

“Solid-Liquid” Vitrimers Based on Dynamic Boronic Ester Networks

Sheng Wang^{a,b}, Lu-Lu Xue^a, Xiao-Zhuang Zhou^a, and Jia-Xi Cui^{a,c,*}

^a INM – Leibniz Institute for New Materials Campus D2 2, Saarbrücken 66123, Germany

^b Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^c Institute of Fundamental and Frontier Sciences, University of Electronic Science and Technology of China, Chengdu 610054, China

Electronic Supplementary Information

Abstract The “solid-liquid” behavior of vitrimers have not been systematically investigated. Herein, a series of “solid-liquid” vitrimers bearing varying contents of dynamic boronic ester bonds were synthesized *via* thiol-ene click reactions. These vitrimers allow for flexible modulation of their network structures and thus show a range of intriguing properties including high stretchability, flexible transition from elasticity to plasticity, strong strain rate dependence, and solid-liquid performance. The dynamic association rate of boronic ester bonds within these vitrimers could be apparently accelerated *via* increasing the content of boronic ester, which could be used to shape-program the flat vitrimer films into various complex 3D structures just with external force. Materials with such versatile dynamic behavior may open up a range of new applications.

Keywords Solid-liquid; Dynamic covalent bond; Boronic ester bond; Strain-rate dependent; High stretchability

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INTRODUCTION

“Solid-liquid” material, which can flow as a highly viscous liquid at a low strain rate but behave like an elastic solid at a high strain rate under room temperature, is attracting enormous attention owing to its potential applications in artificial skin,^[1] flexible electric devices,^[2–4] battery electrode binders,^[5] and multifunctional sensors,^[6–9] etc., Polyborosiloxane (PBS), nicknamed as “silly putty”, is the mostly studied “solid-liquid” material because of the reversible association/dissociation of the boron/oxygen dative bond.^[10–12] Moreover, the strain rate dependent “solid-liquid” behavior could also be observed in the polymer materials when introducing hydrogen bonds^[13] or ion bonds.^[14] However, these materials commonly exhibit weaker mechanic strength due to the weak noncovalent interactions, which greatly limits their practical applications. On the other hand, vitrimers, which can change the topology while maintaining a constant number of chemical bonds, have generated considerable interest as they offer increased mechanical properties and solvent resistance while maintaining malleability/reprocessability.^[15–18] In the last decades, various dynamic covalent motifs, such as transesterification,^[19–23] olefin metathesis,^[24] silyl ether metathesis,^[25,26] trans-

amination of vinylogous urethanes,^[27] boronic ester^[28] or boroxine exchange,^[29,30] imine exchange,^[31] etc., have been employed in vitrimer designs. Compared to the non-covalent bonds, dynamic covalent bonds are usually more stable. Although the associative exchange reactions of dynamic covalent bonds can take place under external stimuli, the “solid-liquid” behavior have rarely been carefully investigated in vitrimers.

Boronic ester (BE) bonds are a kind of thermally stable and robust dynamic covalent bonds, which can undergo associative exchange reactions to rearrange network topology in bulk polymers without the need of catalyst compared to other dynamic covalent systems.^[28,32–35] In this work, we report a class of novel vitrimers bearing various BE contents which can exhibit high stretchability, strong strain rate dependence, and unique “solid-liquid” performance. The dynamic association equilibrium nature of BE bonds serves as the mechanistic basis for these dynamic mechanical properties (Fig. 1c). When the external force is applied slowly (a low strain rate), the exchange reactions between BE bonds have sufficient time to take place, thus relaxing the inner stress and leading to a low modulus. Under this condition, the vitrimer presents plasticity and behaves like a “liquid”. When the external force is applied quickly (a high strain rate), however, the timescale may be sufficiently short so that the BE association is practically negligible. The inner stress is unable to relax in time, resulting in a high modulus. The vitrimer behaves like an elastic solid. This “solid-liquid” behavior can be well modulated by varying the contents of BE bonds and crosslinkers (Fig. 1b).

