Received: 30 June 2023 | Revised: 27 July 2023 | Accepted: 27 July 2023
DOI: 10.1002/pol.20230446

RESEARCH ARTICLE

JOURNAL OF POLYMER SCIENCE WILEY

Tuning material properties of covalent adaptable networks containing boronate-TetraAzaADamantane bonds through systematic variation in electron density of ring substituents

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Funding information
Nederlandse Organisatie voor Wetenschappelijk Onderzoek, Grant/Award Number: 016.Vidi.189.031

Abstract

An outstanding challenge in modern society remains how to make crosslinked polymers (thermosets) more recyclable. A breakthrough solution to this challenge has been the introduction of dynamic covalent bonds in polymer networks, yielding covalent adaptable networks (CANs). Ongoing research is focused on finding new suitable dynamic covalent chemistries and on how to tune the material properties of CANs derived from these new chemistries. Here, we first compare two different dynamic boronic acid based covalent adaptable networks, namely, a conventional boronate-diol and a novel boronate-TetraAzaADamantane (TAAD) system. We show that incorporating boronate-TAAD bonds in networks results in stiffer materials, as seen in a slower relaxation and higher shear and storage moduli. This offers access to more mechanically robust boronate-based materials, compared to conventional boronate-based gels. Next, we investigate the effect of molecular tuning via the electron density of *meta*-positioned ring substituents on the macroscopic material properties for the boronate-TAAD network. By comparing relaxation experiments on materials with different substituents, we show that the macroscopic network relaxation can be tuned through the Hammett parameter of the *meta*-substituent and the activation energy of the boronate-TAAD exchange. This enables subtle control over the (dynamic) material properties of these novel, robust boronate-based networks.

KEYWORDS
boronic ester, covalent adaptable networks, dynamic covalent chemistry, Hammett, TetraAzaADamantane

1 | INTRODUCTION

Polymer waste is becoming an increasingly larger problem in modern society.[1] Part of the solution lies in improving polymer waste stream management. However, not all polymers can currently be recycled. Those polymers are currently mainly disposed by landfilling or incineration.[2] These nonrecyclable polymers largely consist of thermosets. Thermosets, with their permanent covalent crosslinks, are polymers with excellent material properties. However, the same permanent crosslinks that give thermosets their excellent material properties also

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hinder their recyclability. A solution to this problem is to design recyclable thermoset-like materials by replacing the permanent crosslinks with dynamic covalent crosslinks, leading to materials that have been called covalent adaptable networks (CANs).[3] Their crosslinks can be based on a variety of dynamic covalent bonds such as esters,[4] imines,[5] diketoenamines,[6] disulfides,[7] vinylogous urethanes,[8] acylsemicarbazides,[9] and boronic esters.[10] Because these covalent bonds are dynamic, they can exchange when exposed to the appropriate stimulus, thus, allowing polymer networks built using dynamic covalent bonds to be reprocessed, recycled or to display self-healing behavior.[11] Here, we will focus on materials containing boronic esters because of their general biocompatibility[12] and their fast exchange reactions.[13]

In order for boronic ester-based CANs to become a more competitive option compared to conventional thermosets, more research is needed into the performance and tunability of these dynamic materials. While major advances have been realized in successfully integrating dynamic covalent bonds into polymer networks, thus, newly prepared covalent adaptable networks should have the correct material properties (e.g., in terms of mechanical strength, creep-performance, solvent resistance, and/or (re-)processability) for them to become true substitutes for conventional thermosets (that currently lack the ability be reprocessed or recycled). Having a versatile toolbox with (molecular) handles to fine-tune the macroscopic material properties from the molecular level upwards would help design (boronic ester-based) CANs for specific applications. In recent years, the molecular tuning of CANs has proven to be a powerful strategy.[14] Many different (molecular) handles have been found that can used to control the macroscopic properties of boronic ester-containing materials, such as linker length,[15] internal catalysis,[16] crosslinking degree,[17] dual crosslinking,[18] or the steric hindrance of reactive groups.[19]

Despite the great potential of fine-grained control as a result of a large range of possible substituents, the potential of molecular tuning in CANs by installing electron donating or withdrawing ring substituents, which can be quantified via the Hammett equation,[20] has received an increasing amount of attention. There have been studies into the electronic effect on the material properties for only a few CANs, specifically for imine,[21] thia-Micheal reactions,[22] thiol-yne[23] and thiol-ene.[24] For boronic esters structure–property relationship studies remain limited to small-scale molecule studies for structure variation in the boronic acid[25] and the structure of the diol,[26] or focus only on two different boronic acids, where the focus is not specifically on electronic effects.[27]

