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Tuning the Viscoelastic Properties of Dioxazaborocane Vitrimers via Chemical Design of the Functional Groups

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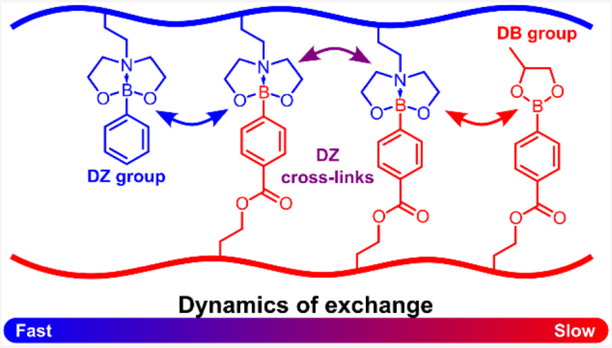

ABSTRACT: Vitrimers are polymer networks that can rearrange their topology via thermally triggered dynamic covalent bonds. While their versatility offers interesting paths for developing new applications, one needs first to understand how their dynamics depends on the topology of the network to exploit their large potential. These past few years, boronic esters, especially dioxaborolanes, have been widely studied as moieties to create reversible covalent bonds. Recently, dioxazaborocanes, moieties featuring a labile N−B bond, have also been proposed, showing much faster dynamics at high temperatures compared to dioxaborolanes when incorporated in vitrimers. Herein, we study the viscoelastic properties of vitrimers obtained from linear precursors bearing complementary dioxazaborocane and dioxaborolane moieties. By playing with the density of these two different moieties, we can accurately control the proportion of free functional groups present in the vitrimers and therefore study their influence on the dynamics of the reversible network. It is found that the network dynamics can be either slowed down or accelerated in the presence of dioxaborolane or dioxazaborocane free functional groups, respectively, regardless of the total density of functional groups. The results also show a nonmonotonic dependence of the network relaxation time as a function of the cross-linking density, which we attribute to the antagonistic effects of the subdiffusion process of the dynamic moieties and the restricted mobility of the polymer chains within the network.

1. INTRODUCTION

Dynamic covalent bonds (DCBs) are chemical links that can break and reform under certain conditions in a reversible way under thermodynamic control.[1,2] These bonds can be used to link polymer chains and to endow new properties on the material, such as self-healing, improved mechanical performance, and stimuli responsiveness, thanks to the exchange dynamics between cross-links (also called stickers).[3−6] This exchange may occur via either a dissociative or associative mechanism that dictates not only the thermomechanical performance of the material but also its viscosity profile and, as a consequence, its processability.[7] To encompass networks featuring both types of exchange mechanisms, covalent adaptable networks (CANs) were coined and defined as macromolecular structures able to adapt their topology in response to an external stimulus and exhibit the aforementioned properties.[8]

Vitrimers are CANs maintaining a constant average cross-linking density regardless of the temperature thanks to an associative exchange mechanism between DCB. For amorphous vitrimers, this exchange process is hindered at temperatures below their glass transition temperature (T_g) because of the restricted segmental dynamics and becomes activated at temperatures above the topology freezing transition temperature (T_v), leading to the network topology rearrangement. Therefore, the behavior of these materials switches from an elastic solid to a viscoelastic liquid at high temperatures when the kinetics of exchange is fast enough to make the material flow, following an Arrhenian behavior. In this context, vitrimers featuring a wide variety of dynamic chemistries have been exploited in the literature for many different applications, pointing out the versatility of these materials.[7−12]

Among the large library of dynamic moieties available to make vitrimers, boronic esters present features such as high thermal stability, chemical orthogonality, ease of synthesis, and insertion to polymers,[13−15] rendering them remarkably appealing for industrial applications. Particularly, dioxaborolanes (DBs), i.e., five-membered ring boronic esters, have been largely studied in this context. It has been shown that the viscosity profile of vitrimers based on this chemistry is strongly dependent on the cross-linking density, the architecture, and

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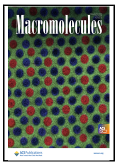

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the chemical nature of the network.[16−21] Moreover, when self-healing properties or a fast dynamics are needed, the introduction of diols (either within the network or as free molecules) speeds up the kinetics of exchange via the transesterification reaction.[22−24]

In addition to dioxaborolanes, another class of boronic esters that has drawn the attention of researchers recently is dioxazaborocanes (DZ). These groups feature a dative N → B bond that can be progressively broken upon applying either a large mechanical load[25] or high temperatures[26] passing from a closed- to an open-ring structure, the latter being a much more reactive species compared to the closed structure. Dioxazaborocanes are also more stable toward hydrolysis and transesterification compared to dioxaborolanes.[27−29] Several CANs incorporating DZ moieties have been reported, including chain-growth polymers,[30,31] epoxy resins,[32] hydrogels,[6,33] and polyurethanes.[26,34−38] Recently, Nicolaÿ and coworkers showed that dioxazaborocanes and dioxaborolanes can undergo metathesis exchange with each other in solvent and in bulk. They harnessed this exchange to make networks from linear precursors bearing complementary DZ and DB functions.[31] They found that these networks exhibit much faster relaxation compared to the majority of dioxaborolane-based vitrimers reported in the literature.