* Corresponding author, E-mail: Jiaxi.Cui@uestc.edu.cn

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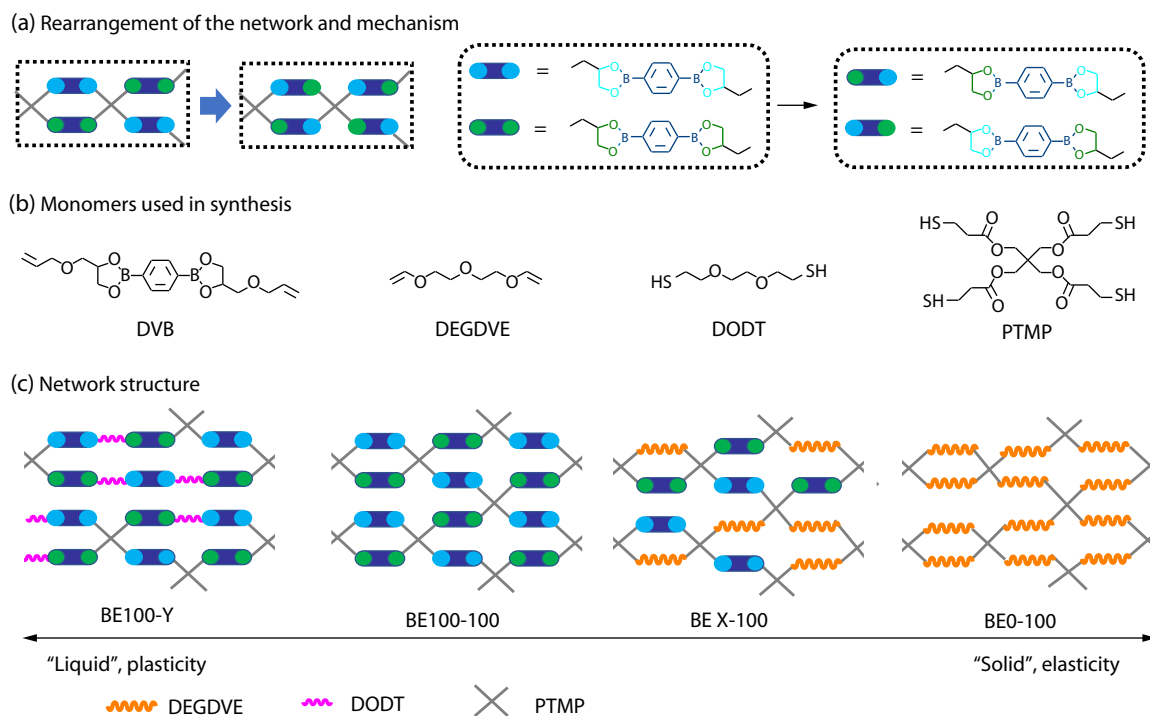


Fig. 1 Design and synthesis of “solid-liquid” vitrimer. (a) rearrangement of the boronic ester network and the inner dynamic mechanism; (b) Chemical structure of monomers used in synthesis; (c) Tunable “solid-liquid” behavior of BE vitrimers by varying the contents of boronic ester bonds and crosslinkers.

Moreover, various 3D shapes of BE vitrimers could be easily obtained under the external force without the need of solvents, molds, or high temperature.

EXPERIMENTAL

Materials

Benzene-1,4-diboronic acid (97%, Sigma-Aldrich), pentaerythritol tetrakis(3-mercaptopropionate) (PTMP, 95%, Sigma-Aldrich), 3-allyloxy-1,2-propanediol (99%, Sigma-Aldrich), Di(ethylene glycol) divinyl ether (99%, Sigma-Aldrich), 3,6-dioxo-1,8-octanedithiol (DODT, 95%, Sigma-Aldrich), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%, Sigma-Aldrich), magnesium sulfate (99.5%, Sigma-Aldrich), tetrahydrofuran (99.9%, Sigma-Aldrich), chloroform-*d* (CDCl_3 , 99.96 atom% D, contains 0.03% (V/V) TMS, Sigma-Aldrich) were used as received.

Instrumentation and Analysis

$^1\text{H}/^{13}\text{C}$ -NMR spectra were recorded on a Bruker ARX 300 instrument using CDCl_3 as the solvent and tetramethylsilane as the internal standard. Tensile tests were performed at room temperature using an Instron 3365 instrument with a 2 kN load cell and different deformation rates from 0.1 mm/min to 10 mm/min. Dog-bone shape samples (5 mm $\times$ 2 mm $\times$ 20 mm gauge length) were used for tensile tests. The modulus was calculated by the slope between the stress and the strain in the strain ranges of 5%–10%.

