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Tuning the Mechanical and Dynamic Properties of Elastic Vitrimers by Tailoring the Substituents of Boronic Ester

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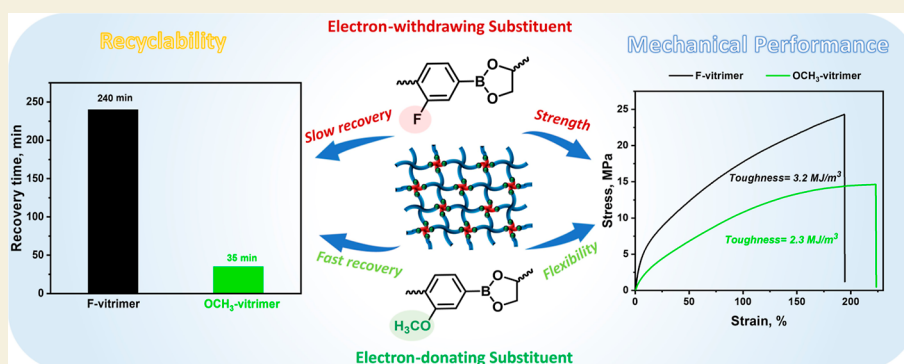
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ABSTRACT: Elastic vitrimers, i.e., elastic polymers with associative dynamic covalent bonds, can afford elastomers with recyclability while maintaining their thermal and chemical stability. Herein, we report a series of boronic ester-based vitrimers with tunable mechanical properties and recyclability by varying the substitute groups of boronic acid in polymer networks. The dynamic polymer networks are formed by reacting diol-containing tetra-arm poly(amidoamine) with boronic acid-terminated tetra-arm poly(ethylene glycol), which possesses different substituents adjacent to boronic acid moieties. Varying the substituent adjacent to the boronic ester unit will significantly affect the binding strength of the boronic ester, therefore affecting their dynamics and mechanical performance. The electron-withdrawing substituents noticeably suppress the dynamics of boronic ester exchange and increase the activation energy and relaxation time while enhancing the mechanical strength of the resulting elastic vitrimers. On the other hand, the presence of electron-rich substituent affords relatively reduced glass transition temperature (T_g), faster relaxation, and prominent recyclability and malleability at lower temperatures. The developed pathway will guide the rational design of elastomers with well-tunable dynamics and processabilities.

KEYWORDS: elastic vitrimer, dynamic covalent bond, binding strength, tunable dynamics, recycled elastomer

1. INTRODUCTION

In recent years, due to the active implementation of polymeric materials in different applications including packaging, electronics, insulation, the automotive industry, etc., the problem with polymer waste has occurred at an unprecedented rate and poses huge challenges with growing populations.[1] Conventional polymeric materials are inherently resistant to degradation and have long-term persistency in the environment; therefore, inappropriate disposal has led to extreme pollution hazards to the environment.[2] Therefore, to facilitate waste management of polymers, recycling is a "greener" option for polymer sustainability.[3,4] Thermoplastic polymers have the potential to be recycled; however, their poor chemical resistance and lack of dimensional stability at elevated temperatures limit their wide range of applications. On the other hand, thermoset polymers are durable materials with high mechanical robustness and exceptional thermal and chemical resistances, allowing their utilization in a wide range of applications; however, the presence of permanent cross-links in their structure limits their chance to be recycled.[5−8] Therefore, to combine the advantages of thermoplastics and thermosets, a new class of polymeric materials owning dynamic covalent cross-links have been developed, exhibiting excellent mechanical performance, solvent resistance, and dimensional stability like thermosets and the
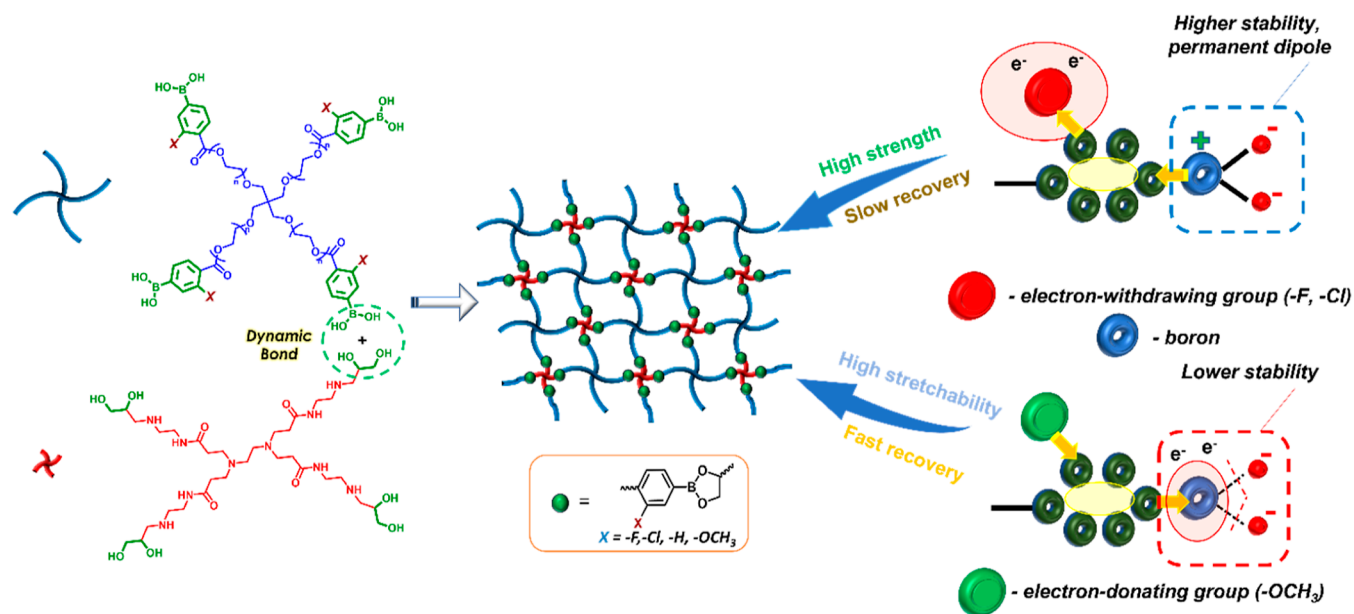
Scheme 1. Illustration of the Chemical Pathway for the Fabrication of Elastic Vitrimers with Variable Boronic Acid Substituents


capability to be reshaped/recycled under exposure of external stimuli such as heat and light.[9−12]

Polymeric materials fabricated via associative dynamic covalent bonds commonly called "vitrimers" have been extensively studied in the past decade due to their prominent advantages including exceptional mechanical performance, chemical/thermal resistance, and good reprocessability.[3,13] The overall performance of vitrimers mainly depends on the chemical structure of polymer segments, the degree of cross-linking, and the type of dynamic bonding. The dynamics and mechanical properties of vitrimers not only rely on structural features of the polymer network but also depend on the nature of dynamic exchange processes.[14−16] To tune the mechanical properties of vitrimers, several strategies have been implemented including but not limited to tuning the cross-link density and mobility of polymer segments, altering the catalyst system and stoichiometric ratio of starting materials, etc.[17−20] Commonly, the presence of external contributors is required for the desired dynamic exchanges. For example, external catalysis, the addition of nanofillers, etc. are employed to afford the vitrimer with on-demand viscoelastic behavior.[21] However, tuning the dynamics by modifying the polymer network or incorporating external fillers or triggers may cause challenges with reprocessability and cross-influences of mechanical reinforcement.[22] Till now, tuning the network kinetics without the use of external contributors still remains a challenge.