Previously, Golovanov et al. reported a new boronate-based dynamic covalent moiety, based on TetraAzaADamantane (TAAD), which is an adamantane containing four nitrogen atoms, three in the bottom ring and one on the top.[28] The three lower nitrogen atoms also have a hydroxyl group, thus, making the TAAD a triol. The top nitrogen can be used to anchor the TAAD to a scaffold via nitrogen quaternization as can be seen in Scheme 1. The TAAD moiety was shown to have strong binding to boronic acids, yet still retain a dynamic pH-sensitive equilibrium.[28a] The strong, yet dynamic, binding of the TAAD moiety to boronic acids and its improved hydrolytically[28a] stability made it an interesting candidate for covalent adaptable network formation, which we showed to be possible in previously published work.[29] The newly emerging boronate-TAAD networks gave rubbery materials, as opposed to the (hydro)gels that are generally obtained when working with boronic esters.

While we previously reported,[29] the promising use of TAAD moieties in CANs, no direct and systematic comparison between the novel boronate-TAAD system and its traditional boronate-diol counterpart was included in this study. For the comparison between the boronate-TAAD and boronate-diol networks two diol linkers, named **BDPE** and **TMPTPE**, and two TAAD linkers, named **bis-TAAD** and **tris-TAAD**, were prepared and crosslinked with a difunctional boronic acid PPG-based linker named **PPG-PBA-H** (Figure 1).

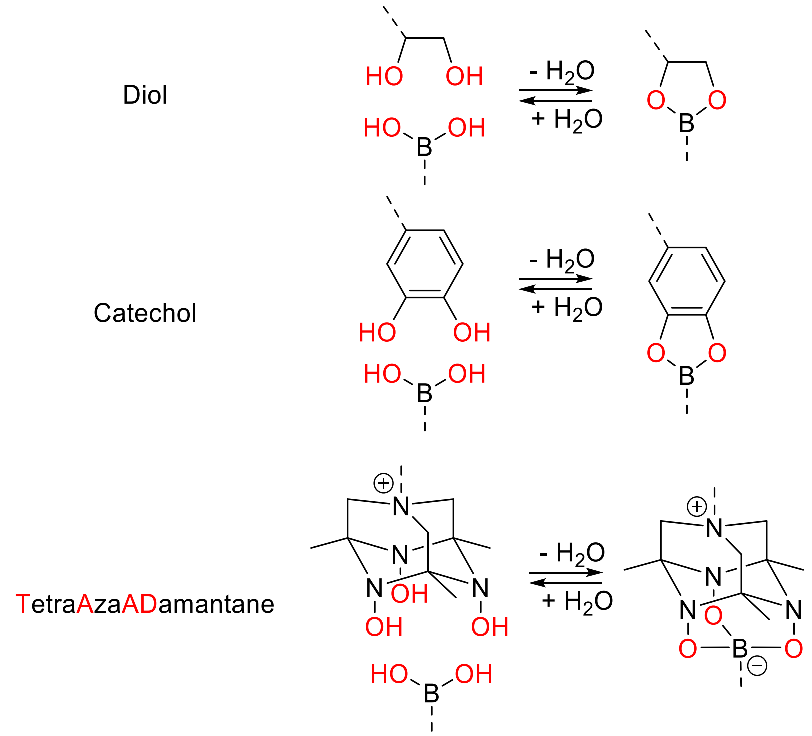
In addition, we also investigated the possibility of using molecular tuning in boronate-TAAD networks through systematic variation in the electronic properties of substituents on the phenylboronic acid and studying its effect on the material properties of these CANs.

To study this, variations of boronic linkers with differently *meta*-substituted phenylboronic acids were prepared and crosslinked. The resulting materials were then characterized using rheology, revealing a relation between their dynamic-mechanical properties (notably, the stress relaxation behavior) and the nature of the substituent (as expressed by its Hammett parameter).

2 | RESULTS AND DISCUSSION

The diol linkers were prepared via epoxy ring opening from the corresponding epoxides. The boronic acid linker was prepared by reacting 4-formylphenylboronic acid with an amine-terminated PPG-2000 and subsequent reduction of the formed imine. The TAAD linkers were prepared as described as previously reported.[29] Details on the synthesis and material preparation are given in the Supporting Information.

