

Linear Viscoelasticity of ABA-type Vitrimer Based on Dioxaborolane Metathesis

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 Electronic Supplementary Information

Abstract In this study, we synthesized a series of ABA-type vitrimers by crosslinking the short A moieties of precursors with a bifunctional crosslinker and evaporating the small molecular byproduct. The vitrimer samples thus prepared exhibit linear viscoelasticity dependent on the length of A moiety as well as the content of the crosslinks. When the average number of A monomers per end moiety $m=1.1$, the crosslinker can only extend the chain but not crosslink the chain. When m becomes 2.8 or higher, introducing a crosslinker first leads to the gelation, whereas excess in crosslinker molecules leads opening of the crosslinking sites and accordingly reentry into the sol regime. Surprisingly, a further increase in the length of the A moieties increases the relaxation time much weaker than the exponential increase seen for the physically crosslinked ABA-type ionomers. We attribute this difference to the distinct relaxation mechanisms: the relaxation of the vitrimer samples is based on relatively independent exchange reactions, which contrasts with the ABA-type ionomers that relax through the collective hopping of connected ionic groups from one ion aggregate to another.

Keywords Polymer rheology; Linear viscoelasticity; ABA-type vitrimer; Relaxation mechanism; Kinetics and thermodynamics

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INTRODUCTION

In 2011, Leibler and coworkers unveiled a specific type of reversible covalent bond chemical reaction system based on transesterification. This system exhibits a drop in viscosity near 10^{12} Pa·s with increasing temperature much weaker than the conventional polymer materials, which mirrors the behavior of inorganic glasses and thus be termed “vitrimer”.^[1] Vitrimers exhibit the properties of traditional thermosets at operational temperatures due to their covalently crosslinked structure. They also offer superior creep and solvent resistances^[2–4] compared with physical networks, such as ionomer or hydrogen-bond networks.^[5–9] In addition, the exchange reaction of a given junction site, either with a functional group or another junction site, is triggered under certain conditions, thereby enabling the topological reconstruction and accordingly the stress relaxation.^[10] The benefits of thermoset and thermoplastic pave the way for applications in shape-memory materials, re-processable and self-healing materials, and 3D printing.^[11–17]

Over the past few years, vitrimers have garnered signifi-

cant interest within the scientific and industrial communities, prompting the identification of various exchange reactions in constructing the vitrimer network. These include transesterification,^[18–21] amine exchange of vinylogous urethanes,^[22–25] silyl ether metathesis,^[26] transamination of diketoenamines,^[27] olefin metathesis,^[28] dioxaborolane metathesis,^[29–32] and so on. Meanwhile, an investigation is also conducted into the impact of exchange reactions on rheology and processability. For example, Tibbitt and coworkers^[33] constructed a robust framework based on dynamic covalent boronic ester to reveal dynamics in covalent adaptable networks. Additionally, they created a physical model to quantify the kinetics and thermodynamics of network rearrangements, paving the way for understanding preferred reaction pathways for dynamic covalent bonds. Hayashi and coworkers^[34] investigated the effects of crosslinking density on the bond exchange property for trans-esterification-based vitrimers under specific conditions, *i.e.*, the same free OH concentration and catalyst concentration. Meng and coworkers^[35,36] explored the rheological properties of vitrimers, emphasizing their behavior across a range of deformations from linear to nonlinear regimes. The study offers analytical expressions that can be used in analyzing the linear viscoelasticity and the creep curves. Recently, Yu and coworkers^[25] introduced a theoretical model to examine the structure of associative intermediates and the kinetic process

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of associative exchange based on vinylogous urethane vitrimers. This model establishes the relationship between the reaction equilibrium constant and the plateau modulus of the associative exchange dynamic polymer networks.

Our previous studies focused on revealing the molecular dynamics of the vitrimer networks by analyzing the linear viscoelasticity.^[10,37,38] We found that the reversible gelation model^[39] can be used in analyzing the linear viscoelasticity of the vitrimer samples based on the dioxaborolane metathesis^[37] to determine a degree of gelation ε that changes with the contents of the reactants, thereby enabling us to study thermodynamics. In addition, the stress relaxation of the networks at a given ε allows the investigation of the reaction kinetics.