Investigating the correlation between small molecule kinetics and the dynamic properties of polymer networks is vital to addressing such a challenge. Formation of dioxaborolane takes place without the presence of a catalyst at relatively low temperatures (e.g., 60 °C), and such cross-link networks are known to have good dimensional stability, efficient dynamic exchange reactions, thermal stability, and high tolerance toward other functional groups.[23] Thus, considering its high dynamics and low activation energy, the dioxaborolane network is a robust platform for us to investigate the effect of internal contributors on the dynamics of vitrimer networks.[24] Till now, several studies have reported the effect of

small molecule design on the dynamics of boronic ester-based vitrimers where the nature of the neighboring group in the boronic acid moiety has a significant effect on exchange dynamics, malleability, and mechanical performance. Yesilyurt et al. developed a range of hydrogel networks containing phenylboronic acid derivatives with different pK_a values that allowed tunable viscoelastic properties via environmental pH changes and the self-healing ability of formed gels.[25] Another study reports the synthesis of dynamic hydrogels with tunable viscoelastic properties by varying the structure of boronate moieties, which directly affects the binding strength between boronic acids and diols.[26] A similar strategy was applied by Chu et al. to evaluate the electronic effect of phenylboronic acid substituents on the properties of biopolymer fibers including tensile strength, ultimate strain, and elastic modulus.[27] However, these studies were mostly focused on the random choice of substituents in the moiety to tune the healing ability and mechanical performance of boronic acid-based vitrimers. Thus, it still remains unexplored how small molecule perturbation, including the electron density of the substituent and its specific location, affects the dynamics of the solvent-free elastic networks and their thermal reprocessability.

Herein, we report a range of boronic ester-based polymer networks with tunable mechanical properties and recyclability by varying the substitutes of boronic acid in the elastic network. This is based on the assumption that the varied electron density of the boronic ester linkage affords different binding strengths, which allows tunable viscoelastic and dynamic behaviors. The presence of the electron-withdrawing group in the phenylboronic moiety like −F and −Cl contributes to the higher binding strength of boronic ester bonds, which enhances the mechanical performance of resulting elastic networks, whereas the decreased electro-negativity of the substituent (−OCH₃) considerably decreases the binding strength of cross-links in boronic ester-based elastic networks, which improves flexibility and recyclability. We are aiming to develop a straightforward method to control the strength and recyclability of these elastic networks via the
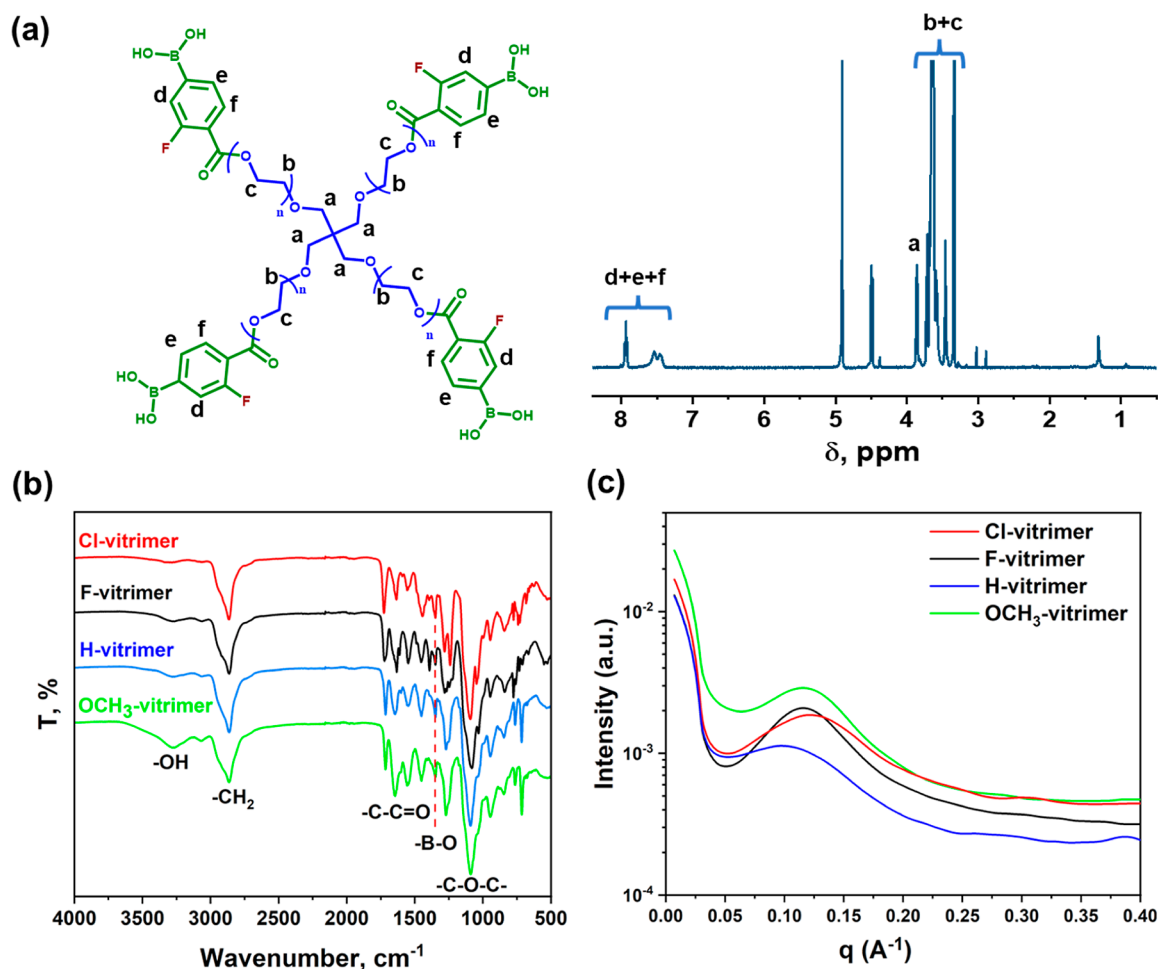
Figure 1. ¹H NMR spectra of phenylboronic acid-functionalized 4-arm polyethylene glycols (a), FTIR spectra (b), and SAXS spectra (c) of boronic ester-based vitrimers (red: Cl-vitrimer, black: F-vitrimer, blue: H-vitrimer, green: OCH₃-vitrimer).

introduction of neighboring groups with different electron densities. The recyclable elastic networks with controlled mechanical properties and recyclability without the presence of external contributors may serve as a durable platform for next-generation smart functional materials.

2. RESULTS AND DISCUSSION

2.1. Synthesis of Boronic Ester-Based Vitrimers

Considering a wide range of applications and outstanding properties, boron-containing polymers have been extensively explored for the design of self-healing polymers.[28,29] The great interest in using boron (B) lies in the fact that it is an inherently electron-deficient and tricoordinate atom, which provides many unique features to the resulting B-containing materials.[30] Commonly, the B—O bond has been utilized in the polymer design to control their healing properties due to the combination of thermodynamic stability and kinetic tunability.[31] The boron-containing dynamic polymer shows fast exchange kinetics, malleability, and a self-healing performance. However, their malleability and self-healability usually require the assistance of water molecules or high temperatures to trigger the effective bond exchange.[32] Therefore, tuning the exchange rate via modifying the intrinsic binding strength of boronic ester is vital to control the mechanical performance and dynamics of the resulting elastic networks.[33] While most studies of boronic ester-containing vitrimers are focused on

tuning self-healing properties, the goal of current research is to demonstrate an effective approach to tune the recyclability of those vitrimers via the introduction of neighboring groups.[26,27]

The presence of substituents and their location in phenylboronic moieties have a significant impact on the electron density of the boron atom, which therefore impacts the stability of the boronic ester bond and its binding strength with diols.[34,35] Hence, the introduction of electron-withdrawing or electron-donating substituents contributes to the inductive and resonance effects, which directly correlates with the unbinding process during the exchange reactions.[36] The existence of electron-withdrawing substituents like −F and −Cl with high electronegativity can attract the electron from covalent bonds, providing a more stable boronic ester bond.[35] The charge transmission within the phenylboronic moiety results in the formation of the dipole. On the other hand, electron-donating substituents like methoxy (−OCH₃) provide migration of electrons to the boron atom, resulting in low binding strength of boronic ester (Scheme 1). Therefore, varying its electron density by performing small molecule perturbations will provide a robust platform for controlling the binding strength and the exchange rate of polymer networks.