Samples of both the boronate-diol and boronate-TetraAzaADamantane (TAAD) networks were prepared by making stock solutions of the different linkers in methanol, mixing them by vortexing and casting them



SCHEME 1 Formation of boronic esters using different diols or triols.

in circular silicon molds (10 mm diameter, 1 mm height). Boronic acids and diol/TAAD were added stoichiometrically and 10 mol% crosslinker was added in all cases. An immediate observation made while casting both the boronate-diol and the boronate-TAAD materials in methanol was that network formation in the boronate-diol materials was hindered through the strong uptake of atmospheric water, thus resulting in the formation of a soft gel instead of a proper elastomer. In contrast, the boronate-TAAD networks were hardly impacted by the uptake of atmospheric water and were able to form bench-stable elastomers. However, since water also affects the network properties this would result in an unfair comparison of the two systems. For this reason, all samples were prepared under nitrogen atmosphere to prevent the uptake of water and allow for a proper comparison of the two systems.

First the shear stress over strain behavior of the two networks was compared. In Figure 2, it can be seen that the boronate-diol network shows a more gradual increase of shear stress compared to the relatively sharp increase of the boronate-TAAD network resulting in a significantly higher shear modulus for the boronate-TAAD networks (0.3 kPa for the boronate-diol networks; 3.5 kPa for the boronate-TAAD networks). Second, the obtained yield plateau is slightly higher for the boronate-TAAD network.

Also, frequency sweeps were performed to gain further insight into the network properties. In Figure 3, frequency sweeps for both networks are shown. The first observation was that the moduli of the boronate-TAAD network were higher than the moduli of the boronate-diol network, suggesting the formation of a stronger network. Second, the moduli of the boronate-TAAD network remained largely constant over the applied frequency range, in contrast to the boronate-diol network, which shifted over an order of magnitude. Third, the boronate-diol network showed cross-over points for the storage modulus (G') and the loss modulus (G'') indicating a transition of a more solid-like material to a more viscous-like material. This cross-over point also shifted to higher frequencies at higher temperatures. No cross-over points were observed for the boronate-TAAD network. In all, these measurements confirm—in a quantitative manner—the increased mechanical stability that can be achieved by replacing the traditional boronate-diol crosslinks with the boronate-TAAD crosslinks within the covalent adaptable network structure.

The stress relaxation of the two networks was also vastly different as can be seen in Figure 4. Boronate-diol networks, when subjected to a 0.5% strain, showed complete relaxation in approximately 10 s at room temperature. In stark contrast to this, for boronate-TAAD networks complete relaxation, at equal strain, was only reached around 20 min at 130 °C.

In these relaxation, experiments all materials showed a temperature dependency on their relaxation behavior. By assuming a Maxwell model for the stress relaxation, we could obtain the relaxation time (τ) of the material at the time point at which the normalized relaxation curve crosses $1/e$ ($\approx$0.37). By plotting the (natural logarithm of