Specifically, we introduced bifunctional crosslinkers to unentangled polymer precursors with randomly incorporated functional groups. The degree of gelation ε first increased upon adding crosslinker molecules to the precursor and then decreased when the crosslinker molecules are excessive and open the crosslinking sites. The crosslinking reaction proceeded in two steps: the first step was the reaction of the polymer precursor with the bi-functional crosslinker, where the crosslinker replaced one of the precursor's functional groups, generating a small-molecule byproduct. The second step was the reaction of the suspended crosslinker with another functional group belonging either to the same chain or another chain, creating a crosslinking point and another small-molecule byproduct. Analyzing a change ε with the contents of reactants revealed reaction equilibrium constant $K=1$ and $K>1$ for the first and second steps of the crosslinking reaction. This feature contrasted with the naive expectation of $K=1$ for both steps because no change in functional groups occurred in either step. Later, Ran Ni and coworkers^[40] rationalized this feature. Since either the reactants or products were composed of one polymer chain and one small molecule in the first step, the entropy remained nearly unchanged, leading to $K=1$. Nevertheless, two polymer sites formed a crosslinking point and a small molecule in the second-step reaction. The generation of the small molecule increased the entropy, thus driving the reaction towards the products to give $K>1$.

This study is an extension of previous research. Differing from the previously investigated random crosslinked vitrimers, ABA-type vitrimers are investigated here. Conventional telechelic polymers have only one functional group at each end, so this system cannot react with bifunctional crosslinkers to form a network structure (because the crosslinker can only serve as a chain extender). Therefore, we choose to polymerize several functional monomers at each of the two end moieties, allowing the moiety to react with more than one polymer chain simultaneously to form a network structure. Introducing the crosslinker leads to the sol-to-gel transition, and later to the gel-to-sol transition when the crosslinker is in excess. The relaxation mechanism of this ABA-type vitrimer is different from the conventional ABA-type physical networks like the ionomer. The difference in relaxation mechanism has been discussed.

EXPERIMENTAL

Materials

The monomer styrene (St, 99%) was purchased from Aladdin,

and purified by passing through a column of basic alumina to remove inhibitors. 2,2'-Azobis(isobutyronitrile) (AIBN, 99%) was purchased from J&K, and recrystallized from ethanol before use. K_3PO_4 (Energy chemical, 95%) was dried in a muffle furnace at 350 °C for 10 h before use. CS_2 , $C_{12}H_{25}SH$ and 1,4-bis(chloromethyl)benzene were purchased from Energy Chemical and used as received. 4-Vinylphenylboronic acid, phenylboronic acid, 1,2-propanediol, 1,10-decanedithiol and 3-butene-1,2-diol were purchased from Aladdin and used as received. The extra dry *N,N*-dimethylformamide (DMF) and extra dry tetrahydrofuran (THF) with molecular sieves were purchased from Energy Chemical. Toluene (analytical purity, Beijing Chemical Reagents Co.) and Dichloromethane (DCM, analytical purity, Beijing Chemical Reagents Co.) were dried with powdered calcium hydride (CaH_2) and then distilled before use. Methanol, ethanol, ethyl acetate, and *n*-hexane were purchased from Beijing Chemical Reagents Co.

Synthesis of Vitrimer Samples

Four different ABA-type telechelic polystyrene precursors were synthesized *via* reversible addition-fragmentation chain transfer (RAFT) polymerization to prepare the vitrimer samples. The synthesis routes of the ABA precursor samples and the crosslinker are shown in Fig. 1, with the details in the electronic supplementary information (ESI). The precursor samples are denoted as TPS-*m*, with *m* being the average number of crosslinkable A monomers per end moiety and determined from M_n change between TPS and TPS-*m*. Their important parameters are summarized in Table 1. All TPS-*m* samples have M_w much lower than $M_e=1.8\times10^4$ g/mol reported for PS,^[41] and thus the vitrimer samples are likely to be unentangled. The crosslinker, 1,1-bis(((2-phenyl-1,3,2-dioxaborolan-4-yl)methyl)thio) decane of $M=526$ g/mol, was synthesized *via* click reaction between sulphydryl groups and double bonds and denoted as C. The moderately high *M* is chosen to suppress evaporation during the sample preparation. The oligomeric nature also endows the crosslinker molecule with a certain flexibility, which would facilitate the exchange reaction at its two ends.

TPS-*m* and C are mixed in anhydrous THF (10 mL) at predetermined molar ratios in a flask at 60 °C. After 10 h of reaction, the raw product was purified through evaporation. The final products were dried under vacuum at 140 °C for more than 48 h. This process, as described in the literature,^[42] appeared to distill out the small molecular byproducts produced during the crosslinking reaction.