Today, despite the different works investigating the properties of vitrimers, the influence of free functional groups on the dynamics of the network remains unclear. These groups are usually cross-linked upon reaction with “small molecule cross-linkers” either in solution or in bulk,[14] but the total number of reactive groups along the polymer backbone remains constant. Several works have shown that the dynamics of exchange between the reversible covalent bonds may be affected by the distribution and the density of functional groups as a closer proximity of these reversible bonds is supposed to facilitate their exchange.[39−42] However, it is not clear whether the lifetime of the exchange between a reversible cross-link and a free functional group is similar to the exchange lifetime between two reversible cross-links. Chen’s group[17,43] concluded that the presence of free functional groups seems to influence the rate of exchange of the cross-links. However, a systematic study of these parameters still needs to be conducted to better exploit the tunability of these materials.

Herein, we aim to study the impact of the chemical nature of the free functional groups, being either free DZ or free DB functions, on the dynamics of exchange of dioxazaborocane-based vitrimers. We also want to understand the influence of the density of cross-links and functional groups on the flow properties of these samples. To this end, we synthesized unentangled monodisperse precursors bearing either DZ or DB groups. Then, we made three sets of vitrimers with only DZ cross-links (no pendent groups) or either DZ or DB free pendent groups while keeping the same chemical nature of the cross-links and the same total density of functional groups. Rheological studies show that vitrimers with free pendent DB groups exhibit slower dynamics with respect to their counterparts with DZ pendent groups, regardless of the cross-linking density. In fact, for the same density of dynamic moieties, vitrimers with DB free pendent groups were demonstrated to be even slower than networks bearing only DZ cross-links (i.e., with no free pendent groups). The effect of temperature on these exchange mechanisms is also studied. The results obtained herein demonstrate the large tunability we can reach with vitrimers containing two types of nonidentical exchangeable boronic ester groups.

2. EXPERIMENTAL SECTION

2.1. Materials

Triethanolamine (99%), triethylamine (TEA, 98%), propane-1,2-diol (99.5%), methacrylic anhydride (>94%), 4-(dimethylamino)pyridine (DMAP, 99%), oxalyl chloride (98%), magnesium sulfate ($MgSO_4$, >99.5%), aluminum oxide activated basic Brockmann I, and 2,2-azobis(2-methylpropionitrile) (AIBN) were purchased from Sigma-Aldrich. 2-Ethylhexyl methacrylate (EHMA, 99%), phenylboronic acid (97%), and anisole were purchased from TCI Europe. 2-Cyano-2-propyl benzodithioate was purchased from BLD Pharm. Sodium bicarbonate ($NaHCO_3$, >99.7%), sodium sulfate (Na_2SO_4, >99%), and sodium hydroxide (NaOH, >98%) were purchased from Alfa Aesar. Hydrochloric acid (37% in water, 98%) and the solvents were purchased from VWR. AIBN was recrystallized from methanol twice before being used. All other reagents and chemicals were used without further purification.

2.2. Nuclear Magnetic Resonance (NMR) Spectroscopy

^1H spectra were recorded at 25 °C on a Bruker AVANCE spectrometer at 400 MHz. The reference used for ^1H spectra was the residual solvent peaks (^1H NMR: δ 7.26 in $CDCl_3$).

2.3. Size Exclusion Chromatography (SEC)

Molecular weights of polymers were estimated based on conventional calibration with monodisperse PMMA standards on an Agilent Technologies 1200 series GPC/SEC equipped with a PSS Gram column connected to a refractive index detector. Measurements were performed at 1 mL/min and 35 °C with THF as the mobile phase.