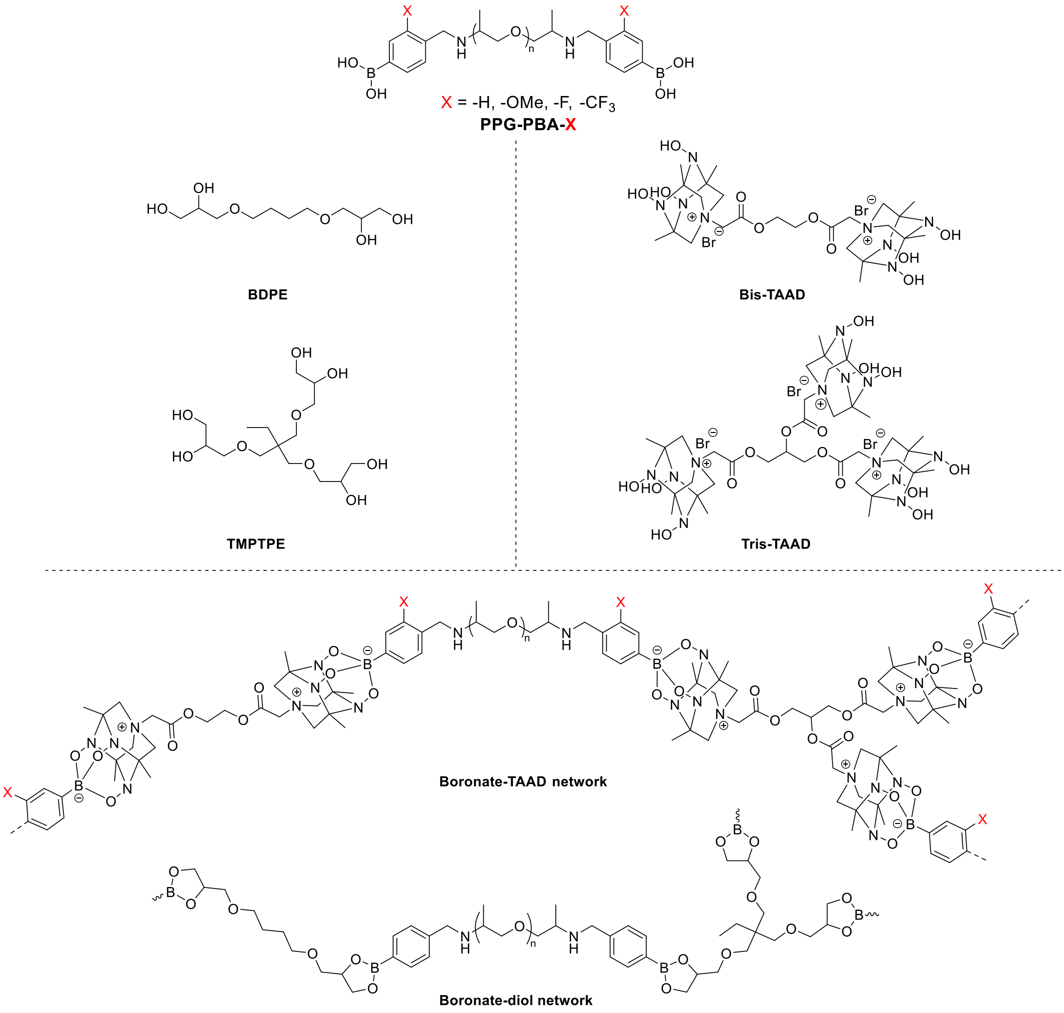


FIGURE 1 The structure of the variable boronic acid linker **PPG-PBA-X**, the two diol linkers **BDPE** and **TMPTPE** (left) and the two TetraAzaADamantane (TAAD) linkers (right). The network structures for both the boronate-diol and boronate-TAAD is given below.

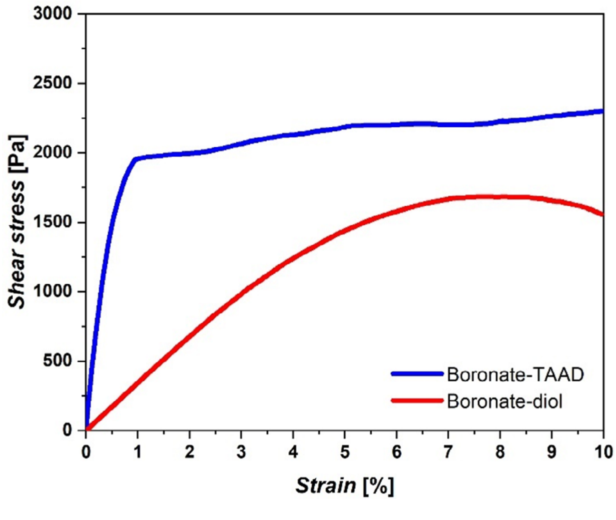


FIGURE 2 Shear stress as function of applied strain for a boronate-diol and a boronate-TetraAzaADamantane (TAAD) 10% crosslinked network at 25 °C. The shear modulus of the boronate-diol network was 0.3 kPa; the shear modulus of the boronate-TAAD network was 3.5 kPa.

TABLE 1 Observed shear moduli for the different **PPG-PBA-X** networks.

PPG-PBA-X	Shear modulus [kPa]
–H	3.5 ± 0.1
–OMe	3.1 ± 0.1
–F	2.3 ± 0.1
–CF_3	3.5 ± 0.2

the) relaxation times against the inverse of the temperature, Arrhenius plots can be constructed for the different two materials. From the slope of these Arrhenius plots, we can then calculate the activation energy (E_a) of the dynamic exchange, with the help of the gas constant (R). This gave an activation energy of $14.5 \pm 1.6\,\mathrm{kJ\,mol^{-1}}$ for the boronate-diol network, which is in accordance with existing literature,[10d,13a,16b,16d] versus an activation energy of $77.3 \pm 2.3\,\mathrm{kJ\,mol^{-1}}$ for the boronate-TAAD network. The higher activation energy of the boronate-

TAAD exchange compared to the boronate-diol network reduces the dynamicity of the network and thus results in sturdier materials, while still keeping the network dynamic enough to relax stress over time.