In this study, the vitrimer samples are coded as TPS-*m*/C-*n*, where *n* represents the molar ratio between C and TPS-*m*. Since (1) each TPS precursor molecule has two ends and accordingly an average number of crosslinkable sites of $2m$ and (2) each crosslinker molecule has two functional groups, $n = m$, $n < m$, and $n > m$ represent the stoichiometric point, excess in precursor and crosslinker, respectively. Important parameters of the precursors TPS-*m* and vitrimers TPS-*m*/C-*n* as shown in Table S1 of Supplemental File.

Characterization

^1H -NMR and ^{13}C -NMR spectra were recorded with a Bruker AV 400-MHz spectrometer using $CDCl_3$ as a solvent and tetramethoxysilane as an internal standard. ^1H -NMR and ^{13}C -NMR spectra of didodecyl-1,2-phenylene-bis(methylene) bistrithiocarbonate, 4-vinylphenyl-2,3-dioxaborolanepropyl, 4-phenyl-

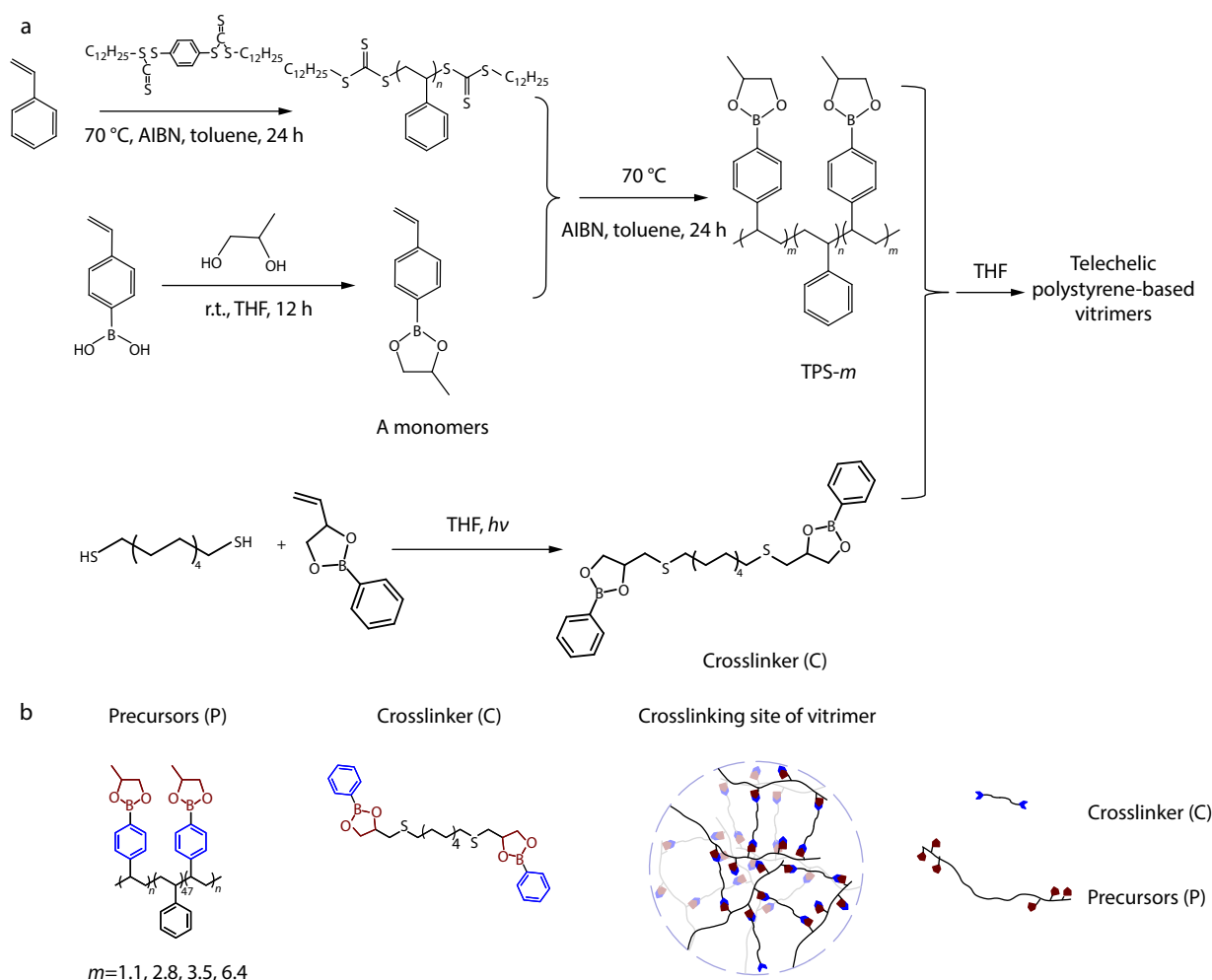


Fig. 1 (a) Synthesis routes of telechelic vitrimers TPS- m /C- n ; (b) Schematic illustration of the network formed through crosslinking the end groups.

