult to control.[4] Therefore, a new method to prepare macromolecular antioxidant was urgently required.

Nucleophilic addition reaction between —OH group and —NCO group provides an attractive method for preparing macromolecular antioxidant as it is not affected by anti-oxidative group and easy to obtain products with controllable structures. In addition, isophorone diisocyanate (IPDI) is known to have considerable selectivity of the primary NCO group and the secondary NCO group. It was often used as a linkage to prepare

functional polymer by a two-step nucleophilic addition reaction.[17–23] In our previous work, a macromolecular antioxidant, hydroxyl-terminated polybutadiene-bound 2,2′-thiobis(4-methyl-6-tert-butylphenol) (HTPB-IPDI-TPH), was prepared via a two-step nucleophilic addition reaction with IPDI.[24] When the content of hindered phenol structure units in the HTPB-IPDI-TPH were almost equal to that of TPH, the HTPB-IPDI-TPH in natural rubber exhibited better thermo-oxidative aging resistance than TPH by accelerated thermal aging test and oxidation induction time (OIT), and it had excellent extraction resistance and thermal stability. However, because the HTPB only had two —OH groups which could be used to bind TPH, the proportion of antioxidant moieties in HTPB-IPDI-TPH was relatively low. This required a higher addition amount than that of commercial antioxidants. Therefore, anti-oxidative efficiency of the HTPB-IPDI-TPH needed to be further improved. As we know, secondary antioxidants, such as thioether and phosphites, have a good synergistic effect with hindered phenol. Therefore, both increasing relative proportion of antioxidant moieties and introducing thioether groups are good choices to improve anti-oxidative efficiency of macromolecular hindered antioxidants.[25] Therefore, a polyhydroxylated polybutadiene containing thioether (PHPBT) was synthesized by a thiol-ene click reaction between HTPB and 2-mercaptoethanol in our reported study.[26]

In this research, a macromolecular hindered phenol antioxidant, polyhydroxylated polybutadiene containing thioether binding 2,2′-thiobis(4-methyl-6-tert-butylphenol) (PHPBT-b-TPH), was prepared via a two-step nucleophilic addition reaction using IPDI as linkage. First, —OH group of PHPBT reacted with the secondary —NCO group of IPDI to form the adduct PHPBT-NCO. Then the PHPBT-b-TPH was obtained by one phenolic —OH of TPH reacting with the adduct PHPBT-NCO. The PHPBT-b-TPH was characterized by Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance (NMR), and thermogravimetric analysis (TGA), and its antioxidant activity in natural rubber was studied by an accelerated thermal aging test. In addition, influences of reaction conditions on the formation of adduct PHPBT-NCO and macromolecular antioxidant PHPBT-b-TPH were investigated in detail. Moreover, catalytic mechanism of catalyst (DBTDL and TEA) for the reaction between PHPBT-NCO and TPH was discussed.

EXPERIMENTAL

Reagents and Materials

PHPBT ($M_n = 4.00 \times 10^3$, $M_w/M_n = 1.18$) with a hydroxyl value of 3.29 mmol g^{-1} was obtained in our lab. IPDI was obtained from BASF Co. Ltd., Germany. 2,2′-Thiobis(4-methyl-6-tert-butylphenol) (TPH) was supplied by Zibo Debaiyi Industral & Trading Co. Ltd., China. Dibutyltin dilaurate (DBTDL) was purchased from GE Co., The United States. Triethylamine (TEA), toluene and methanol were obtained from Guangzhou Chemical Reagent Factory, China. The TEA and toluene was dried by 4A molecular sieves for 1 week.

Synthesis of PHPBT-b-TPH

First, PHPBT was obtained via a thiol-ene click reaction between hydroxyl-terminated polybutadiene (HTPB) and 2-mercaptoethanol (ME) with 2,2′-azoisobutyronitrile (AIBN)
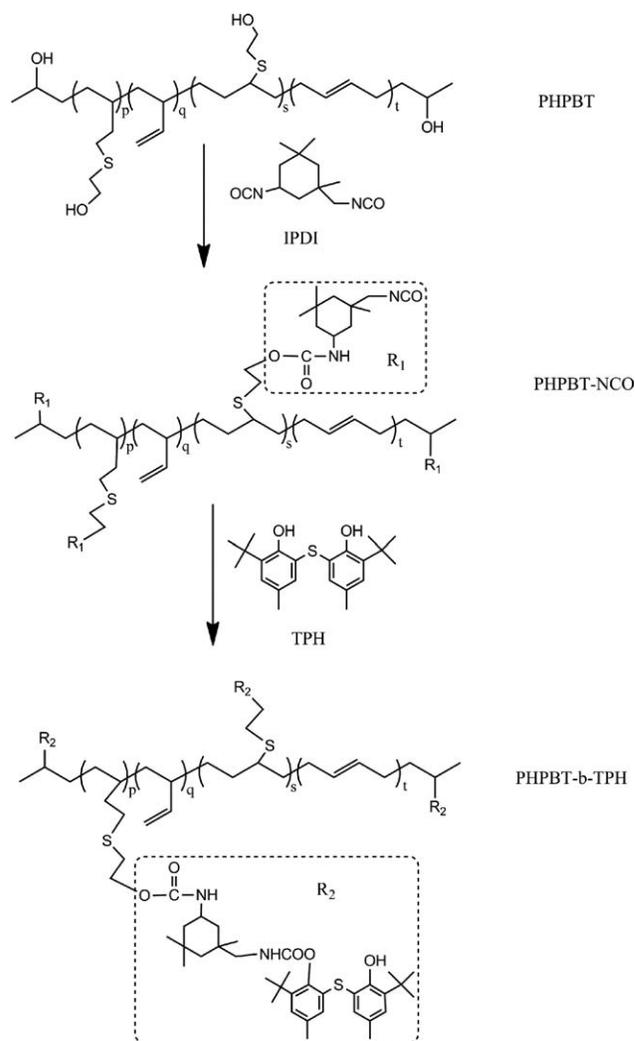
Scheme 1. Synthesis route of PHPBT-b-TPH.

as initiator. The details of the synthetic process was reported previously.[26] The synthesis of PHPBT-b-TPH was described as follows.