Herein, we designed a range of phenylboronic acid-functionalized 4-arm polyethylene glycols (4-arm-PEG, MW = 2000 g/mol) where the electrophilic character of the substituent in the phenylboronic moiety was varied. For this
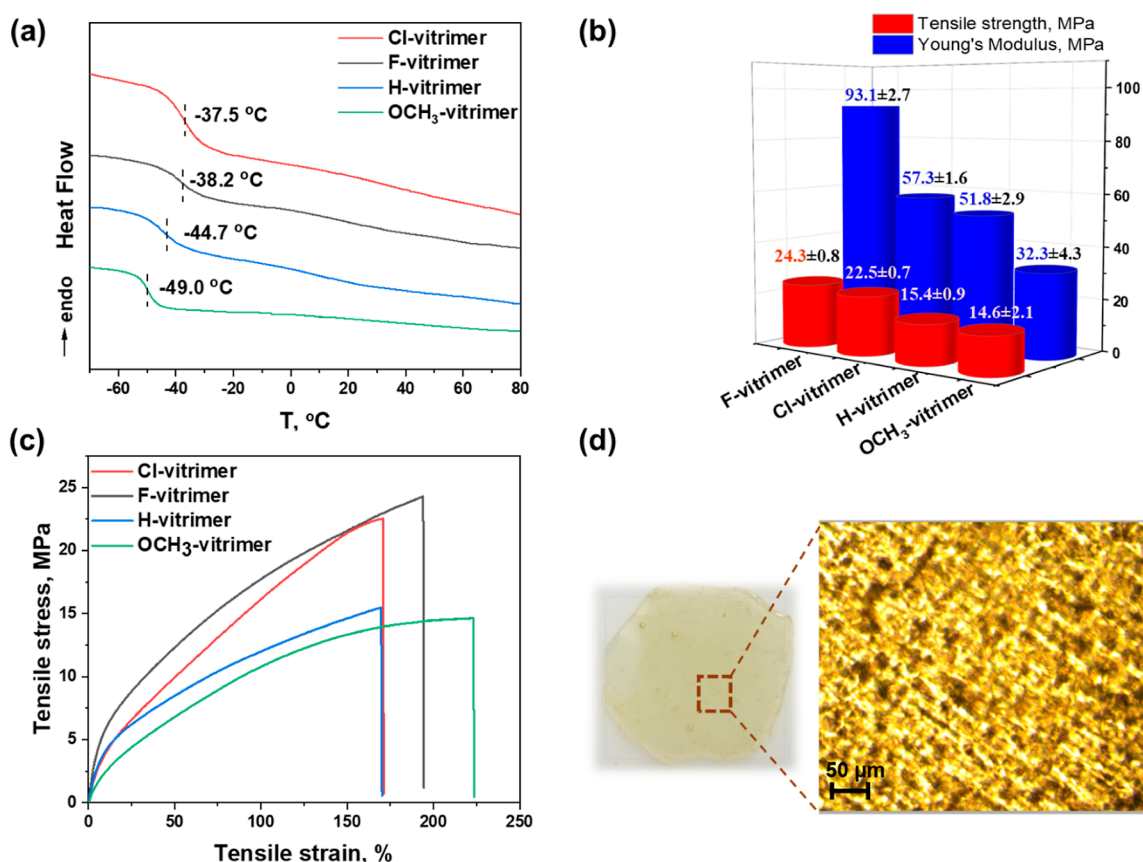
Figure 2. DSC curves (a), Young's modulus/tensile strength (b), and tensile stress−strain curves (c) of boronic ester-based vitrimers with variable neighboring groups. Optical image of the OCH$_3$-vitrimer (d).

purpose, carboxyphenylboronic acids with different neighboring groups including fluorine (−F), chlorine (−Cl), and methoxy (−OCH$_3$) along with the unsubstituted were utilized for the synthesis of phenylboronic acid-functionalized 4-arm polyethylene glycols (Figure S1). The chemical structure of phenylboronic acid-functionalized 4-arm-PEGs was confirmed using ^{1}H NMR spectroscopy (Figures 1a and S2a). The electron density of the substituent was a key parameter to trigger the binding affinity and exchange rate of the vitrimer networks. The resulting boronic acid-functionalized 4-arm-PEG molecules were cross-linked with the diol-functionalized polyamidoamine dendrimer (PAMAM) to form a series of boronic ester-based vitrimers [see the Supporting Information for synthesis details and ^{1}H NMR spectra (Figure S2b)]. As shown in Scheme 1, the boronic ester was formed between boronic acid moieties and diols to deliver a range of polymer networks. The resulting vitrimers are cross-linked networks in which the substituted group affects the stability of such a dioxaborolane bond. As illustrated by the attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra, the presence of a vibration peak at 1300−1350 cm^{-1} corresponding to the asymmetric B−O stretching indicates the formation of boronic ester cross-links (dioxaborolanes) (Figure 1b). The nature of the substituents in phenylboronic moieties has a distinctive effect on the formation and stability of dioxaborolane linkages and hence the ratio of unreacted diols. The relative amounts of unreacted diols were studied by integrating the peaks corresponding to the diol group in the FTIR spectra. It was found that the unreacted diols increased in the range −Cl < −F < −H < −OCH$_3$, which was expected

