

Electronic Supplementary Information

Hydrogenated hydroxy-terminated butadiene-acrylonitrile copolymer-based polyurethane elastomer with improved mechanical properties and aging resistance

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Experimental

Materials

HTBN, with a hydroxyl group value of 0.6833 mmol/g, a number average molecular weight (M_n) of 8700 $\text{g}\cdot\text{mol}^{-1}$ (Figure S1, ESI[†]), and a polydispersity index (PDI) of 2.31 (table S2, ESI[†]), was purchased from Zibo Qilong Chemical Co., Ltd. TDI (reagent grade) was purchased from Chengdu Union Chemical Reagent Research Institute. DMTDA (reagent grade) was purchased from Tianjin Sheehan Biochemical Technology Co., Ltd. Xylene (equilibrium mixture) and ethanol of analytical grade was purchased from Beijing Chemical Company, China. The Rh-SiO₂ fiber catalyst used in the hydrogenation of HTBN was prepared according to our previous study.

Hydrogenation of HTBN

The synthesis of HHTBN with a degree of hydrogenation of nearly 100 % is as follows: The Xylene solution of HTBN (60 g HTBN in 60 g xylene) and the Rh-SiO₂ fiber catalyst were added to a 500ml-stainless steel autoclave which is not lined. The autoclave was purged with N₂ and H₂ three times each. Then, the reaction was initiated by heating the autoclave to the reaction temperature of 120 °C, flushing H₂ to the reaction pressure of 4 MPa, and adjusting the agitation rate to 1000 rpm. The reaction time is 12 h. The molar ratio between the Rh in the Rh-SiO₂ fiber catalyst and the C=C in the HTBN is 1: 500. During the reaction, the reaction temperature was kept constant, and the H₂ pressure was also kept constant by using an automatic gas flow meter. After the reaction, the catalyst was separated from the product by centrifugation. The HHTBN with a degree of hydrogenation of nearly 100 % was obtained by heating the Xylene solution of HHTBN in vacuum at 80 °C for 24 h to remove the xylene.

Synthesis of polyurethanes

The HHTBN (16.9 g) was put in a one-neck, round-bottom flask and dewatered at 100 °C for 1 h. When the HHTBN was cooled down to 80 °C, TDI (1.51 g) was added into the round-bottom flask. Then the mixture was degassed for 30 min, and the chain extender DMTDA (0.618 g) was added into the system. After being stirring for 30min, the mixture was cast into molds (size: 10cm×10cm×2mm) and cured for 1 h in plate vulcanizing machine at 110 °C to carry out the reaction between HHTBN, TDI, and DMTDA, and form the HHTBN-based PUEs. The HTBN-based PUEs were prepared by the same method but without the hydrogenation of HTBN. The samples were kept at room temperature for a week before testing.

Characterizations

To investigate the effect of thermal oxidative aging on the mechanical properties of HTBN-based PUEs and HHTBN-based PUEs, dumb bell-shaped specimens were aged in a thermal oxidative aging oven at 120 °C for 0, 24, 48, and 72 h. Then the aged specimens were kept at room temperature for 24 h, and a tensile testing machine (CMT4104, Shenzhen SANS Test Machine, Shenzhen, China) was used to measure the tensile strength

and elongation at break, according to Chinese standard GB/T528-2009 (original length 25 mm). In every measurement, five different specimens were measured. To investigate the effect of ozone aging on the mechanical properties of HTBN-based PUEs and HHTBN-based PUEs, specimens (10×60×2 mm³) with a deformation of 20 % were placed into an ozone aging oven with the ozone concentration of 50 ppm and relative humidity of 50 % at 40 °C for 48 h. The surface crack of ozone-aged specimens was characterized by scanning electron microscope (SEM) (Hitachi S-4800). The structures of HTBN and HHTBN were characterized by ¹HNMR performed on a Bruker AV400 nuclear magnetic resonance instrument with CDCl₃ as solvent. ATR-FTIR spectroscopy was used to characterize the changes in the chemical structure of (H)HTBN-based PUEs during thermal oxidative aging at 120 °C for 0, 48, 96, 144, and 168 h by using a Bruker TENSOR 27 Fourier transform infrared spectrometer in the wavenumber range 600-4000 cm⁻¹. The glass transition temperatures of the PUEs were measured by differential scanning calorimetry (DSC) performed on a Mettler-Toledo DSC instrument. Samples of about 5 mg was heated from room temperature to 100 °C at a rate of 10 °C/min and then kept isothermal for 10 min. Then the temperature was cooled to -100 °C before the scanning run at a heating rate of 10 °C/min from -100 °C to 100 °C. Thermogravimetric analysis (TGA) was carried out on a STARe system from 30 to 700 °C at a heating rate of 10 °C/min in N₂ atmosphere.