About 5 g of PHPBT (including 16.45 mmol hydroxyl groups) was dissolved in 10 g of toluene in a 250 mL four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer, and N$_2$ inlet. Then a mixed solution of 4.02 g IPDI (18.10 mmol), a certain amount of catalyst (1–4 wt % based on IPDI), and 10 g toluene was added dropwise into the flask within 30 min at a relatively low temperature (30°C–45°C) under N$_2$ atmosphere. The reaction was monitored by FT-IR and determining isocyanate (NCO) content. After the mixture reacted for a certain time, an adduct with primary —NCO groups (PHPBT-NCO) was obtained. Then, another mixed solution including a certain amount of TPH (molar ratio of TPH to NCO in PHPBT-NCO was 1 : 1–3 : 1) and catalyst (3 wt % based on IPDI) was added dropwise into the adduct PHPBT-NCO within 60 min at a relatively high temperature (70°C–80°C). When all —NCO groups were consumed which was monitored by FT-IR, the mixture was concentrated by rotary evaporation under reduced pressure and then was purified five

times by a dissolving-precipitation method with toluene and methanol to remove impurities. The polyhydroxylated polybutadiene binding 2,2′-thiobis(4-methyl-6-*tert*-butylphenol) (PHPBT-b-TPH) was obtained after being dried to a constant weight under vacuum at 60°C. The synthesis route of the PHPBT-b-TPH is represented in Scheme 1.

Characterization

Fourier Transform Infrared Spectroscopy (FT-IR). FT-IR spectra were recorded by a Tensor 27 spectrometer (Bruker, Germany). The measurements were carried out in the range of 4000–400 cm^{-1}. The number of scans per spectrum was 16, and the spectral resolution was 4 cm^{-1}. The sample of PHPBT-b-TPH was mixed with KBr powder, and the mixture was pressed into a tablet. Other samples were prepared by solution casting on KBr tablets.

Nuclear Magnetic Resonance (NMR). ^{1}H-NMR and ^{13}C-NMR spectra were obtained by an AV 300 spectrometer (Bruker, Germany). CDCl$_3$ and TMS were used as solvent and internal standard substance, respectively.

Determination of Isocyanate (NCO) Content. Isocyanate group (NCO) content of reaction mixture was determined by standard dibutylamine back-titration method (ISO 14896:2009). The procedures were as follows. About 2 g (accurate to 0.1 mg) of reaction mixture and 25 mL of toluene were added into a 250 mL iodine flask. After the reaction mixture was dissolved completely, 25 mL of 0.1 mol L^{-1} dibutylamine solution was added, and allowed to react for 15 min at ambient temperature. Then, 100 mL of isopropanol and 1 ml of bromophenol blue solution were added and the solution of reaction mixture was titrated using HCl (aq) until the indicator changed from blue to yellow and remained stable for 15 sec. In addition, a blank determination was conducted under identical conditions, but without any test portion. The residual NCO content of the reaction mixture relative to the IPDI was calculated by the eq. (1).

$$\text{NCO wt \%} = \frac{(V_1 - V_2) \times c \times 4.2}{m_0} \times \frac{m_{\text{total}}}{m_{\text{IPDI}}} \quad (1)$$

where V_1 was the volume of HCl required for titration of the blank (mL), V_2 was the volume of HCl required for titration of the test portion (mL), c was the concentration of the HCl (mol L^{-1}), m_0 was the mass of the test portion (g), m_{total} was the total mass of the reaction mixture solution, and m_{IPDI} was the IPDI mass in the reaction mixture solution.

Thermal Gravimetric Analysis (TGA). TGA was carried out on a TG 209 F1 thermogravimeter (Netzsch, Germany) from 30°C to 800°C at a heating rate of 20°C min^{-1} under air atmosphere.

Accelerated Thermal Aging Test. The dumbbell-shaped specimens of vulcanizates were placed in an aging oven (GT-7017, Gotech Testing Machine Inc., Taiwan) at 100°C. After 48 h, the samples were taken out from the aging oven. The changes of the mechanical properties of NR vulcanizates due to thermal oxidative aging were monitored by tensile test. The tensile strength, elongation at break, and tear strength were obtained by a tensile strength tester (UT-2080, U-CAN Dynatex Inc., Taiwan) according to ASTM D412 at a crosshead speed of 500 mm min^{-1}. The performance retention (P) was calculated using eq. (2)
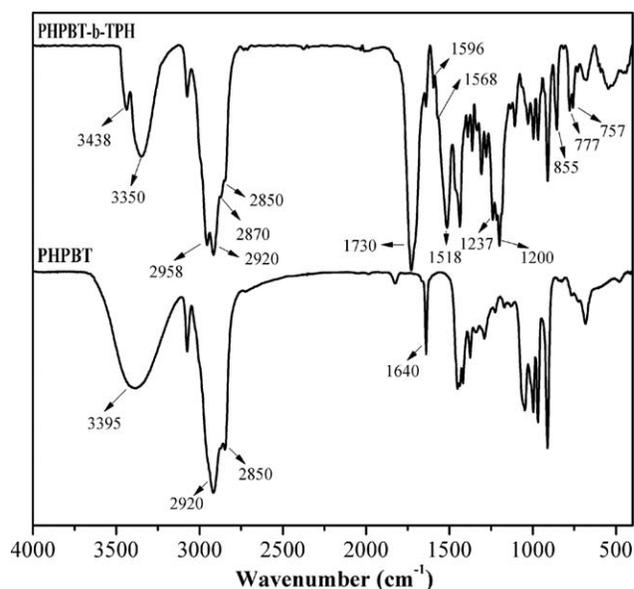

Figure 1. FT-IR spectra of PHPBT and PHPBT-b-TPH.

$$P = (X_1/X_0) \times 100 \quad (2)$$

where X_0 and X_1 is the performance of the vulcanizates before and after aging, respectively.

RESULTS AND DISCUSSION

Structure of PHPBT-b-TPH

FT-IR Analysis. Figure 1 shows the FT-IR spectra of PHPBT and PHPBT-b-TPH. In the PHPBT spectrum, the peak at 3395 cm^{-1} was assigned to the —OH stretching vibration, and its peak intensity was strong, indicating that the PHPBT had many —OH groups. The peaks at 2920 and 2850 cm^{-1} were ascribed to the asymmetric and symmetric stretching vibrations of methylene(—CH$_2$—), respectively. The peak at 1640 cm^{-1} represented the —C=C— stretching vibration.