DMA tester (Q800 DMA, TA Instruments) was employed to characterize the thermomechanical properties in the dual cantilever mode. Samples with the dimension of 50 mm $\times$ 5.0 mm $\times$ 2.0 mm were tested at a frequency of 1 Hz and an amplitude of 50 μm . The temperature was first equilibrated

at -90°C for 5 min, and then increased at a heating rate of $3^\circ\text{C}/\text{min}$. The glass transition temperatures (T_g) were determined from the peak of the $\tan\delta$.

Stress relaxation tests were performed on the DMA tester (Q800 DMA, TA Instruments) using dual cantilever mode on rectangular samples (50 mm $\times$ 5.0 mm $\times$ 2.0 mm). After loading, the sample was equilibrated at the specified temperature (from 0 to 45°C) for 1 min. A constant deflection of 5.0% was applied to monitor the stress relaxation for 120 min.

Rheological measurements were carried out on a TA instruments discovery hybrid rheometer with a PP8, 8 mm diameter parallel plate geometry and a rough surface. The dynamic modulus versus frequency were plotted with the strain of 1%.

Synthesis of Monomer

1,4-Bis(4-((allyloxy)methyl)-1,3,2-dioxaborolan-2-yl)benzene (DVBE)

The divinyl-containing boronic ester (DVBE), was synthesized from the complexation between benzene-1,4-diboronic acid and 3-allyloxy-1,2-propanediol. Briefly, benzene-1,4-diboronic acid (6.0 g, 36.2 mmol) and 3-allyloxy-1,2-propanediol (9.82 g, 74.4 mmol) were dissolved in tetrahydrofuran (120 mL) and water (0.15 mL), to which magnesium sulfate (10.0 g) was added. After stirring at room temperature for 24 h, the mixture was filtered and concentrated to obtain the target compound as colorless oil-like liquid (11.7 g, 90%). ^1H -NMR (300 MHz, CDCl_3 , δ , ppm): 7.76 (s, 4H), 5.83 (ddt, $J=17.2$, 10.4, 5.6 Hz, 2H), 5.16 (dddd, $J=10.4$, 4.0, 3.0, 1.4 Hz, 4H), 4.67 (ddt, $J=8.1$, 6.5, 5.1 Hz, 2H), 4.42–4.30 (m, 2H), 4.12 (dd, $J=9.1$, 6.6 Hz, 2H), 4.03–3.97 (m, 4H), 3.54 (ddd, $J=22.7$, 10.2, 5.1 Hz, 4H). ^{13}C -NMR (75 MHz, CDCl_3 , δ , ppm): 134.35, 134.11, 117.51, 76.22, 72.59, 71.91, 68.51.

Typical Synthesis Procedure of BE Elastomers

Take BE100-100 as an example. DVBE (4.00 g, 11.2 mmol) and photoinitiator I651 (75 mg) were blended with pentaerythritoltetrakis(3-mercaptopropionate) (PTMP, 2.73 g, 5.59 mmol) together, and sonicated for several minutes until a homogeneous solution was formed. Then the mixed solution was quickly poured into Teflon mold and sent for photocuring. During the curing step, the mixed solution was irradiated with 365 nm light at ~ 15 mW/cm² intensity for 30 min per side. By controlling the adding ratios of DVBE, PTMP, DEGDVE, DODT, and DMPA at targeted ratios, various BE samples (BE0-100, BE25-100, BE50-100, BE75-100, BE100-25, BE100-10, BE100-5) with vinyl to thiol functionalities being maintained in a 1:1 ratio were prepared according to the above synthesis procedures. All reactions used 1 wt% DMPA.

RESULTS AND DISCUSSION

To study the effect of BE content and crosslinking density on the dynamic mechanical properties, we designed and synthesized a series of vitrimers bearing various BE contents and crosslinker densities *via* photo-initiated thiol-ene “click” reactions, which is very efficient and simple in material synthesis and modification. As shown in Fig. 1(a), the boronic ester diene (DVBE) was liquid and miscible with the common thiol-ene reagents, di(ethylene glycol) divinyl ether (DEGDVE), DODT, and PTMP, and the photoinitiator (I651). The BE and crosslinker content were varied by altering the ratio of DVBE to DEGDVE and the ratio of DODT to PTMP, respectively, while maintaining a thiol to ene ratio of 1:1. Then the mixed monomer solutions were sent for photocuring with 365 nm UV lamp for about

