

Impact of hydrogen bonds dynamics on mechanical behavior of supramolecular elastomer



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ABSTRACT

Here our special consideration is devoted to the relationship between dynamics and mechanical behaviours of supramolecular elastomer (SE) based on 2-ureido-4[1H]-pyrimidinone (UPy) groups. We find that SE exhibits a new relaxation mode (α' relaxation) which differs from segmental relaxation mode (α relaxation) and normal relaxation mode (NM). Calculated by Arrhenius model, supramolecular interactions are much lower than the bonds energy of covalent bonds; this enables high energy dissipation as the elastomer is subjected to deformation. Moreover, unlike covalent bonds, the hydrogen bonds of UPy groups are dynamic and longer waiting time leads to better re-association efficiency, as evidenced by recovery of hysteresis loop during cyclic tensile tests. This work on the relationship between dynamics and mechanical properties will not only improve the understanding of reversible bonds relaxation, but also provide an idea on preparing mechanically robust SE for us.

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1. Introduction

Supramolecular polymers are assembled from monomeric building blocks through noncovalent interactions, such as hydrogen bonds and metal-ligand interactions [1]. Among such noncovalent bonds, hydrogen bond is a promising candidate because of its intrinsic directionality and versatility. The structural reversibility, caused by the transient nature of secondary interactions, often endows polymers with a wide range of tunable characteristics including self-healing properties, long stacking structure, and shape memory properties [2–12], but hydrogen bonds as weaker physical interactions lead to supramolecular materials with low mechanical properties, limiting their applications [13–15]. To exploit mechanically robust supramolecular elastomers (SE), it is very essential for us to systematically explore the relationship between hydrogen bonds dynamics and mechanical behaviors.

Recently, constructing supramolecular polymers through self-assembly of building blocks has appealed to many researchers' attention. Numerous experimental and theoretical studies have shown that the morphology and domain spacing of separated nanophase can be controlled by varying the degree of

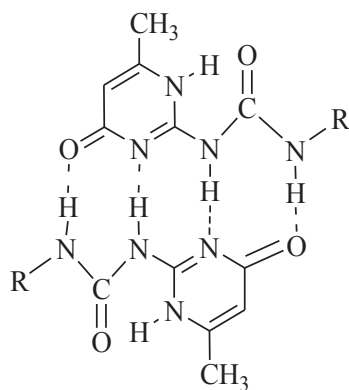
polymerization, the volume fraction, and the interaction parameter between blocks [15,16]. However, less attention has been paid to relate the dynamics with mechanical properties of supramolecular polymers. Previous article has analyzed the dynamics of reversible bonds in detail from theoretical viewpoint, which can be described well by hindered reptation model [17]. For example, enhanced relaxation phenomenon, a new relaxation process combined with an intermolecular association and dissociation process, is observed in reversible bonds [18–23]. This model provides very useful method for us to study the dynamics of supramolecular interactions and calculate the activation energy between them. In addition, inspired by the research methods of double networks toughening mechanism [5,24–27], we can probe the weaker bonds rupture by the energy dissipation. We envision that the dynamics of reversible bonds from microscopic perspective can be considered as the cause for the change of mechanical behaviors. Thus, the bridge is developed between supramolecular interactions and mechanical properties.

Here telechelic oligoisoprene is reacted with 2-ureido-4[1H]-pyrimidinone (UPy) groups, as shown in Scheme 1. The SE is based on the self-complementary quadruple hydrogen bonds of UPy groups. We find that SE exhibits a new relaxation mode (α' relaxation) which differs from segmental relaxation mode (α relaxation) and normal relaxation mode (NM). Calculated by Arrhenius model, supramolecular interactions is much lower than the bonds energy of covalent bonds. That means supramolecular interactions can preferentially break before that rupture of covalent bonds. Thus we

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Scheme 1. UPy groups.

can use energy dissipation to increase mechanical properties such as toughness upon deformation. This work on the relationship between dynamics and mechanical properties will not only improve the understanding of reversible bonds relaxation behavior, but also provide an idea on preparing mechanically robust SE for us.

2. Experimental section

2.1. Materials

Polyisoprene (PI, GPC data: $M_n = 241468$ g/mol, $DPI = 3.893$) was purchased from Shanghai Sanlian Co., Ltd. 3-Chloroperoxybenzoic acid (MCPBA, 85%), periodic acid (99%), sodium borohydride (NaBH_4 , 98%), DCP (98%), 2-amino-4-hydroxy-6-methylpyrimidine (98%), hexyldiisocyanate (98%), and dibutyltindilaurate (95%) were purchased from Adamas Reagent Co., Ltd. Tetrahydrofuran (THF) was purchased from Shanghai Titan Scientific Co., Ltd and used without further purification.