In PHPBT-b-TPH spectrum, the broad peak at 3395 cm^{-1} for —OH in PHPBT spectrum became a narrow peak at 3350 cm^{-1} for —NH— stretching vibration.[27] Meanwhile, new peaks at 3438 and 1200 cm^{-1} were observed, which were attributed to the O—H and C—O stretching vibrations of phenolic —OH, respectively. Peaks at 2958 and 2870 cm^{-1} were ascribed to the asymmetric and symmetric stretching vibrations of methyl (—CH$_3$), respectively. Peaks at 1730, 1518, and 1237 cm^{-1} were attributed to the —C=O stretching vibration, —NH— bending vibration and —C—O— stretching vibration of —C—O—C=O group, respectively,[28] confirming that the —NHCOO— group formed. In addition, the peaks at 1596 and 1568 cm^{-1} were attributed to the skeletal vibrations of benzene ring. The peaks at 855, 777, and 757 cm^{-1} were assigned to the C—H plane bending vibration of benzene ring. From FT-IR analysis, it was suggested that phenolic —OH, —CH$_3$, —NHCOO— groups and benzene ring existed in obtained compound. All these groups belonged to the target product PHPBT-b-TPH.

NMR Analysis. In order to further identify that the structure of obtained PHPBT-b-TPH was consistent with our target product,
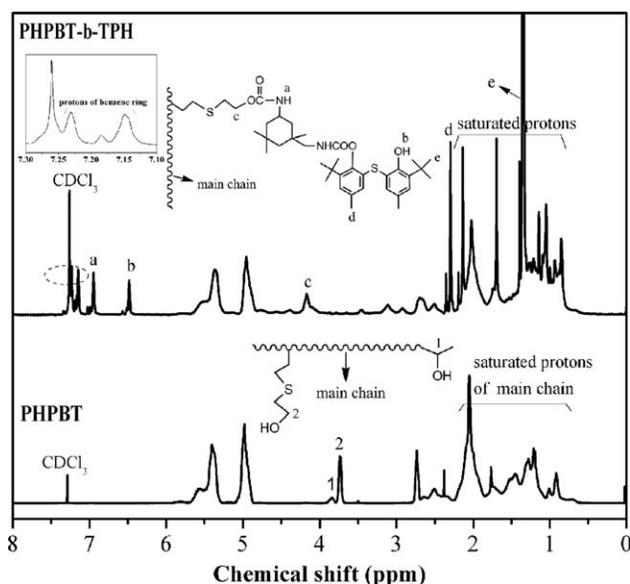
Figure 2. ^{1}H-NMR spectra of PHPBT and PHPBT-b-TPH.

^{1}H-NMR and ^{13}C-NMR of the PHPBT-b-TPH were carried out. Figure 2 shows the ^{1}H-NMR spectra of PHPBT and PHPBT-TPH. Compared with the PHPBT spectrum, both peak at 3.72 ppm assigned to the methylene protons of $-CH_2OH$ and peak at 3.83 ppm belonged to the methine protons of $-CH(CH_3)OH$ disappeared in the PHPBT-b-TPH spectrum. The new peaks at 7.15–7.23 ppm were assigned to the protons of benzene rings. The peak at 6.94 ppm was attributed to the proton of $-NHCOO-$ groups.[29] The peak at 6.47 ppm was attributed to the proton of phenolic $-OH$.[29] The peak at 4.18 ppm was attributed the methylene protons connected to the $-OCONH-$ group.[23] The peaks at 2.30 and 1.35 ppm were attributed to the protons of $-CH_3$ and $-C(CH_3)_3$ in TPH, respectively. These indicated that all alcoholic $-OH$ in PHPBT had reacted with NCO group, and further proved the existences of phenolic $-OH$, $-NHCOO-$ group, and benzene ring in obtained PHPBT-b-TPH.

Figure 3 shows the ^{13}C-NMR spectra of PHPBT and PHPBT-b-TPH. In PHPBT spectrum, the peaks at 142 and 112 ppm were attributed to the $-CH=$ and $=CH_2$ carbons of 1, 2-unit ($-CH=CH_2$), respectively. The peaks at 130 ppm were assigned to the carbons of 1, 4 unit ($-CH=CH-$). The peak at 66 ppm assigned to the methine carbons of $-CH(CH_3)OH$. The peak at 60 ppm assigned to the methylene carbons of the $-CH_2OH$ group. Compared with the PHPBT spectrum, in PHPBT-b-TPH spectrum, the new peaks at 155 and 154 ppm were attributed to the carbons of secondary and primary $-NHCOO-$ groups connected to the IPDI ring, respectively. The peak at 152 ppm was assigned to the carbons connected to the phenolic hydroxyl group. The new peaks at 144, 138, 136, and 126 ppm were attributed to the carbons of benzene ring in TPH. The new peaks at about 44–47 ppm were belonged to the methylene carbons of IPDI structure unit.[30] All these peaks were the characteristic absorption peak of the target PHPBT-b-TPH. Combined with the results of FT-IR and ^{1}H-NMR, it could be concluded

that target product PHPBT-b-TPH had been successfully obtained.