30 min. The obtained samples are named as BE x - y where x and y represent the feeding molar concentrations (mol%) of DVBE in the total vinyl monomers (DVBE + DEGDVE) and PTMP in the total thiol monomers (PTMP + DODT), respectively. The efficient coupling reaction between thiol and vinyl groups was confirmed by FTIR spectra (Fig. S3 in the electronic supplementary information, ESI). For PTMP, the absorption bands at 2570 cm⁻¹ could be ascribed to the stretching vibrations of —SH. In the case of DABE, the absorption bands at 1215 and 928 cm⁻¹ were assigned to the stretching vibration of B—O and the bending vibration of —CH=CH₂, respectively. After mixing PTMP with DVBE but prior to curing, taking BE100-100 as an example, its uncured solution exhibits superimposed spectra of PTMP and DVBE. While the absorptions associated with thiol and vinyl groups completely disappear in cured BE100-100, evincing the success of photocuring.

Dynamic mechanical analysis (DMA) tests were conducted to study the mechanical properties of these BE vitrimers. Fig. 2(a) shows the storage modulus and $\tan\delta$ versus temperature, where the storage modulus describes the elastic response of the material and the peak of $\tan\delta$ indicates the glass transition temperature (T_g). The increase of BE content results in a gradual decrease of the rubbery modulus (the lower modulus plateau at high temperatures), but shifts the peak of $\tan\delta$ to a higher temperature. The intrinsic Young's modulus was obtained from uniaxial tensile tests (Fig. 2b). As depicted in Fig. 2(c), the T_g value and Young's modulus present opposite change with the BE content. From BE0-100 to BE100-100, the T_g value shifts from -12 °C to 31 °C, whereas modulus decreases from 11 MPa to 7 MPa accordingly. The introduction of DVBE might restrict segmental chain mobility

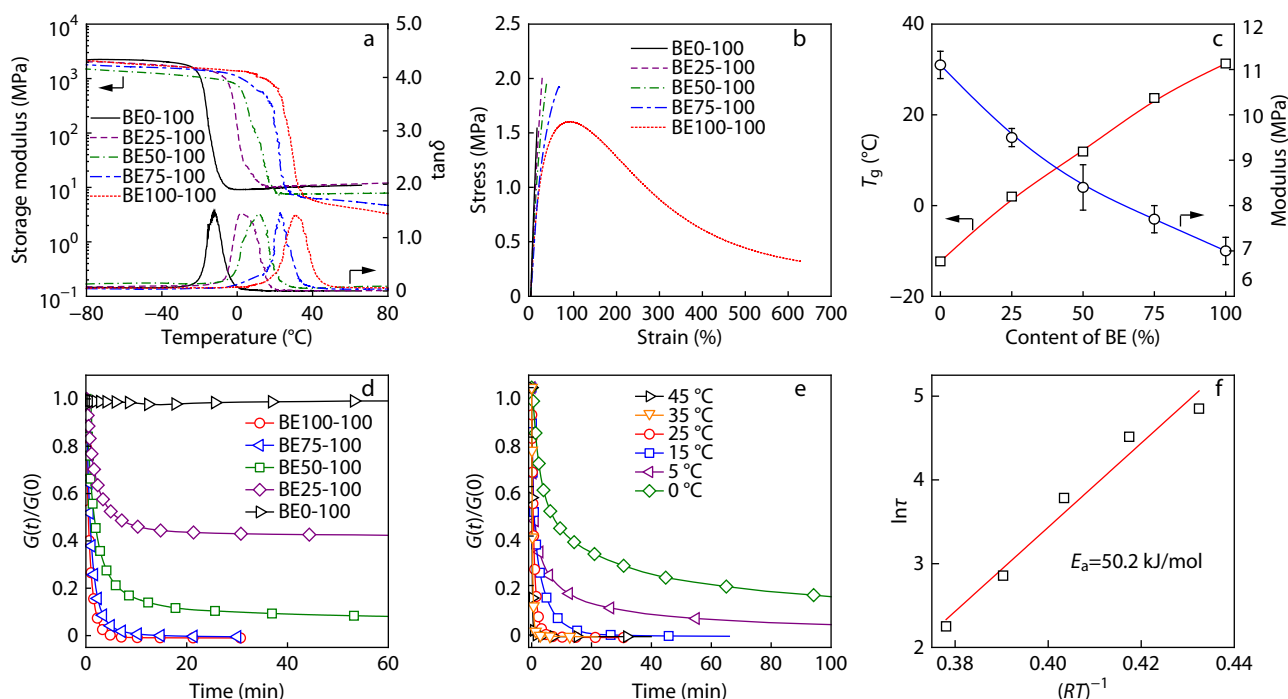


Fig. 2 Mechanical properties. Dynamic mechanical analysis (DMA) tests (a) and uniaxial tensile tests (b) of various BE samples. (c) T_g and Young's modulus changed with the content of boronic ester. (d) Stress relaxation curves of various BE samples at 25 °C. (e) Stress relaxation curves of BE100-100 at different temperatures. (f) Characteristic relaxation time (τ) exhibits an Arrhenius temperature dependence.