2.2. Preparation of HTPI

The synthesis of HTPI was performed according to the previous literature [28,29]. First, we used MCPBA to prepare epoxidized PI in THF. Through oxidative chain cleavage reaction, we used periodic acid to prepare carbonyl telechelic oligoisoprene (CTPI). Through the reduction of CTPI, HTPI was obtained. GPC data of HTPI: $M_n = 23000$ g/mol.

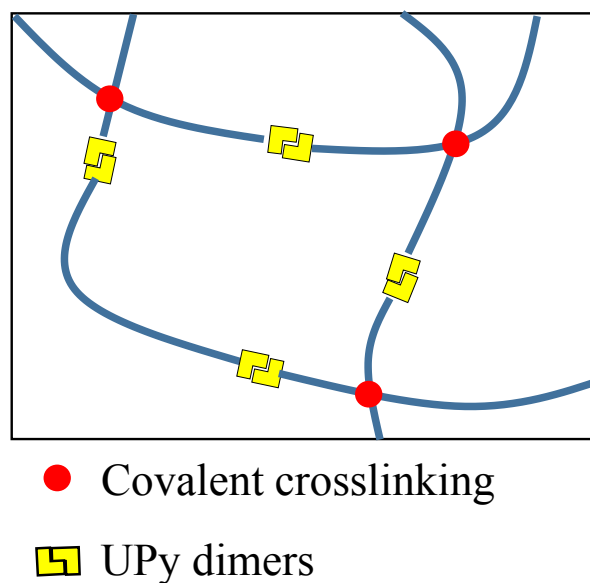
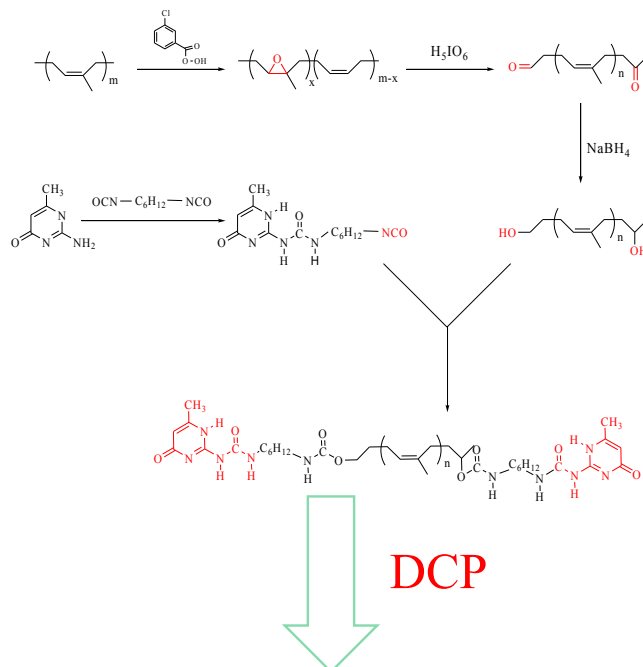
2.3. Preparation of SE

According to the method invented by Sijbesma and Meijer [30], the UPy unit linked to a reactive isocyanate group (UPy-NCO) was prepared. To a solution of HTPI in 700 mL chloroform, UPy-NCO was added. After addition of 2 drops dibutyltindilaurate, the resulting solution was stirred at 60 °C for 16 h. After the end of reaction, chloroform solution was cooled to room temperature. Then 1 phr DCP crosslinker (based on 100 phr SE) was added to chloroform solution. After chloroform was removed, the resulting material was cured in a hydraulic press at 160 °C for 25 min. The synthesis process is shown in Scheme 2.

2.4. Characterization

2.4.1. Fourier transform infrared (FTIR)

The FTIR spectra were measured at room temperature using Thermo Scientific Nicolet iS50 FTIR with a resolution of 4 cm^{-1} . Attenuated total reflection with SeZn crystal was used to obtain the



Scheme 2. Synthesis process of SE.

FTIR spectra. The wavenumber range was from 4000 cm^{-1} to 650 cm^{-1} .

2.4.2. Dynamic mechanical analysis (DMA)

Dynamic mechanical properties were measured in a tensile mode on a Q800 DMA (TA Instruments) under a nitrogen atmosphere. The dimensions of the specimens tested were 12 mm \times 6.5 mm \times 1 mm. The DMA spectra were performed at heating rate of 3 °C/min and a frequency of 1 Hz. The temperature range was -100 °C to 100 °C and a preload force of 0.01 N was applied.

2.4.3. Broadband dielectric spectroscopy (BDS)

Dielectric measurements were performed over the frequency range of 10^{-1} – 10^7 Hz on a Novocontrol Concept 50 system with Alpha impedance analyzer and Quatro Cryosystem temperature control. The disk-shaped film of about 1 mm thickness was placed

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