Influences of Reaction Conditions on the Reaction Between PHPBT and IPDI

Influence of Catalyst Types. IPDI is an asymmetric cycloaliphatic diisocyanate with a primary NCO bonded to a methylene group and a secondary NCO directly bonded to the cyclohexane ring. The reactivity of the secondary NCO is higher than that of the primary NCO. The selectivity of the two isocyanate groups depends on the catalyst types and reaction temperature.[31,32] In order to ensure that only one NCO group of IPDI reacted with the hydroxyl group ($-OH$) of PHPBT and obtain adduct PHPBT-NCO, the catalysts of DBTDL and TEA were chosen in this study. The FT-IR spectra of reaction solution obtained at different reaction time with two different catalysts at 35°C are showed in Figure 4. As can be seen, with the increase of reaction time, the position of NCO absorption peak of the reaction solution using DBTDL as catalyst shifted toward higher wavenumber. However, using TEA as catalyst, the peak of NCO maintained its initial position, and gel easily formed when the reaction time exceeds 3 h. According to previous report,[33] the wavenumber of the primary NCO group is higher than that of the secondary NCO group, and it is impossible to distinguish the peaks of the primary and secondary NCO groups in FT-IR. However, the position changes as the reaction time increase, which can be as an important evidence for the relative content of the primary NCO group and the secondary NCO group. From the result in Figure 4, it could be deduced that when used DBTDL as catalyst, the $-OH$ group of PHPBT mainly reacted with the secondary NCO group of IPDI, thus the adduct PHPBT-NCO could be obtained. When used TEA as catalyst, the reactivity difference between the primary NCO and the secondary NCO was not large enough. As a result, gel easily formed and the adduct PHPBT-NCO failed to obtain. Based on the analysis above, DBTDL was a suitable catalyst for the nucleophilic reaction between PHPBT and IPDI.
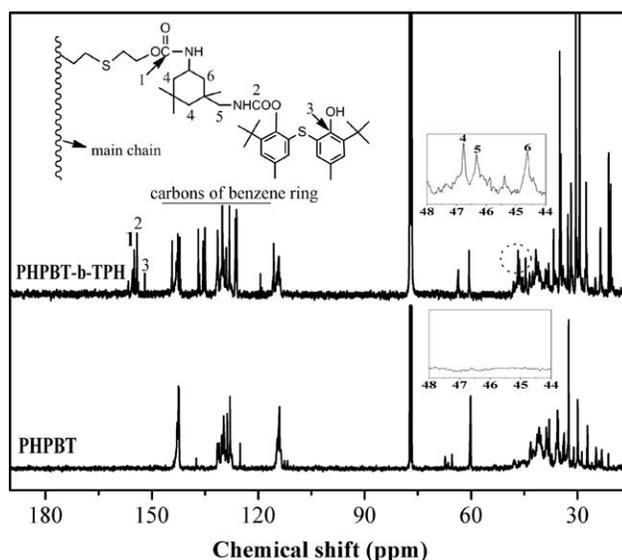
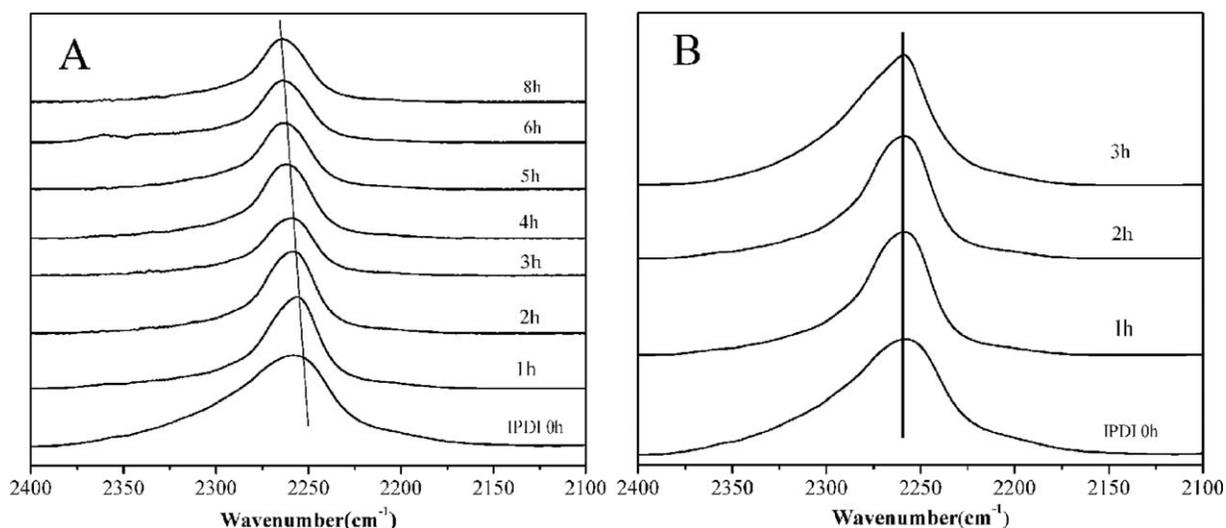

Figure 3. ^{13}C-NMR spectra of PHPBT and PHPBT-b-TPH.

Figure 4. FT-IR spectra in the isocyanate stretching vibration region of reaction solution for the reaction between PHPBT and IPDI using DBTDL (**A**) and TEA (**B**) as catalyst at 35°C.

Influence of DBTDL Amount. The influence of DBTDL amount on the reaction between PHPBT and IPDI at 35°C are showed in Figure 5. As can be seen, the reaction rate increased and the residual NCO content decreased gradually when DBTDL amount increased from 1 to 3 wt % (based on IPDI). However, the reaction rate and residual NCO content hardly changed with further increase of DBTDL amount. Therefore, the suitable DBTDL amount was 3 wt %.

Influence of Reaction Temperature. It was reported that lower temperature would result in higher selectivity of the primary NCO and the secondary NCO group of the IPDI when reaction was catalyzed by DBTDL.[32] However, improving the reaction temperature was necessary to increase the reaction rate due to the low reactivity of NCO group in IPDI to the ─OH group. Therefore, the choice of temperature had a great significance in controlling the reaction between ─OH group and the secondary

NCO group of IPDI to obtain the adduct PHPBT-NCO. Figure 6 shows the influence of reaction temperature on the reaction between PHPBT and IPDI catalyzed by DBTDL. When the temperature was 30°C, the reaction rate was low and the residual NCO content was relatively high. With the temperature was increased to 35°C or 40°C, the reaction rate was increased. When the reaction time reached 6 h, the residual NCO content remained the same, indicating that the ─OH groups of PHPBT had been consumed completely. However, when the reaction temperature increased to 45°C, gel formed after 5 h. This demonstrated that the selectivity of primary and secondary NCO groups was low when the reaction temperature increased to 45°C, which was agreed with the phenomenon of decreasing selectivity with increasing temperature.[32] In order to obtain the adduct PHPBT-NCO and have a higher reaction rate, the suitable temperature was 35°C.
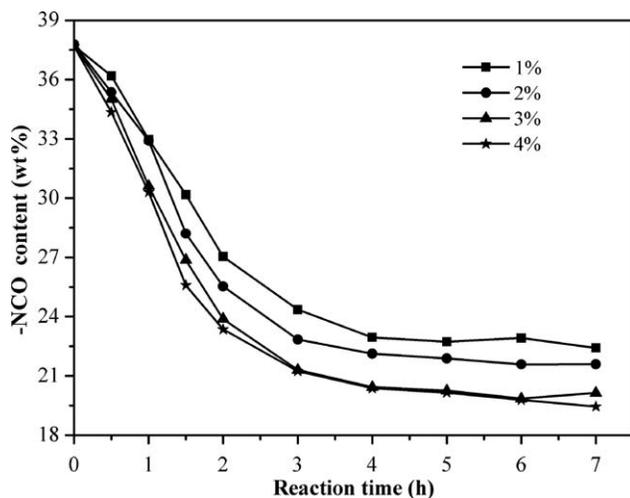

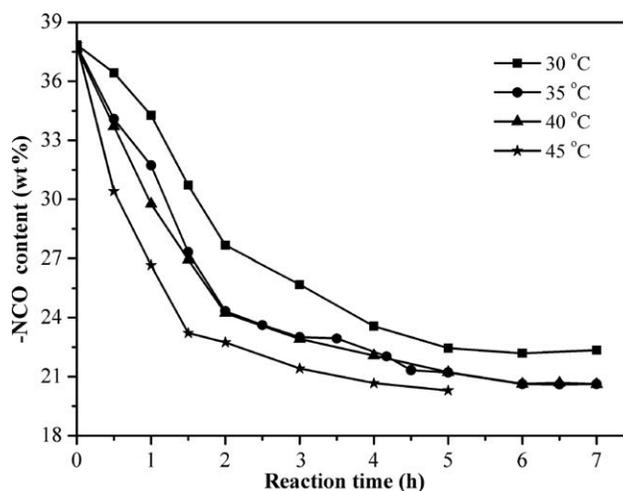**Figure 5.** Influence of DBTDL amount on the reaction between PHPBT and IPDI at 35°C.