Finally, the networks were also compared in terms of temperature stability by subjecting the samples to TGA measurements. Supporting Figures S79 and S80 show that both the boronate-TAAD and the boronate-diol network

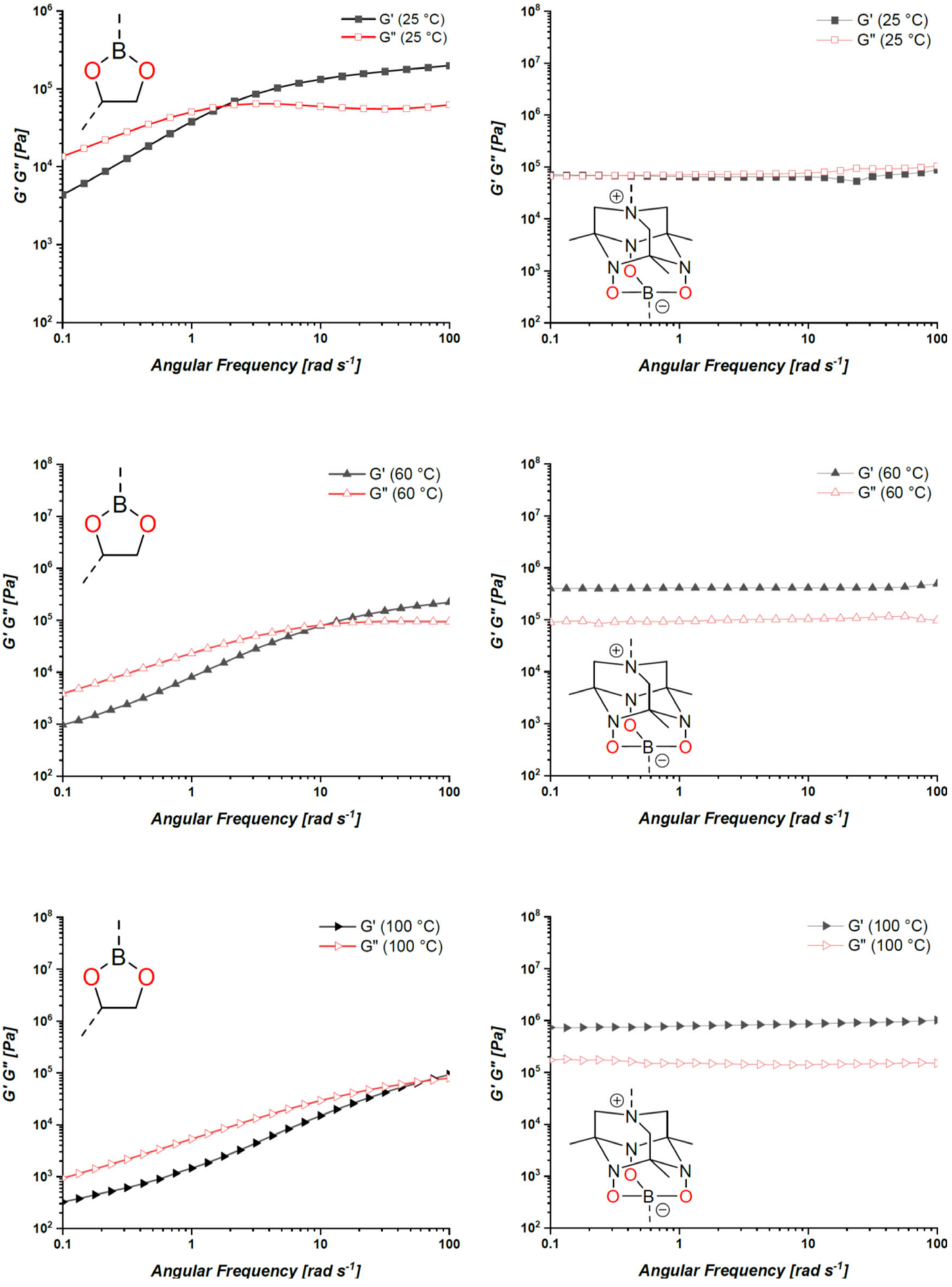


FIGURE 3 Frequency sweeps at different temperatures of a 10% crosslinked boronate-diol network (left) and a 10% crosslinked boronate-TetraAzaADamantane (TAAD) network (right).