2.4. Differential Scanning Calorimetry (DSC)

Samples with masses ranging from 5−15 mg of polymers were loaded into a hermetically sealed disposable aluminum pan. Experiments were carried out on a Mettler Toledo DSC 1 STAR System equipped with an autosampler and a nitrogen gas cooling system. The following protocol was applied: stabilization of the temperature at 100 °C for 5 min, cooling ramp at −20 °C/min from 100 to −80 °C, isotherm for 2 min, heating ramp at +20 °C/min from −80 to 100 °C, isotherm for 2 min, cooling ramp at −10 °C/min from 100 to −80 °C, isotherm for 2 min, and heating ramp at +10 °C/min from −80 to 100 °C. T_g was estimated from the second heating at 10 °C/min.

2.5. Rheological Characterizations

Shear rheological experiments were conducted on an Ares rheometer (TA Instruments) equipped with a heat exchanger. Measurements were performed at temperatures ranging from 180−20 °C on cooling with a parallel plate geometry (8 mm diameter) under a nitrogen atmosphere. The samples were stabilized depending on the cross-linking density of the networks. Thus, the equilibration time varies from 20 min to more than 1 h prior to conducting the frequency sweep experiments. Certain measurements were repeated to confirm that no significant aging of the materials occurred in the experiments.

2.6. Polymerization Protocol

The functional boronic ester monomers DBM and DZM were synthesized following the protocols described by Van Zee, Nicolaÿ and coworkers. The synthetic pathway and protocols can be found elsewhere.[31] EHMA was first passed through a column of activated basic aluminum oxide to remove the inhibitors before performing the copolymerization with either DBM or DZM. The polymers were made by reversible addition−fragmentation chain transfer (RAFT) polymerization by using AIBN as the initiator (solution in DMF at 40 mg/mL), 2-cyano-2-propyl benzodithioate as the chain transfer agent (CTA solution in DMF at 20 mg/mL), and a mixture of anisole:DMF (v:v = 4:1) as the solvent in a ratio of 1:1 with respect to the monomers. The monomer conversions and final compositions of the polymers were confirmed by ^1H NMR spectroscopy. M_n and dispersity of each polymer were determined by SEC using narrow