Figure 6. Influence of reaction temperature on the reaction between PHPBT and IPDI catalyzed by DBTDL.
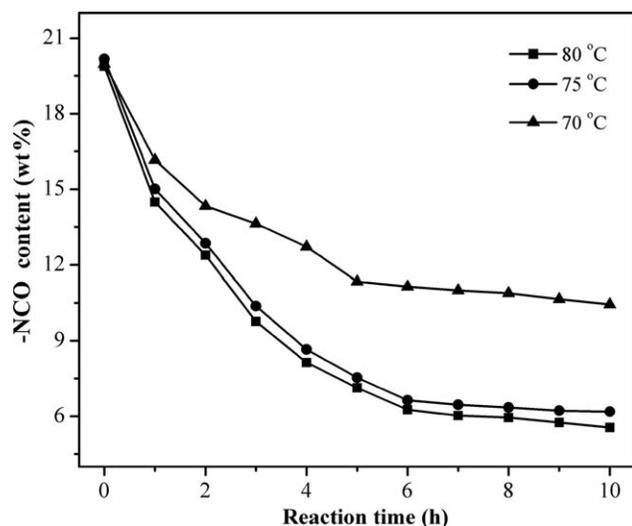
Figure 7. Influence of temperature on the reaction between PHPBT-NCO and TPH catalyzed by DBTDL.

Influences of Reaction Conditions on the Reaction Between PHPBT-NCO and TPH

Influence of Reaction Temperature. The primary NCO group in IPDI has lower reactivity than the secondary NCO group. In addition, the reactivity of phenolic hydroxyl is lower than that of alcohol hydroxyl. In order to ensure that the nucleophilic addition reaction between primary NCO and phenolic OH could be carried out, reaction temperature was necessary to increase. Figure 7 shows the influence of temperature on the reaction between PHPBT-NCO and TPH catalyzed by DBTDL. It was obviously observed that the residual NCO content decreased greatly when the reaction temperature increased from 70°C to 75°C, while there was only a slight change when the reaction temperature further increased to 80°C. It demonstrated that the reaction between the phenolic —OH of TPH and NCO group of PHPBT-NCO was not easy to take place at 70°C. The reactivity could be improved by increasing the reaction temperature. Considering the influence of the temperature on the reaction degree and the risk of forming gel, the suitable temperature for the reaction between PHPBT-NCO and TPH was 75°C.

Influence of Molar Ratio of TPH to NCO. Table I shows the influence of molar ratio of TPH to NCO in PHPBT-NCO on the reaction between PHPBT-NCO and TPH catalyzed by DBTDL at 75°C. When the molar ratio was 1 : 1, the reaction was easy to form gel. With the molar ratio increasing, the gel was not observed and the residual NCO content decreased gradually. After the molar ratio exceeded 2 : 1, the residual NCO content decreased slightly with further increase of TPH amount. It could be explained as follows. When the TPH amount was large enough, the PHPBT-NCO tended to only react with one phenolic —OH of TPH. This was because the reactivity of another phenolic —OH would be greatly reduced due to the steric hindrance effect of the PHPBT chain. Meanwhile, reactivity of the residual NCO decreased significantly with the increase of reaction degree because of the large steric hindrance. Thus, the residual isocyanates were present even for large TPH

Table I. Influence of Molar Ratio of TPH to NCO on the Reaction Between PHPBT-NCO and TPH at 75°C

	Residual —NCO content (wt %)		
$n_{(TPH)} : n_{(NCO)}$	0 h	5 h	10 h
1 : 1	19.98	–	–
1.5 : 1	19.86	10.34	7.53
2 : 1	20.17	8.65	6.18
3 : 1	19.97	8.33	5.83

amounts. However, another phenolic —OH of some TPH would also react with the NCO if the phenolic —OH was not excessive, so the gel formed when the molar ratio was 1 : 1. In this study, taking into account the risk of forming gel and the influence of molar ratio on the residual NCO content, the suitable molar ratio of TPH to the NCO group was 2 : 1.

Influence of Catalyst TEA. As mentioned previously, both the temperature and TPH amount influenced the reaction between the PHPBT-NCO and TPH. However, either improving the temperature or increasing the TPH amount could not make the NCO group to react completely with the phenolic hydroxyl using DBTDL as catalyst. In order to improve reaction degree, another kind of catalyst TEA was used for the reaction between PHPBT-NCO and TPH at 75°C. The FT-IR spectra of reaction solution at different time are showed in Figure 8. Before TPH was added into PHPBT-NCO solution, the peak intensity of NCO group at about 2260 cm^{-1} was very strong. After PHPBT-NCO reacted with TPH for 2 h, the peak intensity of NCO group declined obviously. After 5 h, the peak of NCO group disappeared completely. From the change of the peak intensity of NCO group, it demonstrated that TEA was more suitable than DBTDL for the reaction between PHPBT-NCO and TPH.
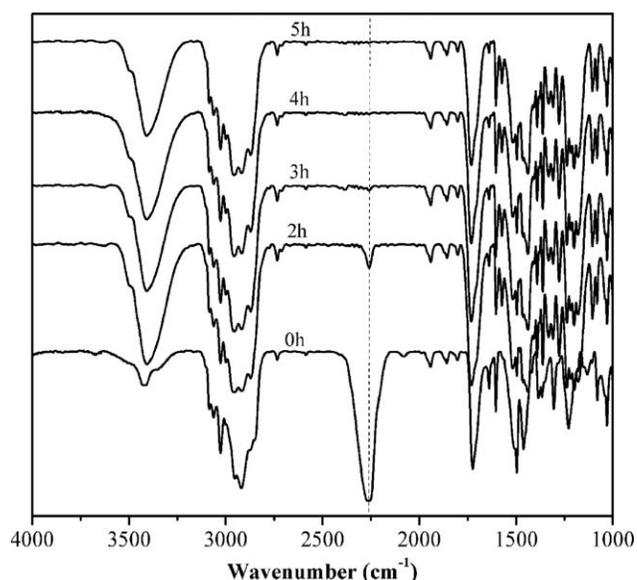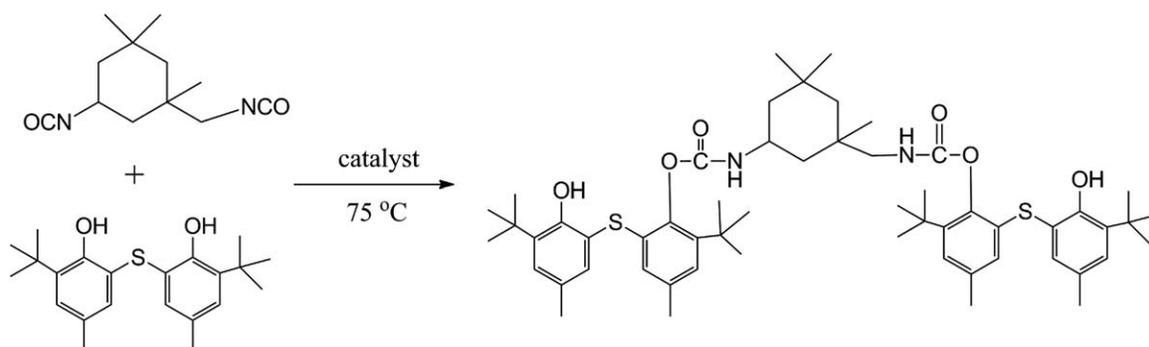

