Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

How chemical cross-linking and entanglements in polybutadiene elastomers cope with tearing

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EXPERIMENTAL

Materials: Both-end hydroxyl group-terminated hydrogenated polybutadiene (BHH-PB) (GI2000, molecular weight, Mn ~ 2000) was obtained from Nippon Soda Co., Ltd., polybutadiene adducted with maleic anhydride (PAMA) (Ricon 130MA8, number average molecular weight, Mn ~ 3100) was purchased from Cray Valley Chemical Co., Ltd. Hexamethylene diisocyanate (HDI), dibutyltin dilaurate (DBTDL), pentaerythritol tetrakys 3-(3,5-ditert-butyl-4-hydroxyphenyl)propionate (RALOX 630), and dichloromethane were obtained from Aladdin Inc. All materials were used as received without further processing.

Methods

B-H-P elastomers. BHH-PB (1.1 eq. of -OH), HDI (1 eq. of -NCO), DBTDL (0.005 eq. of -NCO), and 5 mL dichloromethane were added to a flask, the mixture was stirred for 3 h at 25 °C to form intermediate product (B-H). Subsequently, PAMA (0.25 g, 0.5 g, 0.75 g, 1 g) and RALOX 630 (1 wt%) was added to the flask, followed by pouring the mixture into a Teflon mold. The mixture was cured for 2 h at 150 °C to obtain the B-H-P elastomers.

Optical images. The optical images were obtained with an iPhone.

Tensile and tear test. Mechanical tensile-stress experiments were carried out by a SUNS UTM4000 instrument at room temperature (25 °C) with a displacement rate of 10 mm min^{-1}. The tear test is to control the crack speed at 0.017 mm s^{-1}, 0.067 mm s^{-1}, 0.25 mm s^{-1}, 0.83 mm s^{-1}, and 2.5 mm s^{-1}.

Dynamic mechanical analysis. Dynamic mechanical analysis was performed on a TA

Instruments RSA-G2 Solids Analyzer. Samples were cut into square for characterization. For stretching cycle tests, a 0.83 mm s^{-1} speed was applied on the samples to stretch to 100%, and then keep the speed 0.83 mm s^{-1} to 0%.

Rheology test. The dynamic viscoelasticity of the samples was measured by an Anton Paar model MCR-302 rheometer. The samples were placed under a 25 mm diameter parallel plate. In the frequency sweep tests, the angular frequency (ω) was from 100 to 0.01 rad s^{-1} at 25 °C with the shear strain (γ) of 1%.

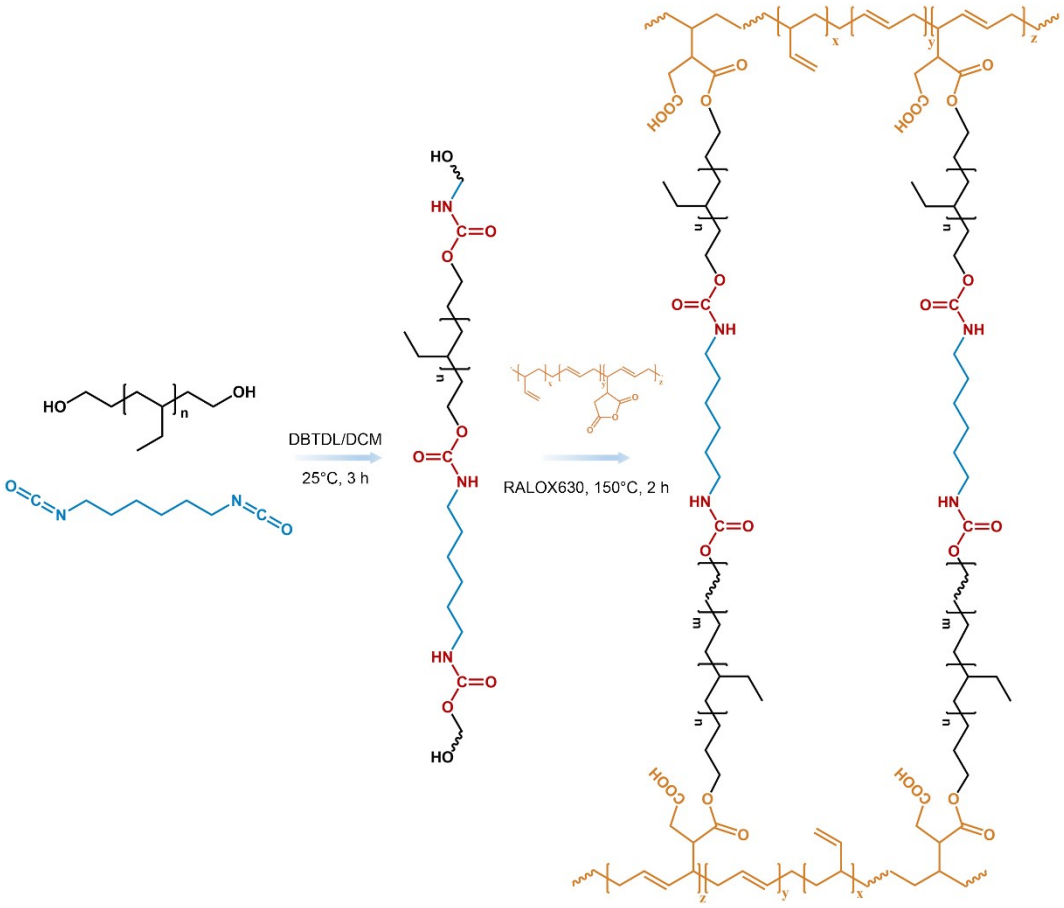

Fig. S1 Chemical reaction flow diagram for the preparation of B-H-P$_x$ elastomers.