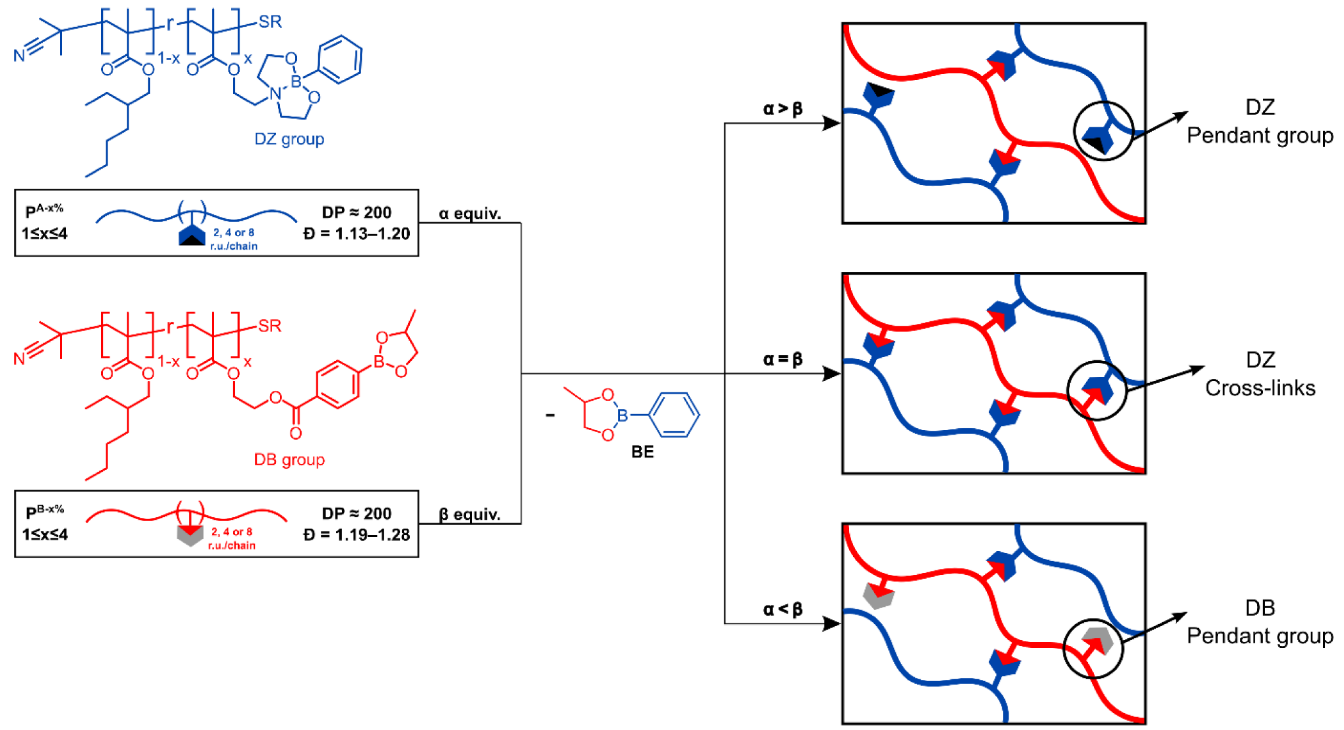

Figure 1. Schematic representation of the precursors bearing dioxazaborocane ($\mathbf{P}^{A}$) and dioxaborolane ($\mathbf{P}^{B}$) moieties and the ideal vitrimer topologies accessible from in- and off-stoichiometric mixing.

PMMA standards. More details about the synthesis can be found in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Design and Conception of the Vitrimer Model Systems

To systematically study the influence of parameters such as the cross-linking density and the chemical nature of the exchangeable groups on the flow properties of boronic ester-based vitrimers, we synthesized unentangled monodisperse precursors (200 repeating units per chain in average) based on EHMA and either dioxazaborocanes (DZM) or dioxaborolanes (DBM) methacrylates as comonomers to have a T_g close to ambient temperature. These polymers bearing either DZ or DB groups will be called from now on $\mathbf{P}^{A-x\%}$ and $\mathbf{P}^{B-x\%}$, respectively, where $x\%$ stands for the molar functionality ranging from 1 to 4 mol %, leading to a number between 2 and 8 of functional moieties per chain in average. Then, we prepared three sets of vitrimers with either (i) DZ or (ii) DB free pendant groups or (iii) (theoretically) only cross-links. The networks were prepared by mixing $\mathbf{P}^{A-x\%}$ and $\mathbf{P}^{B-x\%}$, analogous examples can be found elsewhere.[16,20,31,43,44] The cross-linking is achieved through a metathesis reaction between DZ and DB pendent groups and releases a small molecule BE (see Figure 1). This reaction can quickly reach the equilibrium as demonstrated by model studies.[31] We restrict this study to networks made from precursors with the same functionality to discuss how the viscoelastic properties of these vitrimers can be tuned just by playing with the stoichiometry of the precursors.

Thus, the cross-linking density as well as the functionality of free side groups within the network can be tuned simply by choosing the composition of the precursors and adjusting their stoichiometry in the mixture (more details in the Supporting Information). For the purpose of readability and to give insight into the chemical nature and the number of the pendent groups, vitrimers are labeled as $\boldsymbol{\alpha}\mathbf{P}^{A-x\%}+\boldsymbol{\beta}\mathbf{P}^{B-x\%}$, where α and β represent the equivalents of $\mathbf{P}^{A}$ and $\mathbf{P}^{B}$ precursors. So, when $\alpha > \beta$, vitrimers have DZ free functional groups. Otherwise, if $\alpha < \beta$, free functional groups are DB. In the last scenario, when $\alpha = \beta$, we consider that no free functional groups are present within the network. However, it is very likely that few unreacted DZ and DB free pendent groups still remain within the vitrimer in this case. Figure 1 illustrates the chemical composition of the precursors and the vitrimers, considering the ideal case with no pendent groups or defects.

The viscoelastic properties of these vitrimers were assessed by frequency sweeps and are discussed in the next sections. On the other hand, we decided not to perform swelling tests because the low molar mass of the precursors and the fast dynamics of exchange of these vitrimers in a good solvent would lead to their eventual dissolution, as reported elsewhere for other networks based on boronic esters.[31,39]

3.2. Viscoelastic Properties of the Precursors and the Vitrimers

First, to fairly compare the precursors, we built pseudomastercurves by using the time−temperature superposition (TTS) principle.[45] We applied horizontal shift factors (a_T) to the frequency sweep data while considering an iso-frictional temperature (T_{iso}) as a reference ($T_{iso} \approx T_g + 55$ °C) to compensate for the difference of T_g resulting from the copolymerization of EHMA with the boronic ester monomers.

We confirm that the viscoelastic moduli of all the sets of precursors collapse in Figure 2a (representative example) and S9, and they behave like unentangled linear polymers since no rubbery plateau is observed.