Figure 8. FT-IR spectra of reaction solution at different time for the reaction between PHPBT-NCO and TPH using TEA as catalyst at 75°C.

Scheme 2. The reaction between IPDI and TPH.

Catalytic Mechanism of the Catalyst for the Reaction Between PHPBT-NCO and TPH

In section "Influence of catalyst TEA", catalyzed by TEA, the NCO group in PHPBT-NCO could react with TPH completely, whereas the residual NCO content was relatively high using DBTDL as catalyst. As we know, to obtain the adduct PHPBT-NCO, the catalyst DBTDL was needed to be used for the first step nucleophilic reaction between PHPBT and IPDI. Therefore, DBTDL existed when the reaction between PHPBT-NCO and TPH was catalyzed by TEA. In order to determine whether the DBTDL promoted the reaction between PHPBT-NCO and TPH catalyzed by TEA, reactions between IPDI and TPH (Scheme 2) catalyzed only by TEA or DBTDL were carried out. The reaction temperature was 75°C and the molar ratio of NCO in IPDI to TPH was 1 : 2. Figure 9 shows the FT-IR spectra at different time of the reaction solutions. When only TEA was used as catalyst, the peak intensity of NCO group at 2260 cm^{-1} became very weak after IPDI reacted with TPH for 2 h. After 4 h, the peak of NCO group disappeared completely. It demonstrated that the reaction between IPDI and TPH was carried out completely within 4 h. However, when only DBTDL was used as catalyst, an obvious peak of NCO group at 2260 cm^{-1} still could be observed although the reaction time reached 10 h. These

results suggested that the reaction between PHPBT-NCO and TPH catalyzed only by TEA could be carried out completely. The catalytic activity of TEA for this reaction was much higher than that of DBTDL.

The reasons why the catalytic activity of TEA was much higher than that of the DBTDL for the reaction between PHPBT-NCO and TPH may be attributed to their different catalytic mechanism and steric hindrance effect. The reaction mechanism of nucleophilic addition between phenol and NCO catalyzed by TEA is shown in Scheme 3(A). First, an anionic phenol formed by TEA, and then the anionic phenol attacked isocyanate to form a complex. Finally, the proton transferred to the complex and the NHCOO was obtained.[34] However, when a reaction between phenol and NCO was catalyzed by DBTDL, the isocyanate compound was first activated by DBTDL to form carbocation center, and followed by the nucleophilic attack of the hydroxyl group and obtained a complex. Then urethane was formed by a rearrangement of the complex. The mechanism of nucleophilic addition catalyzed by DBTDL is showed in Scheme 3(B).