Table 1 Important parameters of the Macro-CTA polystyrene (TPS) and the precursors TPS- m of the vitrimer samples.

Samples	M_w (kg/mol)	M_n (kg/mol)	M_w/M_n	m^a	T_g (°C)
TPS	5.1	4.8	1.07	0	72
TPS-1.1	5.6	5.2	1.08	1.1	73
TPS-2.8	6.4	5.8	1.1	2.8	80
TPS-3.5	6.8	6.1	1.12	3.5	81
TPS-6.4	8.7	7.2	1.21	6.4	82

^a Actual number of functional group-containing monomers at each chain end determined from M_n

2,3-dioxaborolanebutene, and 1,1-bis(((2-phenyl-1,3,2-dioxaborolan-4-yl) methyl) thio) decane and $^1\text{H-NMR}$ spectrum of *Macro-RAFT* are shown in Figs. S1–S9 in ESI. Gel permeation chromatography (GPC) measurements were conducted at ambient temperature on Wyatt Optilab, which is equipped with light scattering and refractive index monitors to determine the weight average molecular weight (M_w) and polydispersity index (M_w/M_n) of the *Macro-RAFT* and precursor samples, as shown in Fig. S10 and Table S1 in ESI.

DSC

Differential scanning calorimetry (DSC) analysis was conducted using a DSC Q20 calorimeter (TA, USA). All samples were subjected to three heating runs in the temperature range of -80 °C

to 150 °C with heating or cooling rates of 10 °C/min. The glass transition temperature was determined from the third heating run utilizing the commercially available Universal Analysis Software.

Rheology

All linear viscoelastic measurements were conducted on a strain-controlled rheometer (ARES G2, TA, USA) using 8 mm diameter parallel plates. All samples were loaded at 200 °C or lower temperatures. The frequency sweep measurements were conducted in a range of 20 °C to 200 °C within the linear region, as confirmed by the strain amplitude sweeps, in an environment of highly purified N_2 to avoid degradation and water absorption. The frequency sweep measurement was conducted in

a frequency range of 10^2 rad/s to 10^{-2} rad/s from the highest T (200 °C or lower) to the lowest T (20 °C or higher) at 10 or 20 °C each step. To ensure the achievement of a steady state, we conducted the frequency sweep measurement during annealing at the loading temperature (200 °C or lower). After all dynamic oscillatory frequency sweep measurements, we set the temperature back to loading temperature to check the reproducibility of the frequency sweep measurement.

RESULTS AND DISCUSSION

Glass Transition Temperatures

Fig. 2 compares glass transition temperature T_g obtained for the precursor and vitrimer samples (a) TPS-1.1/C- n , (b) TPS-2.8/C- n , (c) TPS-3.5/C- n , and (d) TPS-6.4/C- n . For TPS-1.1 (Panel a), increasing the content of the crosslinker leads to a significant reduction in T_g (indicated by the arrow). This feature is due to its low $m = 1.1$, a chain has only about one functional group per

end and can only be extended, but can hardly be crosslinked by the crosslinker. Even at the lowest $n=2$, the crosslinker is already in excess. As a result, further increasing the content of the crosslinker only strengthens the plasticizing effect.