due to its more rigid structure compared to DEGDVE. Therefore, BE100-100 exhibits the highest T_g value. While its lowest modulus was probably related to the fast BE bond exchange. As shown in Fig. 2(b), the strain at break increases with the BE content. For BE100-100, the stress is continuously increasing at the initial stage of stretching, and then presents the decrease tendency with strain. The yielding point appears at the strain of 90%, which is probably attributed to the inner chain exchange under stress. By contrast, for the other vitrimers with the lower BE contents, they showed quite fragile and were broken at the lower strains. No obvious yielding point was observed at the strain rate of 10 mm/min, probably attributed to its slower chain exchange rate. These samples were unable to rearrange network and release the inner stress through BE transesterification reaction in time before fracture.

The dynamic chain exchange of BE linkages could well reflect in the stress relaxation behavior. As shown in Fig. 2(d), all BE samples except BE0-100 can significantly release stress with time at room temperature although they are covalently crosslinked. The sample BE100-100 with the highest BE concentration relaxes its stress quickly to 0 within a few minutes. Upon decreasing the BE content, the samples resist the complete stress relaxation, due to the increasing fraction of the permanent network. The eventual relaxation extent increases with the BE content. For BE0-100 without any BE linkages, it cannot release any stress with time, which provided convincing evidence that BE played a key role in the rearrangement of the crosslinked network in BE vitrimers. Moreover, the stress relaxation of BE samples was a temperature-dependent process. As shown in Fig. 2(e), the relaxation rate of BE100-100 slows down with the decrease of temperature. It was because the relaxation process was essentially controlled by the thermo-activated BE transesterification reaction, which could be further accelerated at the elevated temperature. Its characteristic relaxation time (τ^*) exhibits an Arrhenius-like temperature dependence (Fig. 2f), indicating the associative exchange mechanism of BE transesterification reaction.^[32] Accordingly, the activation energy (E_a) was calculated as 50.2 kJ/mol based on the inverse Arrhenius rate equation. This fast

stress relaxation rate of BE100-100 was in a good agreement with its above unique mechanical behavior like the highest T_g value but with the lowest modulus and the largest stretching ratio, as well as the appearance of yielding point.

Hereafter, the dynamic aspect of the mechanical performance was probed by varying the strain rate for each BE vitrimers. Their resulting stress-strain curves are remarkably different under different strain rates (Fig. 3a and Figs. S4–S7 in ESI). BE0-100 exhibits negligible strain rate dependence when the strain rate changes from 1 mm/min to 20 mm/min (Fig. 3a). It suggested that BE0-100 was elastic without energy-dissipation ability, thus its strain at break was independent on the strain rates (Fig. S4 in ESI). By comparison, other BE elastomers showed strong strain rate dependence. At the BE content of 25%, the modulus of BE25-100 exhibits obvious decrease with the stretching rate, but the elastomer remains fragile with the lower rupture elongation (Fig. S5 in ESI). Although the stretching rate decreases to 0.1 mm/min, the strain at break is still lower than 40%, which was attributed to the lower BE content. The distance between two adjacent BE groups is large, resulting in the slow association rate as well as weak energy-dissipation ability. While for BE50-100, the rupture elongation increases from 47% to 350% with the decrease of strain rate (Fig. S6 in ESI), suggesting that the dynamic BE network had enough time to reorganize at the small strain rate and thus delayed the fracture of the materials. Meanwhile, the modulus decreases from 8.7 MPa to 5.4 MPa accordingly. The obvious yielding point appears at the stretching rate of 1 mm/min (Fig. S6 in ESI), ascribed to the accelerated chain exchange reaction. For elastomers with the higher BE contents, this dynamic BE transesterification reaction could be further accelerated. The yielding point is even observed at the high strain rate for BE75-100 (Fig. S7 in ESI) and BE100-100 (Fig. 3a). At the slower strain rate, BE75-100 and BE100-100 present the lower modulus and show obvious self-stiffening ability with strain rate (Fig. 3b), which was similar to the behavior of traditional “solid-liquid” materials. This strain rate dependence arose from the relative timescale of the BE association kinetics versus the rate at which the strain was applied and magnitude was strongly dependent on the