due to the reduced binding strength of boronic ester linkages caused by the presence of substituents with different electrophilic characters. Herein, the OCH$_3$-vitrimer with the electron-donating group has shown an almost four times higher amount of unreacted diols compared to the Cl-vitrimer that contains the electron-withdrawing group. The extent of dioxaborolane cross-links in the vitrimer network and its stability are mainly controlled by the nature of substituents in phenylboronic moieties. The solubility tests showed that the resulting elastic vitrimer with electron-withdrawing substituents has a high gel content (>85%) whereas the vitrimers with −H and OCH$_3$ exhibit a decrease in the gel fraction because of lower stability of dioxaborolane linkages and possible hydrolysis during the test (Figure S3). Moreover, in the presence of alcohol (CH$_3$OH), a noticeable decrease in the gel fraction of vitrimers was observed in the order of −Cl > −F > −H > −OCH$_3$ (74.5% > 70.9% > 38.8% > 29.9%) because favorable transesterification between dioxaborolanes and alcohols leads to vitrimer hydrolysis in such conditions where the impact of the substituent also takes place. Thus, the obtained data from FTIR spectroscopy and the solvent resistance test clearly confirm that the nature of the substituent in phenylboronic moieties not only affects the stability of dioxaborolane but also the extent of its conversion during the vitrimer formation process. Morphological characterization of the resulting vitrimers was examined by small-angle X-ray scattering (SAXS). The distinctive peak in the range of the scattering vector 0.11−0.12 Å^{-1} corresponds to the spacing of 5.1−5.9 nm (Figure 1c). The observed spatial distance can be attributed to the formed mesh size of the vitrimers, which
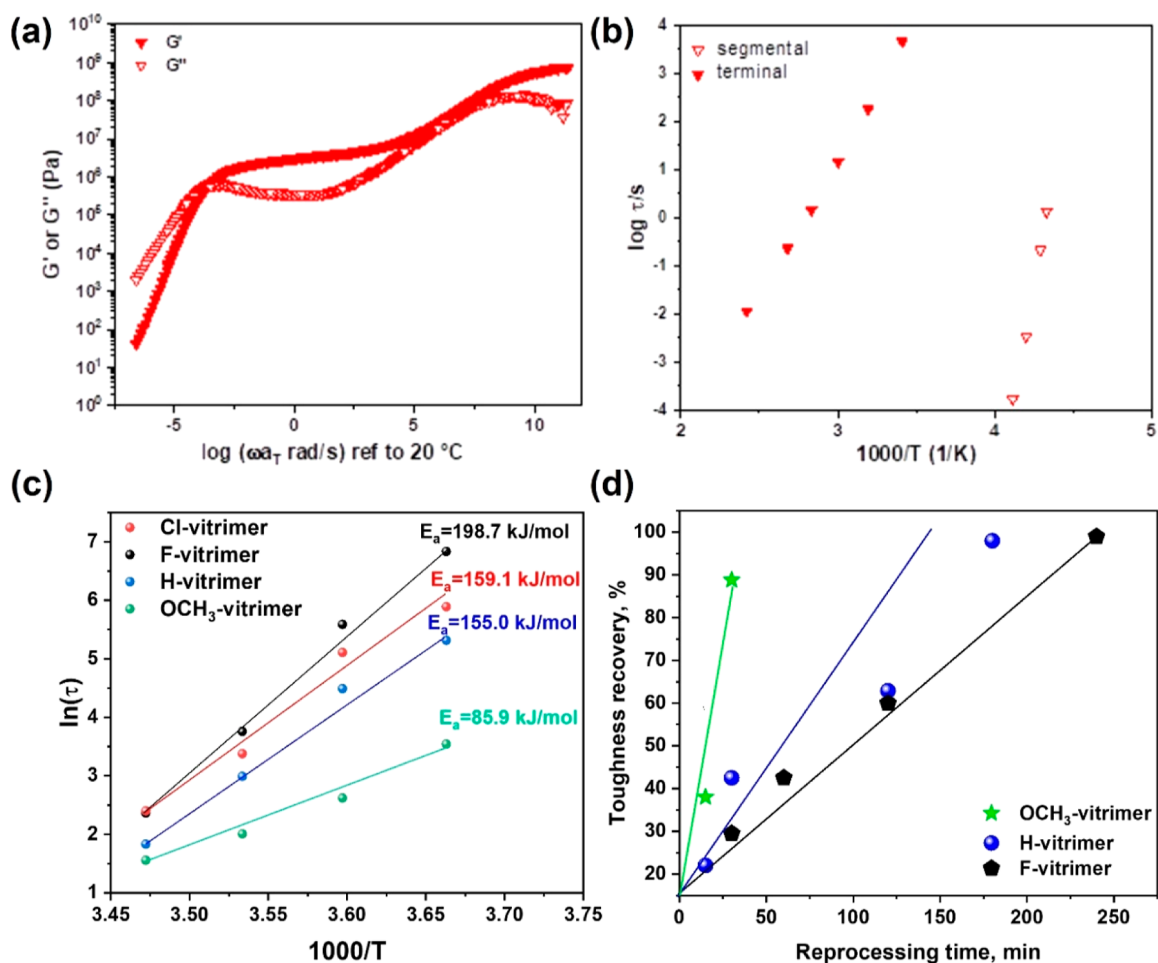
Figure 3. Rheological master curve at the reference temperature T_R = 293 K (a) and the dependence of relaxation time vs temperature (b) for the Cl-vitrimer. Apparent activation energy profiles (c) and comparative toughness recovery with reprocessing time (d) are for elastic vitrimers with different substituents.

should be around 5.6 nm according to the extended coil model calculations. The optical image of resulting elastic vitrimers shows a uniform surface structure without visible defects or phase separation (Figure 2d).

2.2. Thermal and Mechanical Properties

The thermal properties of boronic ester-based vitrimers were studied using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA curves indicate the outstanding thermal stability of such elastic vitrimers with no significant decomposition at lower temperatures ($T_{d50\%}$ in the range 400−409 °C, Figure S4a). The initial decomposition of resulting boronic-ester-based vitrimers starts at ∼200 °C where $T_{5\%}$ is determined to be 197.4, 192.6, and 209.7 °C for F-, H-, and OCH$_3$-vitrimers, respectively. Small decomposition corresponding to the peaks at 200−220 °C in derivative thermogravimetric (DTG) curves (Figure S4b) was observed for elastic vitrimers with H and OCH$_3$ neighboring groups in the boronic acid moiety, attributed to the removal of hydroxyl groups that could be introduced through partial hydrolysis of boronic ester bonds or incomplete conversion to dioxaborolanes.[37] Such an effect was not observed for elastic vitrimers with the F neighboring group, potentially due to the high binding strength and enhanced water resistance. Moreover, as illustrated by the DSC curves of elastic vitrimers, the substituents of boronic acid moieties significantly affect the

chain mobility of these dynamic polymer networks. The presence of electron-withdrawing substituents (−F and −Cl) in boronic acid moieties in vitrimers suppresses the polymer dynamics, leading to higher T_g values, whereas the introduction of a methoxy substituent as a neighboring group considerably improves the chain mobility, as indicated by the lower T_g value (Figure 2a).

The small molecule perturbations in phenylboronic acid moieties are designed to tune the mechanical properties of the resulting elastic vitrimers. Herein, static uniaxial tensile measurements were performed under ambient conditions for a range of boronic ester-based vitrimers (Figure 2c). The ultimate tensile strength of boronic ester-based vitrimers increases with the following order: −F > −Cl > −H > −OCH$_3$, which could be explained that the presence of neighboring groups with electron-withdrawing character leads to the formation of nodes with high binding strength of polymer networks, therefore allowing to withstand higher loads under stress. Moreover, elastic vitrimers with a wide range of Young's modulus (from 32 ± 4.3 to 93 ± 2.7 MPa) are also achieved by varying the chemical substitution of a single site on the phenylboronic acid moiety (Figure 2b).

2.3. Viscoelasticity and Dynamic Behavior

A rheometer is utilized to reveal the effect of substituents on the chain dynamics and viscoelasticity of the elastic vitrimers.

A typical time-resolved oscillatory shear master curve is shown in Figure 3a for the Cl-vitrimer. The validity of time–temperature superposition was verified by the van Gurp–Palmen plot (Figure S5c), and the shift factors were also provided (Figure S5d) for all of the obtained elastic vitrimers.[38] At 20 °C, a glassy state was noticed around 10^9 rad/s with a modulus around the level of 1 GPa. As the frequency decreases, a transition region was followed by the rubbery plateau at the level of 4 MPa, which was slightly higher than the H- and OCH$_3$-vitrimers (see the Supporting Information). With a reference temperature of 20 °C, the terminal crossover was observed at 10^{-3} rad/s, indicating the observable exchange of ester bonds as well as the flow regime. It was found that the electrophilic character of the substituent has a significant effect on the chain dynamics and viscoelastic properties of the elastic vitrimers. The elastic vitrimers with electron-withdrawing groups (−Cl, Figure 3b) showed decelerated polymer dynamics, especially for the terminal dynamics. The polymer dynamics at the glassy state were not significantly affected because the ester bonds exhibited a minor contribution to the mobility of polymer segments at low temperatures, whereas a differentiation started to show up as the temperature increased. Moreover, the elastic modulus at the rubbery plateau was increased for Cl-vitrimers, although the designed networks should have the same cross-linking density. This result can be explained by the stronger resistance of the Cl-vitrimer to hydrolysis, which shows higher apparent cross-linking density during the rheology test. They also showed a relatively broader rubbery region (high resistance to flow), attributed to the higher dissociation energy barrier that extended the terminal relaxation time. On the other hand, the electron-donating substituent (−OCH$_3$) affords faster polymer dynamics and lower resistance to flow. The onset temperature for the flow of resulted vitrimers decreases in the following range: −Cl > −F > −H > −OCH$_3$, which is correlated with the electrophilic effect of the neighboring groups (Table 1). The

Table 1. Viscoelastic Characteristics of Boronic Ester-Based Vitrimers

	F	Cl	H	OCH$_3$
onset temperature of flow (°C)	99.3	105.2	92.3	74.3
apparent E_a (kJ/mol)	109.8	108.0	96.4	96.9
actual E_a (kJ/mol)	61.4	68.3	54.3	50.5
T_g by max G'' (°C)	−37.7	−40.4	−40.5	−40.7

obtained mechanical test results have shown a comparable trend for resulting vitrimers containing electron-withdrawing groups (−F and −Cl), which have shown much higher tensile strength than others. The slight difference in the trend for Young's modulus vs rheology profile of F- and C-vitrimers could be attributed to the difference in moisture absorption because the tensile test was performed at ambient conditions with high humidity levels (60−70%), while the rheology was studied in the dry environment under N$_2$.