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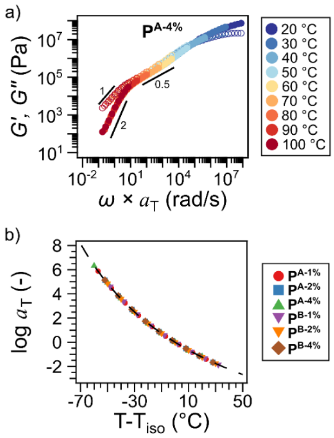

Figure 2. (a) Pseudomastercurve of $\mathbf{P}^{\mathbf{A\text{-}4\%}}$. Filled and open symbols represent G' and G'', respectively. (b) Horizontal shift factors (a_T) as a function of temperature for the precursors. The dashed line represents the expected a_T from the WLF equation.

We used the Williams–Landel–Ferry (WLF) equation (eq 1) to describe and predict the temperature dependence of the shift factors with respect to the temperature (Figure 2b):

$$\log a_T^{\mathrm{WLF}}(T) = \frac{-C_1(T - T_{\mathrm{iso}})}{C_2 + T - T_{\mathrm{iso}}} \tag{1}$$

The values of C_1 and C_2 were fixed to 11.82 and 171.61 °C, respectively.

Pseudomastercurves are also built for the vitrimers, at iso-T_g conditions, to look into the effect of temperature on their viscoelastic response (Figures S10–S18). Besides the horizontal (a_T) shift factors, vertical (b_T) shift factors are also considered to compensate for the apparent change of density (see Supporting Information).

In Figure 3, we show the viscoelastic response of the vitrimers at T_{iso}. All samples exhibit different viscoelastic behavior. We observed that the values of plateau modulus (G_N^0) increase with the density of functional groups, as expected. These were estimated from the corresponding value of G at the minimum of Tan(δ) and are listed in Table S6.

In comparison with the theoretical values determined from the molar mass between two cross-links, it is observed that G_N^0 determined from the experimental data is lower than expected, especially for the poorly cross-linked samples. This is attributed to the low number of functional groups per chain, estimated to be about 2, 4, and 8 for the molar functionality of 1, 2, to 4 mol %, respectively. This means that many chains have only two dynamic covalent bonds and do not contribute to the sample elasticity, their only contribution being to increase the length of the bridging molecular segment to which they participate. Dangling ends, which represent a large weight fraction of the weakly functionalized samples, also do not contribute to the rubbery plateau.

Although we notice that G' overlaps well throughout the experimental temperature window, this is not the case for G''. This discrepancy can be attributed to the thermorheological complexity of the systems as a result of the interplay of different temperature-dependent mechanisms, i.e., a WLF dependence on temperature for the dynamics of the chains and an Arrhenius dependence for the boronic ester exchange. This is much more evident over a large window at low frequencies (high temperatures) since both the segmental motion and the exchange dynamics play a role in the overall

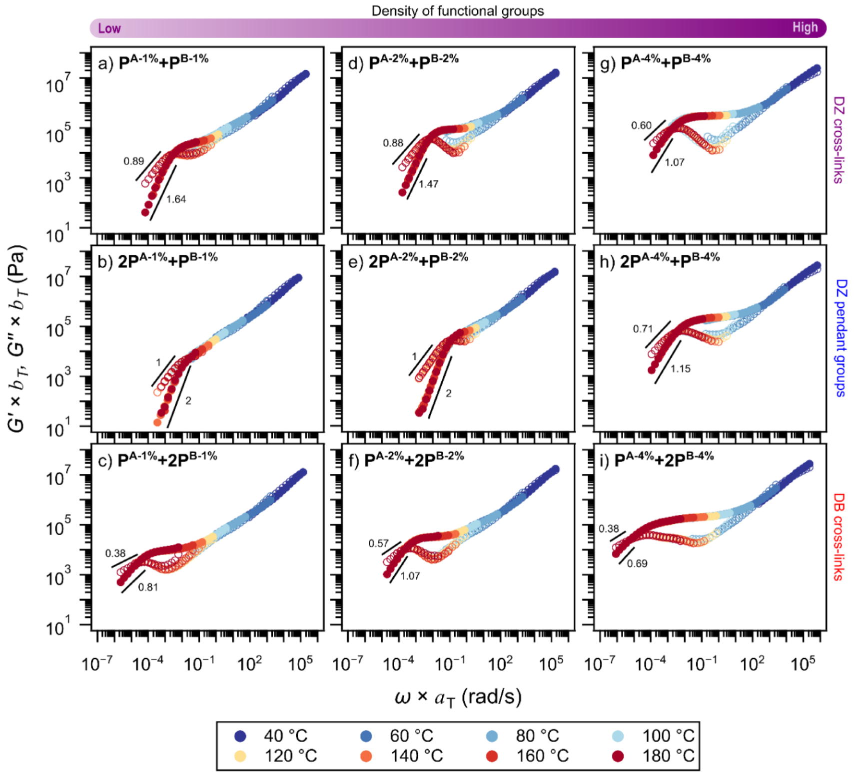

Figure 3. Pseudomastercurves of vitrimers at $T_{ref} = T_g + 55$ °C. Filled and open symbols represent G' and G'', respectively.