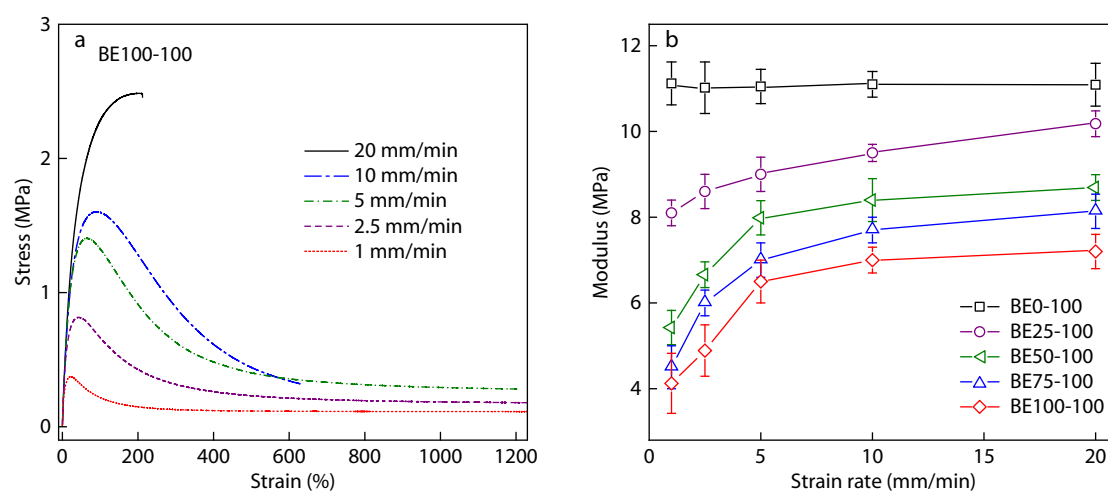


Fig. 3 Strain rate dependence: (a) stress-strain curves of BE100-100 at 25 °C at different strain rates, (b) Young's modulus of BE samples at different strain rates (25 °C).

BE content. Under a slower stretching rate, the large number of BE groups had enough time to associate and relax; as such, they should not contribute to the modulus and instead dissipate energy, resulting in the more liquid-like property and higher extensibility. While under a higher stretching rate, these boronic ester groups would not have enough time to relax, thereby leading to the more solid-like property and relatively lower stretchability. Compared to the reported “solid-liquid” materials like the most studied PBS^[10–12] or supramolecular polymeric networks bearing dynamic UPy unit crosslinkers,^[13] whose modulus is below 0.5 MPa, our “solid-liquid” vitrimers exhibit the higher mechanical strength (>4.0 MPa even at the strain rate of 1 mm/min).

Next, to study the strain rate-responsive solid-liquid property of BE vitrimers, rheological measurements were performed. Dynamic mechanical properties as a function of frequency ranging from 0.001 Hz to 100 Hz at 25 °C are shown in Figs. 4(a)–4(d) and Figs. S8 and S9 (in ESI). According to the frequency sweeps, samples with lower BE contents ($\leq 25\%$) exhibit a noticeably higher storage modulus (G') than the loss modulus (G'') in the whole frequency range (Fig. 4a and Fig. S8 in ESI). The samples containing more BE groups ($\geq 50\%$) present strong shear sensitivity and behaved in a liquid-like manner at low frequency, as G' is lower than G'' . Above a certain frequency, G' becomes higher than G'' , indicating an elastic behavior at high frequency. The crossover point (ω_{cross}) of the transition from the viscous state to elastic state is indicated by the frequency where $G' = G''$. For BE50-100, the ω_{cross} value is 0.002 Hz. It shifts to the higher frequencies with in-

creasing BE bonds (Fig. 4e) and reaches 0.008 Hz for BE100-100 (Fig. 4c), indicating a shorter relaxation time. Such a phenomenon suggested that a higher BE content led to a faster rate of dynamic association of boronic ester bonds within the elastomers. Such results were consistent with the stress relaxation time determined by DMA. Compared to the well-known solid-liquid material PBS, the ω_{cross} value of BE100-100 still appears at a relatively lower frequency, probably ascribed to its higher crosslinking density and the slower association rate of BE bonds than that of boron/oxygen dative bonds within PBS. BE100-100 exhibits higher modulus than PBS.^[7] To further investigate the effect of crosslinking density on crossover frequency, BE100- γ ($\gamma=25, 10, 5$) bearing various fractions of PTMP were prepared. As shown in Fig. 4(f), the ω_{cross} value increases with the decreasing content of crosslinker PTMP. For BE100-5 containing 5 mol% of PTMP, its ω_{cross} value is the largest and up to 0.25 Hz (Fig. 4d), showing a very fast relaxation time. It implied that the decrease of crosslinking density could effectively enhance the molecular motions, and thus increase the dynamic chain exchange rate of BE bonds.