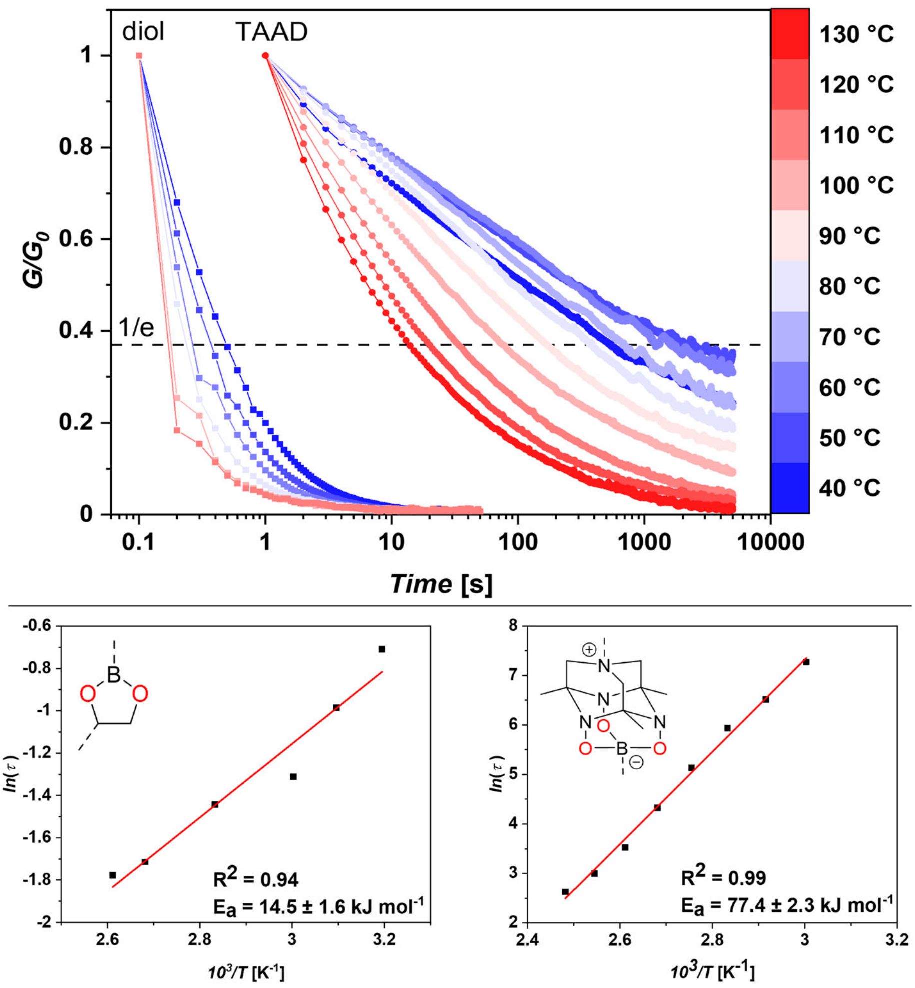


FIGURE 4 Comparison of relaxation behavior (0.5% strain) at different temperatures between dynamic 10% crosslinked boronic diol networks and 10% crosslinked boronate-TetraAzaADamantane (TAAD) networks (top) with their respective Arrhenius plot and activation energy (bottom).

are stable till 150 °C as displayed by the $T_{95\%}$ of 170 °C and 330 °C, respectively. Although the boronate-diol network does show higher thermal stability. we would like to stress that TGA only measures the weight at different temperatures and does not probe the network composition or properties at these temperatures.

The comparison of material properties of the boronate-diol with the boronate-TAAD networks, revealed that the latter displayed superior mechanical properties (as seen in the stress–strain data, the frequency sweeps and the stress relaxation experiments). At the same time, the boronate-TAAD network is dynamic enough to undergo stress relaxation at a temperature far below its thermal stability limit. Also, the boronate-TAAD network was far less impacted by atmospheric water, thus making these networks easier to work with. For these reasons the boronate-TAAD networks were chosen for the molecular tunability experiments.

To study the effect of different ring substituents a series of PPG-PBA linkers was synthesized by replacing the 4-formylphenylboronic acid with a substituted derivative (see Supporting Information). For this study only the *meta* position relative to the boronic acid was varied. This resulted in four PPG-PBA variants containing a –H, –OMe, –F, or a $-CF_3$ as *meta*-substituent, giving networks as depicted in Figure 1.

After preparing all the different 10% crosslinked variant networks it was observed that the color of the different variants was different, ranging from yellow to brownish/red. Investigating the shearing behavior of these different materials, no clear correlation between the observed shear moduli and the substituents (data shown in Supporting Figures S84–S88) could be established. The shear moduli of the networks with –H, –OMe, and –F substituent showed a trend of lower shear moduli with increasing electron withdrawing ring substituent, however materials made with **PPG-PBA-CF$_3$** showed shear moduli similar to networks with **PPG-PBA-H** (Table 1). Of course, there could be other effects, such as sterics combined with the apparent size of the substituent,[30] influencing the shear moduli, but this will require further research.