Due to the reversibility of dynamic cross-link networks, boronic ester-based elastic vitrimers can relax stress and rearrange the network through a boronic ester trans-esterification or exchange with free diols.[33,39] To further examine the effect of neighboring groups on the dynamic properties of bulk elastic vitrimers, stress relaxation studies were performed using dynamic mechanical analysis (DMA) at the temperature range from 0 to 25 °C. The data show that the

relaxation process strongly depends on the nature of the substituent in the boronic acid moiety, which controls the rate of its malleability. The stress release at 1% strain was achieved much faster for the elastic vitrimer with the methoxy substituent that exhibits faster dynamics, in agreement with the rheological data (Figure S6d). However, for elastic vitrimers containing electron-withdrawing groups (−F and −Cl), the relaxation process takes a considerably longer time due to the higher bond stability (Figure S6a,b). The relaxation time, τ, is often obtained by the $1/e$ method using the stress relaxation results within the temperature range of interest. The characteristic relaxation time (τ^*) of vitrimers was defined as the time of 37% ($1/e$) of the applied stress (Figure 3c). As expected, the increasing temperature enhanced the relaxation rate, which follows the Maxwell model i.e., the Arrhenius law (eq 1)

$$\ln(\tau) = E_a/RT - \ln A \tag{1}$$

However, such a method often leads to a misconception of the stretched exponential nature of relaxation processes. Herein, a more rigorous methodology is to use time–temperature superposition (tTS) to reveal the temperature dependence of relaxation dynamics, which has been applied for decades. Our group has clearly demonstrated the difference between the $1/e$ method and the traditional tTS method in another work.[40] The apparent E_a values obtained from tTS applied to rheological terminal flow data are presented in Table 1. There is a significant difference in the activation energies estimated from the $1/e$ method and from rheological tTS. Apparently, the $1/e$ method provided the relaxation time that significantly deviated from the actual value.[41]

Although we have shown the correct method to estimate the relaxation time, there is one more piece of the puzzle that is still missing because the apparent E_a seems to be still higher than the bond energy of the esterification process.[42] Our group has also shown that the segmental relaxation dynamic (τ_α) is non-negligible, and one should consider τ_α as the prefactor of bond exchange

$$\ln(\tau) = E_a/RT + \ln(\tau_\alpha) \tag{2}$$

where τ_α can be extrapolated from the segmental dynamics using the Vogel–Fulcher–Tammann equation. By taking τ_α into consideration, the actual E_a for bond exchange is much lower than the apparent E_a (Table 1), which agrees with the energy landscape of the esterification process. Moreover, the actual E_a showed a consistent trend with the apparent E_a for terminal relaxation (Table 1), which indicated that the segmental dynamics was comparable among different systems in comparison with the bond exchanges. Moreover, as electron-withdrawing groups, the elastic vitrimers with Cl and F substituents have a comparable E_a.

The neighboring groups in the phenylboronic ester structure also contributed to the contrast of reprocessing behavior of boronic ester-based vitrimers. The difference in the binding strength of boronic ester bonds in the resulting vitrimers caused by the shift of electron density near the boron atom has significantly impacted the time required for dynamic exchange and reprocessing of polymer films. The reprocessability of a range of boronic ester-based vitrimers was investigated using compression molding. The films were cut and pressed over different periods at 70 °C. Toughness recovery was calculated over different processing times to evaluate the effect of neighboring groups in boronic acid on the kinetics of dynamic
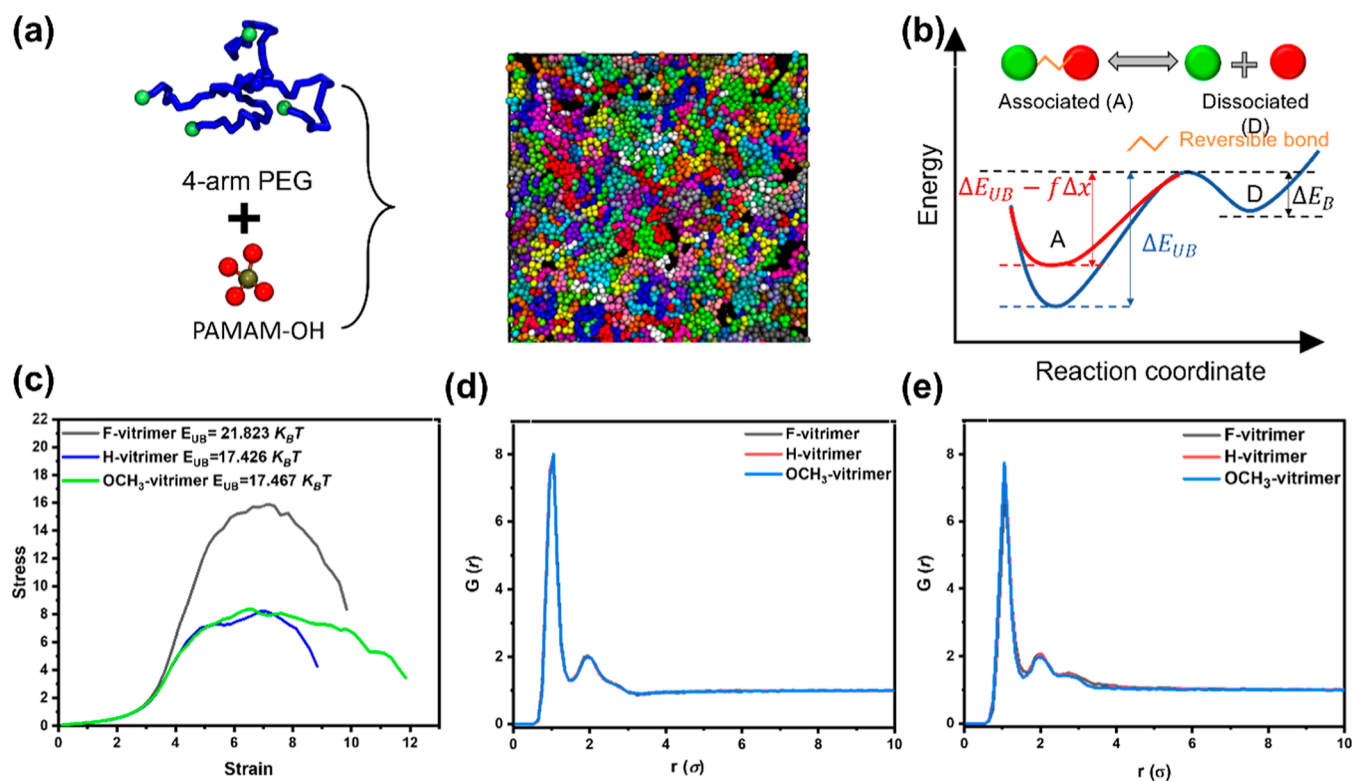
Figure 4. Snapshot of the simulation system and corresponding 4-arm PEG polymer and dendrimer (the green and red beads on the terminal represent a sticker, which is the boronic acid and diol in the experiment) (a), illustration of the reversible interaction for a boronic ester dynamic covalent bond through a Monte Carlo process (b), the stress−strain curve for different substitutes during the uniaxial extensional tests (c), and radius distribution function between stickers during the uniaxial extension process (d,e).

bond exchange in resulting vitrimers (Figure 3d). It was found that network rearrangement and bond reshuffling occurred more slowly in F-vitrimers, which is caused by the shift of electron density from the boron atom providing stabilization of the boronic ester bond. Therefore, the presence of an electron-withdrawing substituent results in the formation of a dioxaborolane with high bond strength, thus slowing the dynamics of bond exchange and malleability overall.