This fast BE transesterification also provides a way to reshape 3D structures in the presence of external forces, which is more like the traditional processing even though no mold and solvent are used. As shown in Fig. 5(a), a flat strip could be reshaped to an extended spiral (Fig. 5a2) after being fixed with external force for about 30 s, which is the enough time for the exchange reactions between boronic esters to quickly relax the inner stress. Then, the formed extended spiral could be subsequently reshaped to another two tighter spirals

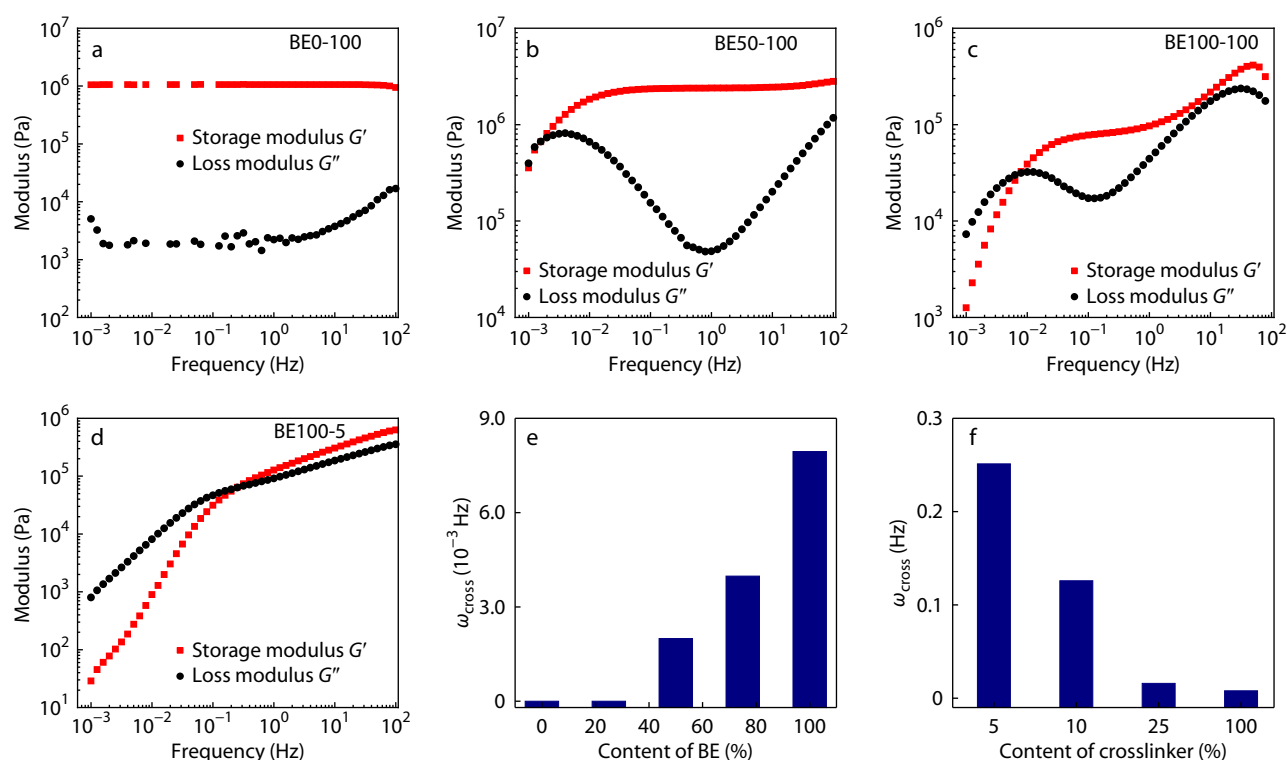


Fig. 4 Rheological properties of BE elastomers. Frequency dependence of storage modulus and loss modulus for BE0-100 (a), BE50-100 (b), BE100-100 (c), BE100-5 (d). The crossover point ω_{cross} of the transition from the viscous state to elastic state changed with the content of BE (e) and crosslinker (f).