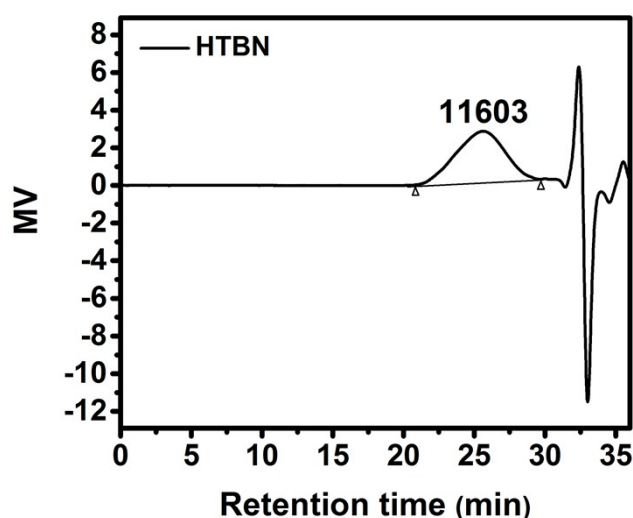


Figure S1. GPC spectrum of HTBN.

Table S1. GPC results of HTBN.

	Mn	Mw	MP	Mz	M _{Z+1}	Mv	Polydispersity	K(dl/g)	alpha
1	8701	20114	11603	42392	69803	17787	2.31	0.0001600	0.7060

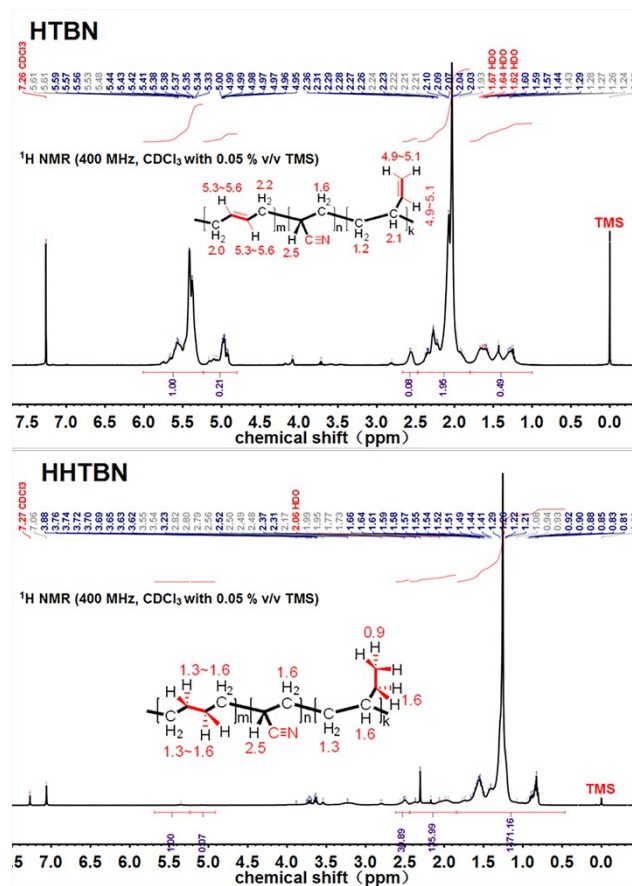


Figure S2. $^1\text{H NMR}$ Spectra of HTBN and HHTBN.