2.4. Simulation Study of Dynamic Behavior

Simulation studies have been conducted to reveal the dependence of binding energy of boronic ester cross-links on the mechanical performance of final materials.[43] Therefore, the hybrid Monte Carlo (MC)/Molecular Dynamics (MD) model has been successfully applied to investigate associative polymer networks (see the Supporting Information).[44] In our coarse-grained model, the PEG polymer model is a linear chain with a monomer number of $N = 20$, with each PEG polymer as an arm in the 4-arm PEG polymer. The terminal of each PEG polymer is a sticker (the green bead in Figure 4a), which can interact with the active sticker (the red bead in Figure 4a) on a small molecule that models the dendrimer. The 4-arm PEG polymers and small molecule have the same chain number in the simulation box with 2000 chains each. The temperature of all of the coarse-grained simulations is controlled as $T = 1.0$ through the Nosé−Hoover thermostat. During the uniaxial tension process, we used a strain rate of $10^{-3}/\tau$ with the Poisson's ratio set as 0.5. All the simulations are performed through the software of LAMMPS.[45] The snapshots are generated by Visual Molecular Dynamics (VMD) software.[46]

Uniaxial extensional tests were performed for different substitutes in the coarse-grained simulations, with the stress−strain curves shown in Figure 4c. During the extensional process, the stress of all elastic vitrimers increases before hitting the maximum values σ_{max}. The maximum stress σ_{max} of the three systems appears around a strain of 7. The σ_{max} of substitute −F is larger than those of −H and −OCH$_3$, while the −H and −OCH$_3$ substitutes almost have the same σ_{max} value. The simulation here is consistent with the experimental tests, and this observation about σ_{max} also indicates that the energy barrier ΔE_{UB} controls the maximum stress. To further confirm that the ΔE_{UB} controls the maximum stress, we test the radius distribution function (RDF) $G(r)$ between the boronic acids (green bead) and diol function (red bead) at strain = 3 and strain = 7. All different substitutes give the same $G(r)$ curve at both strain values, suggesting that the three systems have the same number of dynamic covalent B−O bonds at each strain. On the other hand, the RDF also tells us that the dynamic covalent B−O bond RDF curves maintain their number during the extensional process, which is indicated by the fact that strain = 7 just slightly changes compared to strain = 3. Overall, our simulation results are consistent with experimental tests showing that the dissociative energy barrier controls the maximum tensile stress during tension for different elastic vitrimers.

3. CONCLUSIONS

In summary, we developed a facile and efficient strategy to fabricate boronic ester-based elastic vitrimers with tunable mechanics and dynamics via varying the neighboring group in phenylboronic acid moieties. The presence of electron-withdrawing groups on the dynamic boronic ester linkage endows the elastic vitrimers with higher Young's modulus and

tensile strength. The toughness recovery calculations show that the incorporation of electron-donating groups allows a faster recycling process due to lower binding strength and faster exchange kinetics. The slower segmental (chain) and terminal (bond exchange) dynamics with the side group changing from OCH_3 to F are clearly observed as well as the molecular-level influence on the stress−strain relationship. Also, a series of actual E_a values were calculated based on the rheology shift factor and the bond exchange dynamics and chain dynamics dissociated. The developed hybrid MC/MD model also confirmed that the dissociative energy barrier controls the maximum tensile stress during tension for different elastic vitrimers. The demonstrated approach on tunable elastic vitrimers will pave the way for developing recycled thermoset elastomers with an energy-efficient approach.

4. EXPERIMENTAL SECTION

4.1. Materials

Four-arm polyethylene glycol with hydroxyl as the end group (MW = 2000 g/mol, 99% purity) was purchased from Creative PEGWorks and dried under vacuum at 50 °C overnight. Boronic acid-based precursors including 4-carboxy-3-fluorophenylboronic acid, 4-carboxy-3-chlorophenylboronic acid, 4-carboxy-3-metoxyphenylboronic acid, 4-carboxyphenylboronic acid, diisopropyl carbodiimide (DIC, 99%), and 4-dimethylaminopyridine (DMAP) were supplied were purchased from Millipore Sigma and used as received. Anhydrous dichloromethane (DCM) and methanol as solvents were used without further purification. The PAMAM dendrimer (20% in methanol, 516 g/mol) and glycidol (96%) were supplied by Millipore Sigma and used as received.

4.2. Synthesis of Phenylboronic Acid-Functionalized 4-Arm Polyethylene Glycol (F-Precursor)

4-Arm polyethylene glycol (1.0 g, Mw = 2000 g/mol) was dissolved in 50 mL of anhydrous DCM. A 1.38 g (10 mmol) portion of 4-carboxy-3-fluorophenylboronic acid and 0.95 g of N,N'-diisopropylcarbodiimide (DIC) were added sequentially to the reaction mixture and stirred for 30 min under an argon blanket. Then, 0.917 g of 4-dimethylaminopyridine (DMAP) was added with continuous stirring. The reaction was carried out in an ice bath overnight. After the evaporation of the solvent, the resulting product was diluted with methanol, dialyzed against methanol for 24 h, and then vacuumed to remove the remaining solvent. One H (400 MHz, CDCl3, δ): 7.7−7.85 (m, 12H), 3.6 (br s, PEG).

Other phenylboronic acid-functionalized 4-arm polyethylene glycols (H-, OCH_3, and Cl- precursors) were synthesized following the same protocol described above using 4-carboxy-3-fluoro phenylboronic acid. ^{1}H NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer by using the residual proton resonance of $CDCl_3$ as the internal standard. Chemical shifts are reported in parts per million (ppm).

4.3. Synthesis of the Boronic Ester-Based Vitrimer (F-Vitrimer)

2 g of the F-precursor (0.75 mmol) was dissolved in 10 mL of anhydrous methanol. Then, the cross-linker solution was prepared by dissolving 0.61 g of PAMAM-diol in 3 mL of anhydrous methanol. After full dissolution, the F-precursor was mixed with PAMAM-diol in a molar ratio of 1:1, at which point the polymer samples became more viscous. The polymer solution was then cast into a Teflon mold and allowed to slowly evaporate at room temperature overnight on the benchtop. The cross-linked polymer films were then placed in a vacuum oven at 80 °C. The samples were vacuumed for 24 h to remove any residual solvent and moisture that may lead to bond dissociation and affect the overall cross-linking process. The other boronic ester-based vitrimers were prepared using the above-mentioned procedure.