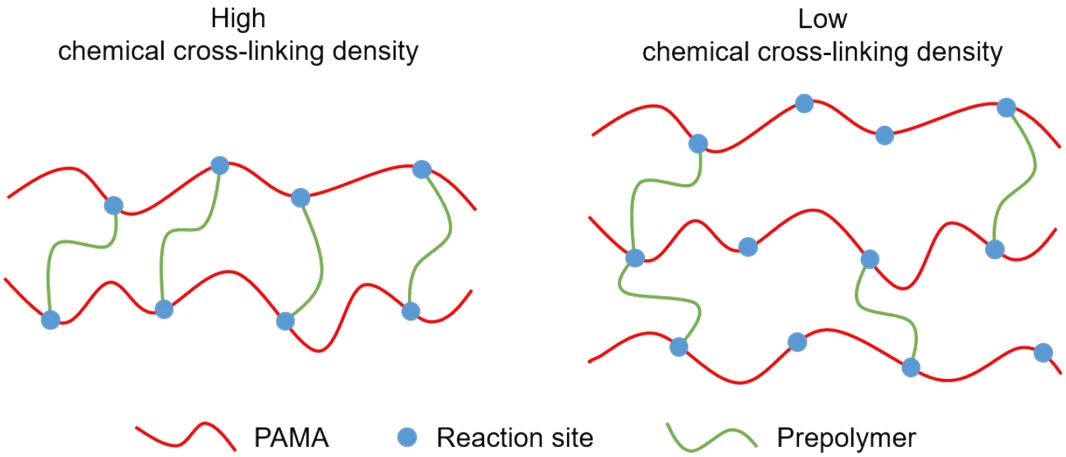

Fig. S2 Schematic diagram of branch points affect the chemical cross-linking density of elastomers.

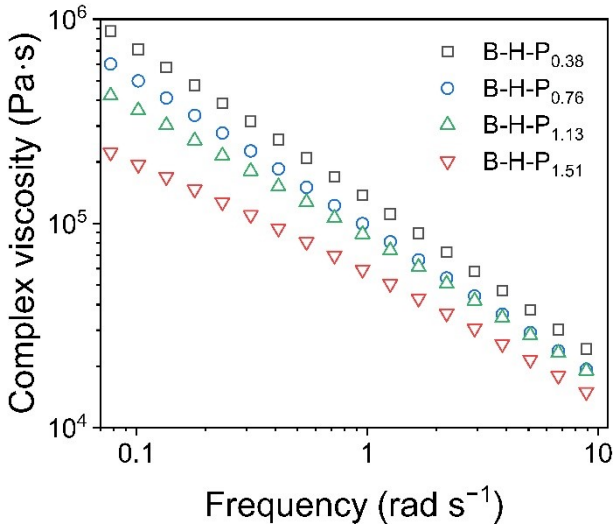

Fig. S3 Complex viscosity of fabricated elastomers.

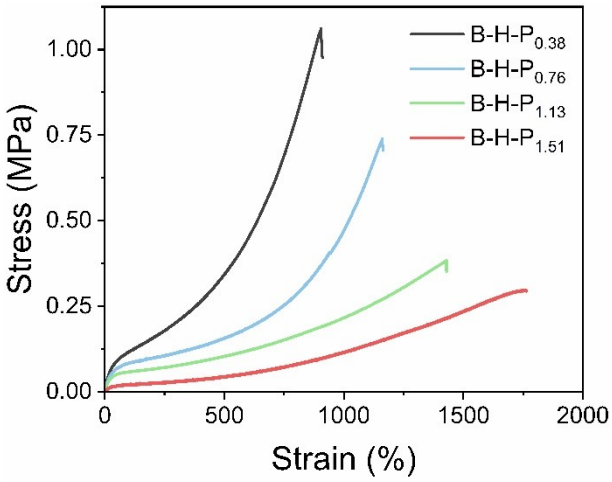

Fig. S4 Stess-strain curves for B-H-P_x elastomers.