From frequency sweeps, (Supporting Figures S89–S93) it was found that all materials displayed a stable storage modulus in the range of 10^5–10^6 Pa with no crossover points.

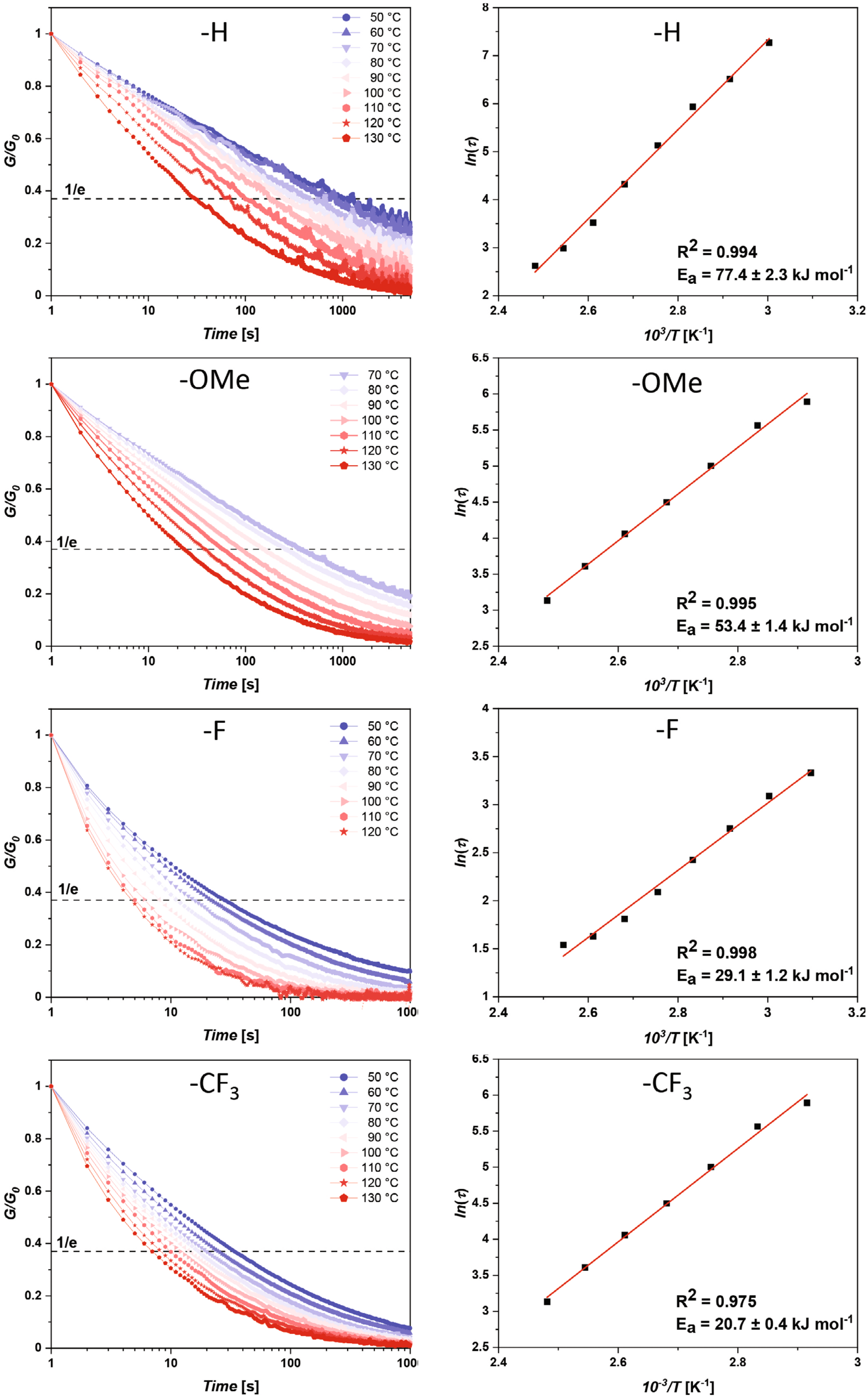


FIGURE 5 Representative relaxation curves at varying temperatures (0.5% strain) for the networks made using different **PPG-PBA-X** linkers (10% crosslinking) and their resulting Arrhenius plot. Duplo measurements can be found in the Supporting Information (Figures S94–S97).