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relaxation process, with the latter becoming more important as temperature increases.

3.3. Influence of the Free Functional Moieties

Focusing, first, on the influence of the free functional moieties, we compare the vitrimers with the lowest cross-linking densities of 1% (Figure 3a,b,c). Unexpectedly, despite having no side groups, sample $\mathbf{P}^{\mathrm{A\text{-}1\%}}$ + $\mathbf{P}^{\mathrm{B\text{-}1\%}}$ exhibits a much faster dynamics than $\mathbf{P}^{\mathrm{A\text{-}1\%}}$ + $\mathbf{2P}^{\mathrm{B\text{-}1\%}}$, a network bearing DB free functional groups. This latter displays a longer plateau with a network crossover relaxation time (τ*) of around 10.3 h, much larger than the 323 s estimated for $\mathbf{P}^{\mathrm{A\text{-}1\%}}$ + $\mathbf{P}^{\mathrm{B\text{-}1\%}}$, and does not reach the terminal flow after its crossover time, as is seen from the slopes of G' and G''. On the contrary, $\mathbf{2P}^{\mathrm{A\text{-}1\%}}$ + $\mathbf{P}^{\mathrm{B\text{-}1\%}}$, which contains the same density of cross-linking junctions as $\mathbf{P}^{\mathrm{A\text{-}1\%}}$ + $\mathbf{2P}^{\mathrm{B\text{-}1\%}}$ but in which the pendent groups are DZ moieties in place of DB moieties, seems to behave like a conventional poorly entangled thermoplastic, with the relaxation of dangling branches at intermediate frequency, followed by the Rouse-like relaxation of the network, G' and G'' progressing parallel to each other until reaching the terminal regime. Even though this behavior seems to be identical to that of the precursors (Figure S9), the viscoelastic response of the vitrimer is slower (τ* equal to 29 s) compared to the precursors (Rouse time, τ_R, of 0.36 s), suggesting a sticky Rouse behavior.[46] As shown in Figure 3, a similar influence of the free functional groups is observed for the vitrimers with a higher density of functional moieties (2% or 4%). From these outcomes, we can conclude that the presence and nature of free functional groups play a crucial role in the network's dynamics: while it is accelerated in the presence of DZ free functional groups, the opposite effect is observed when DB free functional groups are part of the network. If we account for the different weight fractions of precursors bearing DZ moieties in these samples (being equal to 2/3, 1/2, and 1/3 for samples $\mathbf{2P}^{\mathrm{A-}x\%}$ + $\mathbf{PB}^{-x\%}$, $\mathbf{P}^{\mathrm{A-}x\%}$ + $\mathbf{P}^{\mathrm{B-}x\%}$, and $\mathbf{P}^{\mathrm{A-}x\%}$ + $\mathbf{2P}^{\mathrm{B-}x\%}$, respectively), these results suggest that the dynamics of the networks speeds up with an increasing proportion of DZ groups, either as free functional groups or cross-links. The results also suggest that free DB groups hinder in some extent the exchange of DZ groups, which are responsible for triggering fast dynamics of the network.

3.4. Decoding the Mechanisms Involved in the Relaxation of the Vitrimer Network

As shown in Figure 3, comparing the vitrimers with the same proportion of precursors $\mathbf{P}^{\mathrm{A}}$ and $\mathbf{P}^{\mathrm{B}}$, but upon increasing the cross-linking density, reveals the complexity of the mechanisms governing the flow properties of these networks. As summarized in Figure 4a, increasing the cross-linking density leads to, first, a decrease of τ*, followed by an increase of this latter. To evaluate the influence of the shifting of the curves on this result, the values of τ* at 180 °C are also presented (Figure 4b). The nonmonotonic trend is preserved for $\mathbf{P}^{\mathrm{A-}x\%}$ + $\mathbf{2P}^{\mathrm{B-}x\%}$, while for the other networks having 2% of moieties in place of 1% only slows down the network relaxation. The decrease of τ* observed for $\mathbf{P}^{\mathrm{A-2\%}}$ + $\mathbf{2P}^{\mathrm{B-2\%}}$ seems, a priori, counterintuitive since more stickers alongside the chain backbone are expected to restrict the chain diffusion.