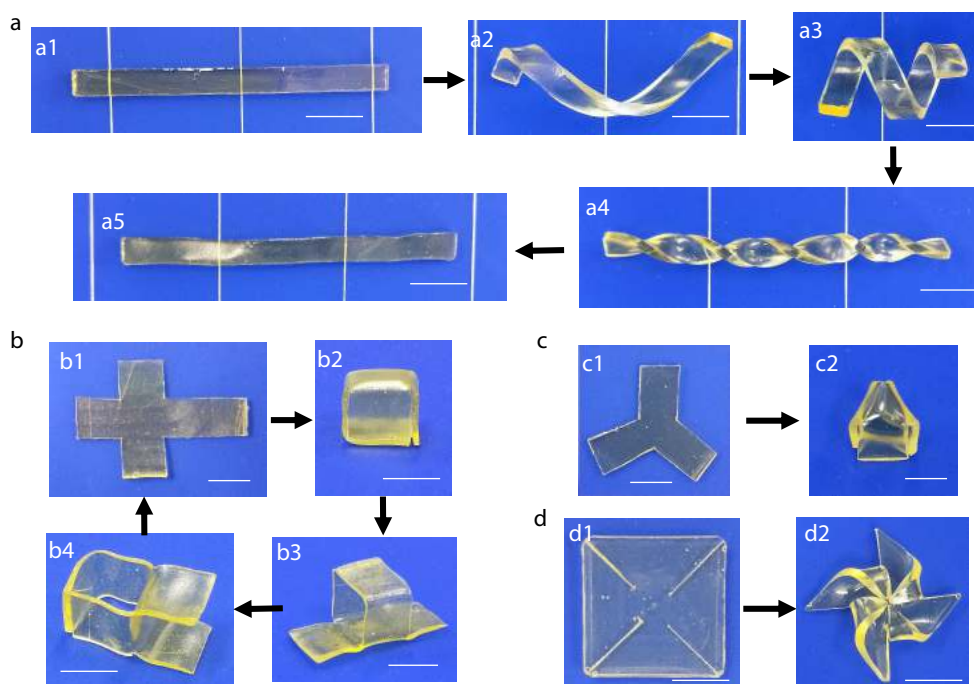


Fig. 5 Force-induced shape programming. (a) Reshaping a flat strip continuously to three different spirals with external force. Then the reconfigured structure was recycled to the initial flat strip with external force. (b) Reshaping a cube vitrimer by applying the external force onto the designed edges simultaneously in each procedure. (c) Reshaping a triangular prism by origami and kirigami with external force. (d) A bended windmill reshaped from a flat film with precuts and the application of the external force. Scale bar: 10 mm.

(Figs. 5a3 and 5a4) and recycled to the initial flat strip (Fig. 5a5) by taking advantage of the external force. It evinced that various 3D shapes could be easily programmed and erased by fast rearrangement of the network topology under external force. In another example, a cubic box could be fabricated from a 2D flat sample *via* simple programming with external force. This 3D cubic box could be reconfigured to new structures again and again without solvents, molds, or a need of high temperature (Fig. 5b). In addition, introducing origami and kirigami into a flat film can increase the flexibility of the final 3D structures (Figs. 5c and 5d). 3D triangular prism (Fig. 5c) and complex windmill shape (Fig. 5d) were easily reshaped from a flat film with precuts and external force.

CONCLUSIONS

In summary, we have designed and synthesized a series of well-defined polymer networks containing various contents of dynamic BE bonds and covalent crosslinks *via* radical-mediated thiol-ene click addition. Adjusting these two molecular parameters allowed continuous fine-tuning of the topological rearrangement kinetics. The dynamic association rate of BE bonds within vitrimers could be apparently accelerated *via* increasing the BE content and decreasing the crosslinking density, which led to polymer networks with several unusual mechanical properties including high stretchability, strong strain rate dependence and solid-liquid properties, and could also be used to shape-program flat vitrimer films into various complex 3D structures just with external force. Materials of such properties might open a new window in future innovations in advanced manufacturing, actuators, shape memory, 3D/4D

printing, flexible electronics, *etc.* In addition, other dynamic covalent bonds with different dynamic properties (*e.g.*, timescale of the bond exchanges) are worth exploring as a way to tune the dynamic macroscopic properties to meet various practical needs.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-021-2592-1>.

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