TPH is a bisphenol which has a high acidity, low nucleophilicity and large steric hindrance due to the *tert*-butyl group. In the
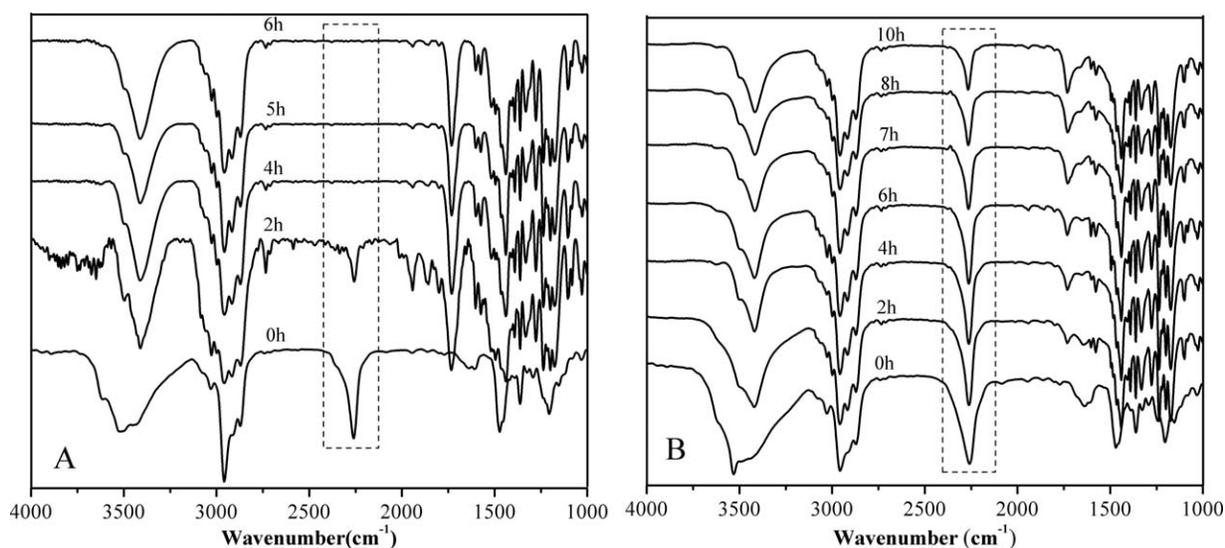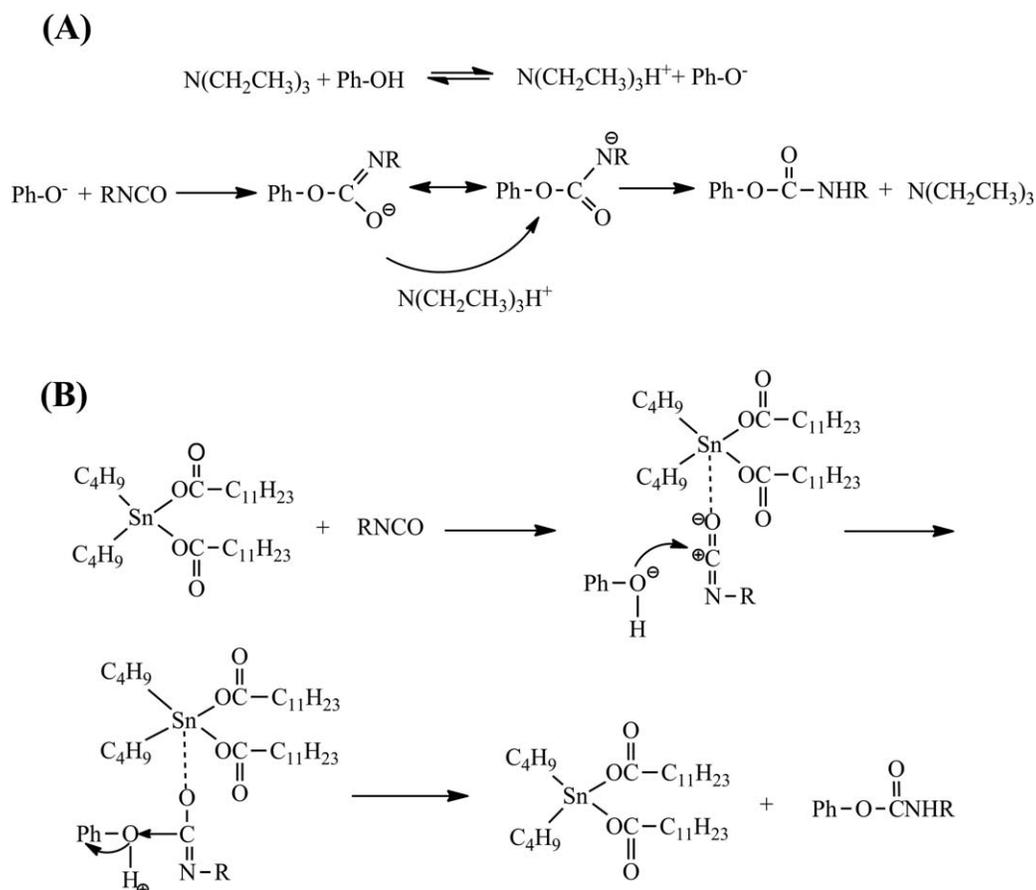

Figure 9. FT-IR spectra of reaction solution at different time for the reaction between IPDI and TPH using TEA (A) and DBTDL (B) as catalyst at 75°C.

(A)

(B)

Scheme 3. Mechanism of nucleophilic addition between isocyanate and phenol catalyzed by TEA (A) and DBTDL (B).

presence of TEA, TPH lost its proton easily and formed a strong nucleophile. Then the nucleophilic addition could be carried out between the strong nucleophile of ph-O⁻ ion and NCO group. However, when DBTDL was the catalyst, the steric hindrance of the NCO was very large because the NCO was bound on the PHPBT chain. On one hand, the NCO was not easy to be activated by DBTDL. On the other hand, the formed complex was not easy to rearrange to obtain urethane.

Furthermore, TPH with low nucleophilicity was difficult to be activated by DBTDL, resulting in its low reactivity. Therefore, due to the large steric hindrance of PHPBT chain and low nucleophilicity of TPH, TEA was more efficient than DBTDL for the reaction between PHPBT-NCO and TPH.

Thermal Stability and Antioxidant Activity of PHPBT-b-TPH

The thermal stability of the samples was evaluated by the initial weight loss temperature (T_i) and the temperature of 50% weight loss ($T_{50\%}$). The T_i is defined as the temperature at which a 5% weight loss occurs. The TG curves of the PHPBT-b-TPH and TPH were showed in Figure 10. The T_i and $T_{50\%}$ of the TPH were only 220°C and 283°C, respectively. Compared with the TPH, the T_i and $T_{50\%}$ of PHPBT-b-TPH increased to 265°C and 347°C, respectively. It demonstrated that the thermal stability of the PHPBT-b-TPH improved remarkably.

Figure 10. TG curves of TPH and PHPBT-b-TPH.

Table II. Retention Rate of Mechanical Properties of NR Vulcanizates (Aged at 100°C for 48 h)

Antioxidants (1 phr[a])	Tensile strength rate (%)	Rate of elongation at break (%)	Tear strength rate (%)
TPH	74	72	83
PHPBT-b-TPH	81	77	87

[a] phr represents the mass parts per 100 mass parts of rubber.
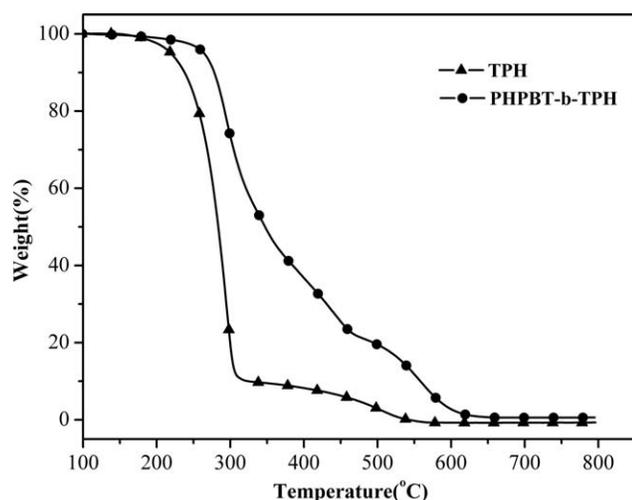
The mechanical properties retentions of natural rubber (NR) vulcanizates were used to evaluate antioxidant activity of the TPH and PHPBT-b-TPH. The mechanical properties retentions of the NR with 1 phr PHPBT-b-TPH or TPH were summarized in Table II. The tensile strength retention, retention of elongation at break, and tear strength retention of the NR vulcanizate with PHPBT-b-TPH were higher than those of the NR vulcanizate with TPH. It demonstrated that the antioxidant activity of the PHPBT-b-TPH was better than that of the TPH. It could be explained as follow. On one hand, the PHPBT-b-TPH had good compatibility with NR, thus it could be dispersed uniformly in NR matrix. On another hand, the PHPBT-b-TPH with high molecular weight could prevent its migration and evaporation from NR, which reduced physical loss of the PHPB-b-TPH. What is more important, the PHPB-b-TPH had many —CH$_2$—S—CH$_2$— and —NHCOO— groups. The synergism effect may occur between —CH$_2$—S—CH$_2$—, —NHCOO—, and phenolic —OH groups.