The origin of the difference in trends comes from the temperature dependence of a_T as the density of the functional groups increases. As will be shown in Figure 5, this temperature dependence is weaker for the vitrimers made from the precursor having 2 mol % of functional groups compared to the others. This implies that the shift factors applied for the vitrimers ($\boldsymbol{\alpha}\mathbf{P}^{\mathrm{A-}x\%}$ + $\boldsymbol{\beta}\mathbf{P}^{\mathrm{B-}x\%}$) to shift the data measured at high temperature to T_{iso} are smaller for x = 2 than for x = 1. This leads to shorter values of τ*. In contrast, when estimating τ* at a temperature far from T_g (e.g., 180 °C), segmental dynamics should have a negligible effect on the overall relaxation.

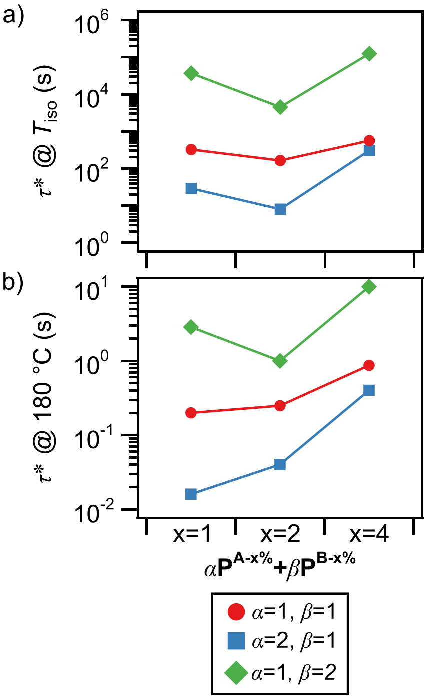

Figure 4. Characteristic crossover relaxation times (τ*) of the vitrimers at: (a) T_{iso} and (b) 180 °C.

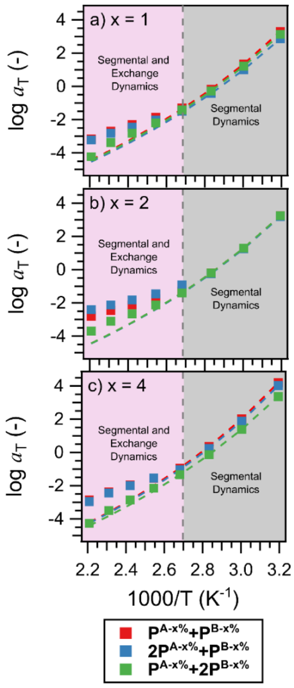

Figure 5. Plots of shift factors (a_T) as a function of the inverse of temperature. Dashed lines represent the expected trend of a_T from the WLF equation.

We attribute this behavior to the subdiffusive mechanism of the reactive groups (cross-links and side groups) described by de Gennes[47] which leads to antagonistic effects at low and high cross-linking densities: when stickers are far from each other at low cross-linking densities, they need longer times to diffuse and find a new partner to exchange, leading to slower relaxation. In contrast, when the number of stickers increases, the exchange becomes easier due to the proximity of the dynamic moieties, which should lead to faster relaxation. However, this effect is counterbalanced by the restricted mobility of the chains upon increasing the cross-linking density, unable to diffuse and relax. Consequently, a delay of the network dynamics may be observed.[39]

Likewise, we can explain the difference between the vitrimers with either DZ or DB free functional groups from the kinetic point of view by considering the approach of Chen and coworkers[43] for vitrimers made of complementary polymers. They demonstrated that the kinetic constants of the exchange reactions (i.e., between 2 cross-links or a free functional group and a cross-links) control τ_s, the bond exchange lifetime, and that the presence of free functional groups should accelerate the dynamics because of lower mobility constraints. Nevertheless, that study is based on the exchange of DB groups. Herein, we demonstrated that the presence of DB free functional groups in place of DZ groups actually slows down the dynamics of exchange of DZ-based vitrimers; so, we infer that the kinetic constant for the exchange between DZ and DB groups is much lower compared to that of identical DB moieties, characterized by longer relaxation times. Additionally, we can also infer that the kinetic constants for the DZ exchange (between a free functional group and a cross-link or between two cross-links) are large enough to accelerate the network relaxation with respect to the networks containing DB free functional groups.