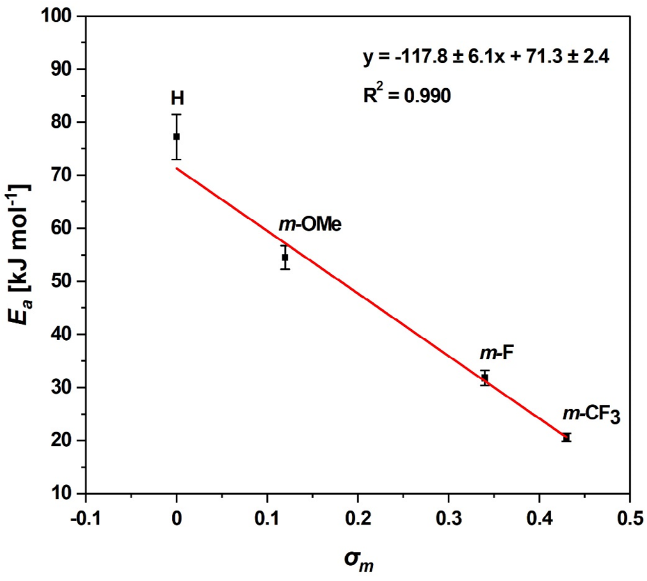


FIGURE 6 Activation energy E_a for the dynamic boronate-TetraAzaADamantane (TAAD) exchange in the networks (10% crosslinked) using different **PPG-PBA-X** linkers against their substituent Hammett constant (σ_m). Obtained activation energies were fitted using a weighted linear fit (see Supporting Information).

Also, the relaxation behavior at different temperatures for the **PPG-PBA-X** material series was investigated, as shown in Figure 5 (duplo measurements are shown in Supporting Figures S94–S97). Here, we see that the different materials all show a different temperature dependence on the relaxation time. When comparing the calculated activation energies for the different **PPG-PBA-X** materials, we can see significant differences in the obtained values. These activation energies range from 77.3 ± 4.3 kJ mol^{-1} for the **PPG-PBA-H** network to 20.6 ± 0.8 kJ mol^{-1} for the **PPG-PBA-CF$_3$** network. These activation energies can then be plotted against the Hammett constant (σ_m) of the ring substituent and fitted with a (weighted) linear fit, resulting in Figure 6. The linear fit shows a good correlation with the activation energies obtained from the network relaxation. This shows that the macroscopic relaxation of the network can be tuned by varying only a few atoms in the molecular structure of the building blocks through the electronic properties of the ring substituents. Considering that these two substituents are part of a large, polymeric building block (with molecular weight of ~2500 g mol^{-1}), this Hammett-based effect seems rather pronounced, and is in contrast with earlier work[22–23] that introduced varying substituents on small-molecule, non-polymeric building blocks. Having a direct, and highly tunable molecular handle to control the activation energy for exchange, will enable further control over the dynamic function (e.g., self-healing, reprocessing and recycling) of covalent adaptable networks.

3 | CONCLUSION

In this study, we showed that dynamic boronic networks can show quite different material properties depending on the dynamic boronic linkage used. A systematic, quantitative comparison allowed us to conclude that the boronate-TAAD networks outperformed the classical boronate-TAAD networks, giving stronger materials as shown in frequency sweeps, shear experiments and temperature sweeps. From there, the tunability of the boronate-TAAD networks was investigated, where we found that (*meta*-positioned) ring substituents on the boronic acid can be used to tune the macroscopic material relaxation through Hammett-based electronic effects by changing the activation energy of the bond exchange. The activation energy of the bond exchange could be changed over almost a full order of magnitude. Also, the shear modulus of the different variants seems to show a trend with decreasing shear modulus for increasing electron withdrawing character of the ring substituent, but further research on other contributing factors is necessary. We foresee that our tunable TAAD-based dynamic bonds can be extended to other polymer networks to help design new covalent adaptable networks that combine robustness with tuneability. Further control over mechanical performance can be obtained by studying the effect of the soft segments within the network; e.g., by replacing PPG by another polymer.

ACKNOWLEDGMENTS

The Netherlands Organization for Scientific Research (NWO) is acknowledged for funding (NWO Vidi grant 016.Vidi.189.031 to Maarten M. J. Smulders). All authors contributed equally to this work.

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How to cite this article: S. van Hurne, T. J. M. Buijsen, M. M. J. Smulders, *J. Polym. Sci.* **2023**, 1. https://doi.org/10.1002/pol.20230446