4.4. Characterization of Vitrimers

FTIR spectroscopy was performed using a Nicolet iS50 FT-IR spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. The transmission spectrum of each vitrimer were obtained with 32 scans in the range 500−4000 cm^{-1} wavenumber. TGA was conducted using TGA Q50 (TA Instruments) to determine the thermal stability of the resulting vitrimers. The measurements were conducted in the range of temperatures from 20 to 800 °C with a 10 °C/min rate in the nitrogen atmosphere. DSC measurements were performed using a DSC 2500 (TA Instruments). The samples were sealed into aluminum hermetic pans and tested using a heat−cool−heat regime in the range from −80 to 80 °C at a rate of 5 °C/min with dry nitrogen purging through of the sample at a 50 mL/min flow rate to analyze their glass transition temperature (T_g). SAXS measurements were performed at the Xeuss 3.0 X-ray Scattering Beamline with the Pilatus 3R 300 K detector at the Joint Institute for Advanced Materials. DMA measurements were performed on a TA Discovery DMA850. The amplitude and frequency in the oscillation model were set to 20 μm and 1 Hz, respectively. The rectangular shape sample specimens were loaded between clamps and soaked at the starting temperature for 5 min before testing. The stress relaxation tests were conducted in the temperature range from 0 to 25 °C by applying a strain of 1%. Rheology studies were performed on a TA AR2000ex rheometer with an angular frequency range of 10^{-3} to 10^3 rad/s using parallel plate geometries with diameters of 4 and 8 mm. Strains of 0.03 to 3% were used depending on the temperatures from −45 to 150 °C. The tTS validity was further verified using the van Gurp−Palmen plot. Tensile properties of boronic ester-based vitrimers were determined according to the ASTM D1708 using an Instron universal testing machine 3343 with 50N cell capacity at a cross-head speed of 1 mm/s. At least five samples were tested from each composition, and the average data of tensile strength and elongation at break were calculated.

4.5. Recycling Process

1 × 1 in. square-shaped films of boronic ester-based vitrimers were broken into small pieces using a razor and loaded into a 0.5 mm thickness square-shaped PTFE mold. Then, the sample was placed in a vacuum oven at 70 °C under applied pressure (500 g) and held for various periods of time. The recycled films were removed from molds, cut to a rectangular shape of $W \times L$ of 3 × 20 mm, and tested using tensile testing according to the ASTM 1708 via the method mentioned above. The toughness recovery ($Toughness_{recov.}$) was calculated by calculating the area under the curve and comparing it to the toughness of virgin samples.

$$Toughness_{recov.} = \frac{Toughness_{recycled\ film}}{Toughness_{virgin\ film}} \quad (3)$$

where $Toughness_{virgin\ film}$ is the toughness value calculated for the vitrimer sample using the area under the stress−strain curve for virgin film, MJ/m^3 and $Toughness_{virgin\ film}$ is the toughness value calculated for the vitrimer sample using the area under the stress−strain curve for film after recycling, MJ/m^3.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialsau.3c00074.

The chemical pathway for the functionalization of 4-arm-polyethylene glycols using carboxyphenylboronic acids with variable substituents in the m-position; synthesis of diol-functionalized PAMAM dendrimers; ^{1}H NMR spectra of phenylboronic acid precursors and PAMAM-diol; solvent resistance test of resulting boronic ester-based vitrimers; TGA and DTG curves of boronic ester-based vitrimers; dynamic master curves of vitrimers, van Gurp−Palmen plots, shift factors used

for rheology master curves, and stress relaxation profiles for F-, Cl-, H-, and OCH$_3$-vitrimers; and simulation modeling of dynamic exchange in boronic ester-based vitrimers (PDF)

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Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Zhiqiang Shen** data curation, investigation, resources, writing-review & editing; **Peng-Fei Cao** conceptualization, formal analysis, project administration, supervision, visualization, writing-review & editing.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Law, K. L.; Narayan, R. Reducing environmental plastic pollution by designing polymer materials for managed end-of-life. *Nat. Rev. Mater.* **2022**, *7*, 104−116.

(2) Kumar, R.; Verma, A.; Shome, A.; Sinha, R.; Sinha, S.; Jha, P. K.; Kumar, R.; Kumar, P.; Shubham; Das, S.; Sharma, P.; Vara Prasad, P. V. Impacts of Plastic Pollution on Ecosystem Services, Sustainable Development Goals, and Need to Focus on Circular Economy and Policy Interventions. *Sustainability* **2021**, *13* (17), 9963.

(3) Luo, J.; Demchuk, Z.; Zhao, X.; Saito, T.; Tian, M.; Sokolov, A. P.; Cao, P.-F. Elastic vitrimers: Beyond thermoplastic and thermoset elastomers. *Matter* **2022**, *5* (5), 1391−1422.

(4) Ignatyev, I. A.; Thielemans, W.; Vander Beke, B. Recycling of polymers: a review. *ChemSusChem* **2014**, *7* (6), 1579−1593.

(5) Asim, M.; Jawaid, M.; Saba, N.; Ramengmawii; Nasir, M.; Sultan, M. T. H. Processing of hybrid polymer composites—a review. *Hybrid Polymer Composite Materials*; Woodhead Publish., 2017; pp 1−22.

(6) Tang, Z.; Chen, Y.; Zhang, C.; Wu, S.; Guo, B.; Zhang, L. Dual dynamic crosslinking of rubber for enhanced mechanical properties and reconfigurable shape memory behavior. *Polym. Int.* **2023**, *72* (9), 783−789.

(7) Zhang, D.; Tang, Y.; Gong, X.; Chang, Y.; Zheng, J. Highly conductive and tough double-network hydrogels for smart electronics. *Smart Mater.* **2023**, No. e1160.

(8) Demchuk, Z.; Zhu, J.; Li, B.; Zhao, X.; Islam, N. M.; Bocharova, V.; Yang, G.; Zhou, H.; Jiang, Y.; Choi, W.; Advincula, R.; Cao, P.-F. Unravelling the Influence of Surface Modification on the Ultimate Performance of Carbon Fiber/Epoxy Composites. *ACS Appl. Mater. Interfaces* **2022**, *14* (40), 45775−45787.

(9) Alabiso, W.; Schlögl, S. The Impact of Vitrimers on the Industry of the Future: Chemistry, Properties and Sustainable Forward-Looking Applications. *Polymers* **2020**, *12* (8), 1660.

(10) Krishnakumar, B.; Sanka, R. P.; Binder, W. H.; Parthasarthy, V.; Rana, S.; Karak, N. Vitrimers: Associative dynamic covalent adaptive networks in thermoset polymers. *Chem. Eng. J.* **2020**, *385*, 123820.

(11) Chen, Q.; Zhao, X.; Li, B.; Sokolov, A. P.; Tian, M.; Advincula, R. C.; Cao, P.-F. Exceptionally recyclable, extremely tough, vitrimer-like polydimethylsiloxane elastomers via rational network design. *Matter* **2023**, *6* (10), 3378−3393.

(12) Stewart, K. A.; Lessard, J. J.; Cantor, A. J.; Rynk, J. F.; Bailey, L. S.; Sumerlin, B. S. High-performance polyimine vitrimers from an aromatic bio-based scaffold. *RSC Appl. Polym.* **2023**, *1*, 10−18.

(13) Denissen, W.; Winne, J. M.; Du Prez, F. E. Vitrimers: permanent organic networks with glass-like fluidity. *Chem. Sci.* **2016**, *7* (1), 30−38.

(14) Zheng, J.; Png, Z. M.; Ng, S. H.; Tham, G. X.; Ye, E.; Goh, S. S.; Loh, X. J.; Li, Z. Vitrimers: Current research trends and their emerging applications. *Mater. Today* **2021**, *51*, 586−625.

(15) Meng, F.; Saed, M. O.; Terentjev, E. M. Rheology of vitrimers. *Nat. Commun.* **2022**, *13* (1), 5753.

(16) Deng, J.; Bai, R.; Zhao, J.; Liu, G.; Zhang, Z.; You, W.; Yu, W.; Yan, X. Insights into the Correlation of Cross-linking Modes with Mechanical Properties for Dynamic Polymeric Networks. *Angew. Chem., Int. Ed.* **2023**, *62* (37), No. e202309058.

(17) Zhang, B.; Yuan, C.; Zhang, W.; Dunn, M. L.; Qi, H. J.; Liu, Z.; Yu, K.; Ge, Q. Recycling of vitrimer blends with tunable thermomechanical properties. *RSC Adv.* **2019**, *9* (10), 5431−5437.