3.5. Influence of Temperature on the Network Relaxation

The horizontal shift factors a_T used to build the pseudo master-curves of Figure 3 are presented in Figure 5. We see that a transition occurs in the temperature dependence of these shift factors, from a WLF behavior at low temperatures, at which the network dynamics is governed by the segmental dynamics to an Arrhenius temperature dependence when the exchange dynamics becomes the dominant relaxation process. Thereby, for the sake of convenience, we propose to call cooperative dynamics transition temperature (T_{tr}) the onset temperature at which the Arrhenius-like behavior becomes predominant. This definition does not contravene in any case T_v.[48]

We can then express the horizontal shifts as

$$a_T(T) = \begin{cases} a_T^{\mathrm{WLF}}(T), & \text{for } T < T_{tr} \\ \exp\left\{ \frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{tr}} \right) \right\}, & \text{for } T \geq T_{tr} \end{cases} \tag{2}$$

Using these equations, we then estimate the effective E_a of the Arrhenius process (Figure S22). It is found that E_a of the vitrimers containing only DZ moieties (either as free functional groups or cross-links) are similar (Figure 6). For instance, the estimated values of E_a for $\mathbf{P}^{A-2\%}$ + $\mathbf{P}^{B-2\%}$ and $2\mathbf{P}^{A-2\%}$ + $\mathbf{P}^{B-2\%}$ are 59.9 and 59.0 kJ/mol, respectively. However, E_a increases for the vitrimers containing DB free functional groups (e.g., E_a for $\mathbf{P}^{A-2\%}$ + $2\mathbf{P}^{B-2\%}$ was calculated to be 90.3 kJ/mol). We attribute this large difference to the ineffective collisions between DZ and DB groups because of the geometrical differences of their molecular structures, i.e., planar five-membered ring dioxaborolanes and three-dimensional eight-membered ring dioxazaborocanes, which lead to a higher energetic barrier to overcome for the exchange between nonidentical boronic esters. On the other hand, we can infer that when none or few DB groups are present, the activation energy mainly depends on the cross-linking density and is apparently independent of the state of the DZ moieties (i.e., free group or cross-link).

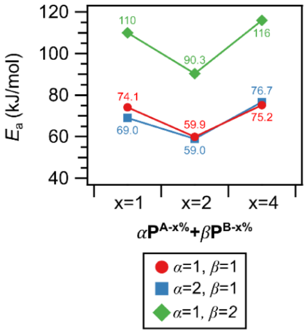

Figure 6. Evolution of the activation energy of the vitrimers.

The values E_a, which describe the temperature dependence of the relaxation of the vitrimers, show a similar nonmonotonic trend to the one of τ^*, i.e., first, a decrease followed by an increase when rising the cross-linking density (Figure 6). This further supports our hypothesis about the subdiffusive mechanism of the reactive groups, which speeds up the relaxation with increasing the cross-linking density, contrary to the diffusion of the whole chains, which slows down the dynamics. Thus, a certain equilibrium between both effects can be found at which the activation energy for the network tends to be the lowest.

In Figure 5, we also observed that, at high temperatures, the temperature dependence is lower than that predicted by WLF. This behavior is interpreted as unexpected since the temperature dependence of a_T should include the contribution of both the segmental motion and the bond exchange dynamics.[48,49] This has been previously reported for some vitrimers,[17,50,51] including dioxaborolane-based vitrimers made by complementary polymers at different cross-linking densities.[43] However, to the best of our knowledge, this is the first time this behavior is reported for networks made of nonidentical exchangeable boronic ester groups.

4. CONCLUSIONS

In conclusion, we showcase that the relaxation time of boronic ester-based vitrimers can be tuned not only by relying on the cross-linking density but also by relying on the chemical nature of the exchangeable groups and on the presence of free functional moieties. Herein, we design vitrimers based on dioxazaborocane cross-links and either dioxaborolane or dioxazaborocane free functional groups by cross-linking polymers bearing complementary functions and show that we can adjust the network design by simply tuning the stoichiometry of the precursors. In particular, we showed that the presence of dioxazaborocane free functional groups accelerates the dynamics, whereas replacing these dioxazaborocane by dioxaborolanes leads to slower dynamics. We also highlighted the nonmonotonic dependence of both the network relaxation time and the flow activation energy upon increasing the density of functional moieties and attributed this behavior to the antagonistic effects of the subdiffusion process of the dynamic moieties and the restriction of diffusion of the chains within the network when the cross-linking density increases. This work brings light to the complex mechanism involving the vitrimer dynamics and the exchange between nonidentical boronic esters and paves the way to design materials with adjustable viscoelastic profiles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.5c03243.

> Detailed polymerization procedures, preparation of vitrimers, thermal characterization, and rheology supplemental data (Figures S1−S22 and Tables S1−S7) (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

DB, dioxaborolane; DZ, dioxazaborocane; EHMA, 2-ethylhexyl methacrylate; RAFT, reversible addition−fragmentation chain-transfer; TTS, time−temperature superposition; WLF, Williams−Landel−Ferry

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