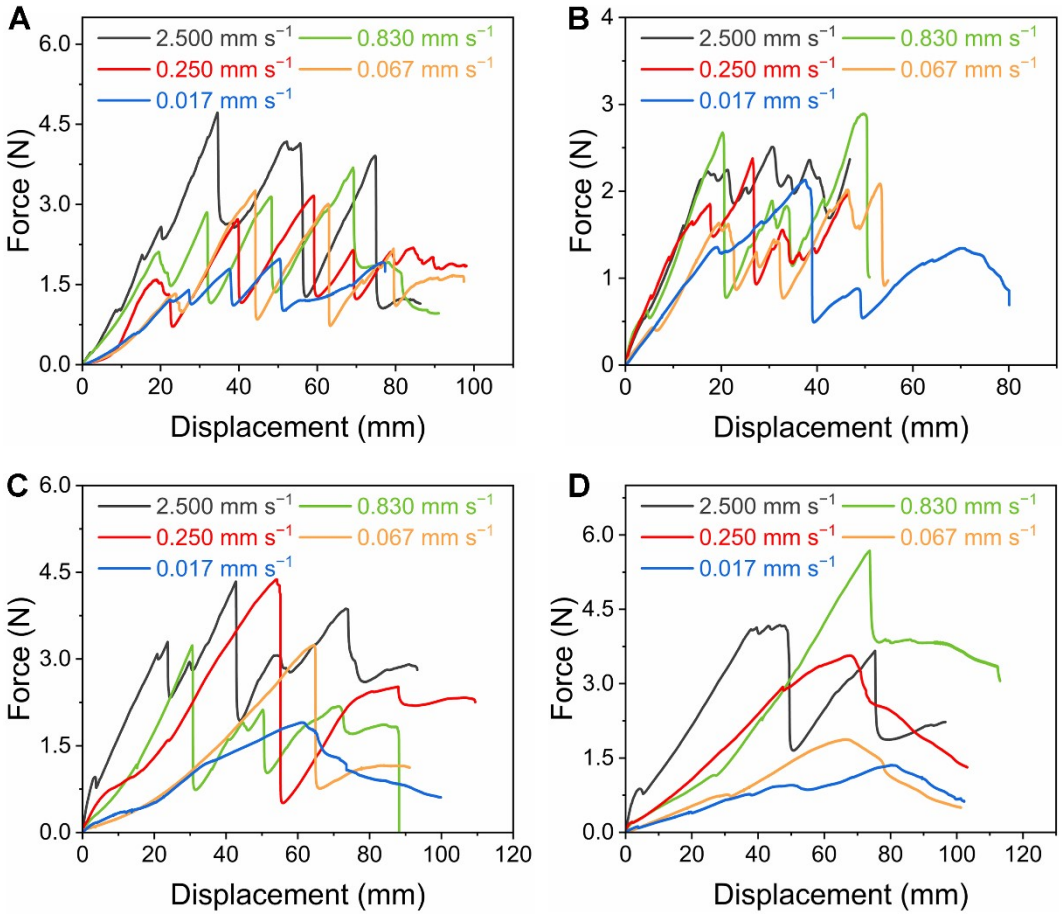

Fig. S5 Force-displacement curves. A B-H-$P_{0.38}$, **B** B-H-$P_{0.76}$, **C** B-H-$P_{1.13}$, and **D** B-H-$P_{1.51}$ elastomers.

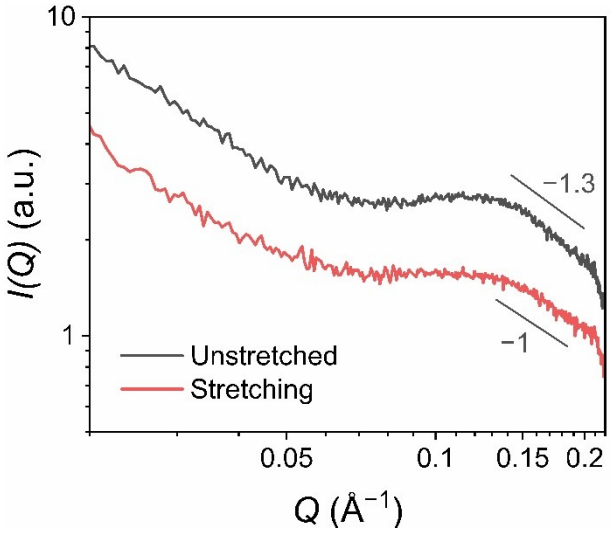

Fig. S6 Small-angle X-ray scattering of B-H-$P_{1.51}$ elastomer.

Table S1 The chemical cross-linking density of the elastomers.

Elastomer	B-H-$P_{0.38}$	B-H-$P_{0.76}$	B-H-$P_{1.13}$	B-H-$P_{1.51}$
Crosslinking density (10^{-4} mol ml^{-1})	56.205	48.463	40.285	30.171

Table S2 The calculated molecular weight between two cross-linkers and molecular weight between two entanglement points of the elastomers.

Elastomer	B-H-$P_{0.38}$	B-H-$P_{0.76}$	B-H-$P_{1.13}$	B-H-$P_{1.51}$
Molecular weight between two cross-linkers (g mol^{-1})	344492	400390	646175	959195
Molecular weight between two entanglement points (g mol^{-1})	27637	32957	46695	148305