(18) Zhou, Y.; Groote, R.; Goossens, J. G. P.; Sijbesma, R. P.; Heuts, J. P. A. Tuning PBT vitrimer properties by controlling the dynamics of the adaptable network. *Polym. Chem.* **2019**, *10* (1), 136−144.

(19) Liu, Y.; Tang, Z.; Chen, J.; Xiong, J.; Wang, D.; Wang, S.; Wu, S.; Guo, B. Tuning the mechanical and dynamic properties of imine bond crosslinked elastomeric vitrimers by manipulating the cross-linking degree. *Polym. Chem.* **2020**, *11* (7), 1348−1355.

(20) Denissen, W.; Droesbeke, M.; Nicolaÿ, R.; Leibler, L.; Winne, J. M.; Du Prez, F. E. Chemical control of the viscoelastic properties of vinylogous urethane vitrimers. *Nat. Commun.* **2017**, *8* (1), 14857.

(21) Guerre, M.; Taplan, C.; Winne, J. M.; Du Prez, F. E. Vitrimers: directing chemical reactivity to control material properties. *Chem. Sci.* **2020**, *11* (19), 4855−4870.

(22) Chen, X.; Li, L.; Wei, T.; Venerus, D. C.; Torkelson, J. M. Reprocessable Polyhydroxyurethane Network Composites: Effect of Filler Surface Functionality on Cross-link Density Recovery and Stress Relaxation. *ACS Appl. Mater. Interfaces* **2019**, *11* (2), 2398−2407.

(23) Röttger, M.; Domenech, T.; van der Weegen, R.; Breuillac, A.; Nicolaÿ, R.; Leibler, L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **2017**, *356* (6333), 62−65.

(24) Breuillac, A.; Kassalias, A.; Nicolaÿ, R. Polybutadiene Vitrimers Based on Dioxaborolane Chemistry and Dual Networks with Static and Dynamic Cross-links. *Macromolecules* **2019**, *52* (18), 7102−7113.

(25) Yesilyurt, V.; Webber, M. J.; Appel, E. A.; Godwin, C.; Langer, R.; Anderson, D. G. Injectable Self-Healing Glucose-Responsive Hydrogels with pH-Regulated Mechanical Properties. *Adv. Mater.* **2016**, *28* (1), 86−91.

(26) Tang, S.; Ma, H.; Tu, H. C.; Wang, H. R.; Lin, P. C.; Anseth, K. S. Adaptable Fast Relaxing Boronate-Based Hydrogels for Probing Cell-Matrix Interactions. *Adv. Sci.* **2018**, *5* (9), 1800638.

(27) Chu, C. K.; Joseph, A. J.; Limjoco, M. D.; Yang, J.; Bose, S.; Thapa, L. S.; Langer, R.; Anderson, D. G. Chemical Tuning of Fibers Drawn from Extensible Hyaluronic Acid Networks. *J. Am. Chem. Soc.* **2020**, *142* (46), 19715−19721.

(28) Cho, S.; Hwang, S. Y.; Oh, D. X.; Park, J. Recent progress in self-healing polymers and hydrogels based on reversible dynamic B-O bonds: boronic/boronate esters, borax, and benzoxaborole. *J. Mater. Chem. A* **2021**, *9* (26), 14630−14655.

(29) Zhang, X.; Wang, S.; Jiang, Z.; Li, Y.; Jing, X. Boronic Ester Based Vitrimers with Enhanced Stability via Internal Boron-Nitrogen Coordination. *J. Am. Chem. Soc.* **2020**, *142* (52), 21852−21860.

(30) Mellerup, S. K.; Wang, S. Boron-based stimuli responsive materials. *Chem. Soc. Rev.* **2019**, *48* (13), 3537−3549.

(31) Niu, W.; O'Sullivan, C.; Rambo, B. M.; Smith, M. D.; Lavigne, J. J. Self-repairing polymers: poly(dioxaborolane)s containing trigonal planar boron. *Chem. Commun.* **2005**, 4342−4344.

(32) Zhao, Z. H.; Wang, D.-P.; Zuo, J.; Li, C. H. A Tough and Self-Healing Polymer Enabled by Promoting Bond Exchange in Boronic Esters with Neighboring Hydroxyl Groups. *ACS Mater. Lett.* **2021**, *3* (9), 1328−1338.

(33) Cash, J. J.; Kubo, T.; Dobbins, D. J.; Sumerlin, B. S. Maximizing the symbiosis of static and dynamic bonds in self-healing boronic ester networks. *Polym. Chem.* **2018**, *9* (15), 2011−2020.

(34) Adamczyk-Woźniak, A.; Sporzyński, A. The influence of ortho-substituents on the properties of phenylboronic acids. *J. Organomet. Chem.* **2020**, *913*, 121202.

(35) Lee, S. M.; Chung, J.; Gong, M. S.; Jun, B.-H.; Kweon, D.-H.; Chung, W.-J. Substituent effects of phenylboronic acid-functionalized resins in pH-controlled separation of catecholic flavonoids. *J. Ind. Eng. Chem.* **2019**, *77*, 164−170.

(36) Zarzeczańska, D.; Adamczyk-Woźniak, A.; Kulpa, A.; Ossowski, T.; Sporzyński, A. Fluorinated Boronic Acids: Acidity and Hydrolytic Stability of Fluorinated Phenylboronic Acids. *Eur. J. Inorg. Chem.* **2017**, *2017* (38−39), 4493−4498.

(37) Hou, J.; Li, G.; Yang, N.; Qin, L.; Grami, M. E.; Zhang, Q.; Wang, N.; Qu, X. Preparation and characterization of surface modified boron nitride epoxy composites with enhanced thermal conductivity. *RSC Adv.* **2014**, *4* (83), 44282−44290.

(38) van Gurp, M.; Palmen, J. Time-Temperature Superposition For Polymeric Blends. *Rheol. Bull.* **1998**, *67*, 5−8.

(39) Wang, S.; Xue, L.-L.; Zhou, X.-Z.; Cui, J.-X. Solid-Liquid" Vitrimers Based on Dynamic Boronic Ester Networks. *Chin. J. Polym. Sci.* **2021**, *39* (10), 1292−1298.

(40) Martins, M. L.; Zhao, X.; Demchuk, Z.; Luo, J.; Carden, G. P.; Toleutay, G.; Sokolov, A. P. Viscoelasticity of Polymers with Dynamic Covalent Bonds: Concepts and Misconceptions. *Macromolecules* **2023**, *56* (21), 8688−8696.

(41) Ricarte, R. G.; Shanbhag, S.; Ezzeddine, D.; Barzycki, D.; Fay, K. Time-Temperature Superposition of Polybutadiene Vitrimers. *Macromolecules* **2023**, *56* (17), 6806−6817.

(42) Gosecki, M.; Gosecka, M. Boronic Acid Esters and Anhydrates as Dynamic Cross-Links in Vitrimers. *Polymers* **2022**, *14* (4), 842.

(43) Yue, T.; He, J.; Tao, L.; Li, Y. High-Throughput Screening and Prediction of High Modulus of Resilience Polymers Using Explainable Machine Learning. *J. Chem. Theory Comput.* **2023**, *19* (14), 4641−4653.

(44) Shen, Z.; Ye, H.; Wang, Q.; Kröger, M.; Li, Y. Sticky Rouse Time Features the Self-Adhesion of Supramolecular Polymer Networks. *Macromolecules* **2021**, *54* (11), 5053−5064.

(45) Plimpton, S. Fast Parallel Algorithms for Short-Range Molecular Dynamics. *J. Comput. Phys.* **1995**, *117* (1), 1−19.

(46) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graphics* **1996**, *14* (1), 33−38.