CONCLUSIONS

A macromolecular hindered phenol antioxidant PHPBT-b-TPH was synthesized successfully by binding 2,2′-thiobis(4-methyl-6-tert-butylphenol) (TPH) onto PHPBT using IPDI as linkage via a two-step nucleophilic addition reaction. The —OH of PHPBT could react with the secondary NCO of IPDI at first to obtain the adduct PHPBT-NCO using DBTDL as catalyst at 35°C. For the reaction between PHPBT-NCO and TPH, the catalytic activity of TEA was much higher than that of DBTDL because of steric hindrance effect. When catalyzed by TEA, the NCO group in PHPBT-NCO could react with TPH completely, whereas the residual NCO content was relatively high using DBTDL as catalyst. The suitable reaction conditions were that the molar ratio of TPH to the NCO group in PHPBT-NCO was 2 : 1, the temperature was 75°C and the catalyst was TEA. Compared with the low molecular weight antioxidant TPH, the PHPBT-b-TPH had more excellent antioxidant activity. Moreover, the thermal stability of PHPBT-b-TPH improved remarkably, whose initial weight loss temperature increased to 265°C from 220°C of the TPH.

REFERENCES

1. Malshe, V. C.; Elango, S.; Rane, S. *J. Appl. Polym. Sci.* **2006**, *100*, 2649.
2. Shehata, A. B.; Nasr, A.; Farouk, T. *Polym. Plast. Technol. Eng.* **2005**, *44*, 1281.
3. Xue, B.; Ogata, K.; Toyota, A. *Polym. Degrad. Stabil.* **2008**, *93*, 347.
4. Xue, B.; Ogata, K.; Toyota, A. *Polymer* **2007**, *48*, 5005.
5. Kim, T. H.; Song, Y. R.; Kim, J. N. *Bull. Korean Chem. Soc.* **2003**, *24*, 1853.
6. Kim, T. H.; Lee, N. *Bull. Korean Chem. Soc.* **2003**, *24*, 1809.
7. Kim, T. H. *J. Appl. Polym. Sci.* **2004**, *94*, 2117.
8. El-Wakil, A. A. *J. Appl. Polym. Sci.* **2007**, *104*, 27.
9. Al-Ghonamy, A. I.; El-Wakil, A. A.; Ramadan, M. *Int. J. Polym. Sci.* **2010**, *2010*, 1.
10. El-Wakil, A. A.; Barakat, M. A. *J. Appl. Polym. Sci.* **2011**, *119*, 2461.
11. El-Wakil, A. A. *J. Appl. Polym. Sci.* **2006**, *101*, 843.
12. El-Wakil, A. A. *Polym. Plast. Technol. Eng.* **2007**, *46*, 661.
13. Podesva, J.; Kovarova, J.; Hrdickova, M.; Netopilik, M. *Polym. Degrad. Stabil.* **2009**, *94*, 647.
14. Podesva, J.; Kovarova, J. *J. Appl. Polym. Sci.* **2003**, *87*, 885.
15. Bozic, M.; Strancar, J.; Kokol, V. *React. Funct. Polym.* **2013**, *73*, 1377.
16. Morshedian, J.; Mohammad, Hoseinpour P.; Azizi, H.; Parvizzad, R. *Express Polym. Lett.* **2009**, *3*, 105.
17. Shen, Y.; Deng, J.; Luo, X.; Zhang, X.; Zeng, X.; Feng, M.; Pan, S. *J. Biomat. Sci., Polym. E* **2009**, *20*, 1217.
18. Chattopadhyay, D. K.; Raju, N. P.; Vairamani, M.; Raju, K. V. S. N. *Prog. Org. Coat.* **2008**, *62*, 117.
19. Prabhakar, A.; Chattopadhyay, D. K.; Jagadeesh, B.; Raju, K. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*, 1196.
20. Han, W.; Lin, B.; Zhou, Y.; Song, J. *Poly. Bull.* **2012**, *68*, 729.
21. Kumari, S.; Mishra, A. K.; Chattopadmay, D. K.; Raju, K. V. S. N. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 2673.
22. Gao, Q.; Li, H.; Zeng, X., *J. Coat. Technol. Res.* **2011**, *8*, 61.
23. Dzunuzovic, E.; Tasic, S.; Bozic, B.; Jeremic, K.; Dunjic, B. *React. Funct. Polym.* **2006**, *66*, 1097.
24. Wang, Y.; Zeng, X.; Li, H.; Guo, J. *J. Macromol. Sci., Part B: Phys.* **2012**, *51*, 1904.
25. Mitrofanova, S. E.; Girfanova, E. N.; Averko-Antonovich, I. Y.; Cherezova, E. N. *Russ. J. Appl. Chem.* **2006**, *79*, 137.
26. Wu, W.; Zeng, X.; Li, H.; Lai, X.; Yan, Z. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2014**, *51*, 229.
27. Kantheti, S.; Sarath, P. S.; Narayan, R.; Raju, K. V. S. N. *React. Funct. Polym.* **2013**, *73*, 1597.
28. Semsarzadeh, M. A.; Navarchian, A. H. *J. Appl. Polym. Sci.* **2003**, *90*, 963.
29. Ahmad, S.; Pawelke, B.; Zulfiqar, S.; Habicher, W. D. *Polym. Degrad. Stabil.* **2001**, *72*, 47.
30. Raghu, A. V.; Jeong, H. M.; Kim, J. H.; Lee, Y. R.; Cho, Y. B.; Sirsalmath, K. *Macromol. Res.* **2008**, *16*, 194.
31. Lomolder, R.; Plogmann, F.; Speier, P. *J. Coat. Technol.* **1997**, *69*, 51.
32. Burel, F.; Feldman, A.; Bunel, C. *Polymer* **2005**, *46*, 15.
33. Sardon, H.; Irusta, L.; Fernandez-Berridi, M. *J. Prog. Org. Coat.* **2009**, *66*, 291.
34. Silva, A. L.; Bordado, J. C. *Catal. Rev.* **2004**, *46*, 31.