For TPS-2.8/C- n (Panel b), TPS-3.5/C- n (Panel c), and TPS-6.4/C- n (Panel d), a change of T_g with increasing n is different from that seen in Panel a; the glass transition temperature T_g first increases and then decreases with increasing crosslinker content. This transition is akin to the feature seen for the random vitrimer in our previous study,^[37] which was attributed to a dominance of the crosslinking effect at low n , leading to the slight increase of T_g . In contrast, the plasticizing effect dominates at high n , particularly when the crosslinker becomes excessive, which opens the crosslinking sites thereby leading to the decrosslinking. One piece of evidence that supports this argument is that the critical value of n for the transition from increase to decrease of T_g , i.e., n between 1.2 and 2.5 for TPS-2.8/C- n , 2 and 3 for TPS-3.5/C- n , and 3 to 6 for TPS-

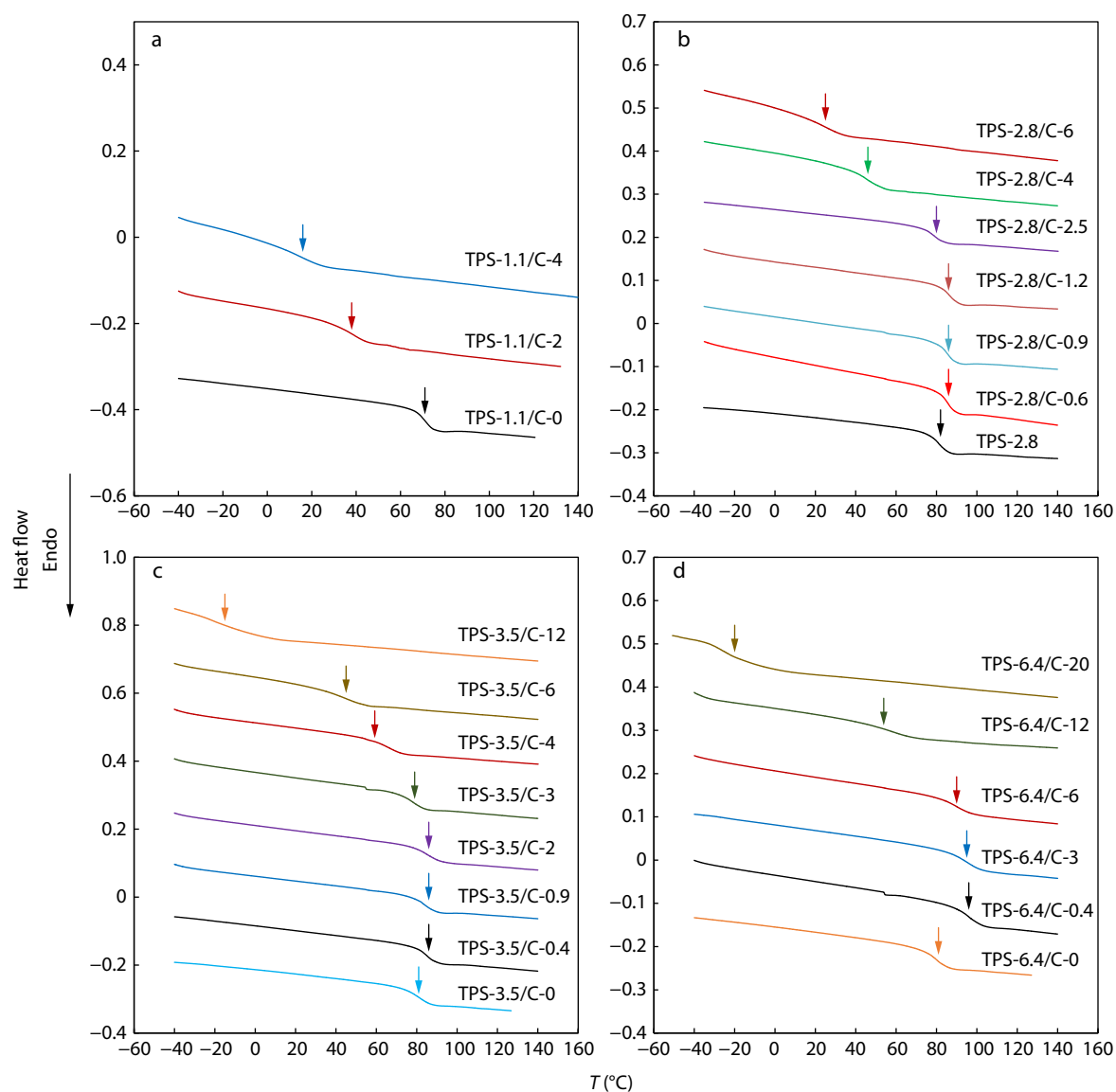


Fig. 2 Comparison of DSC glass transition temperatures (T_g) obtained for (a) TPS-1.1/C- n , (b) TPS-2.8/C- n , (c) TPS-3.5/C- n , and (d) TPS-6.4/C- n .

6.4/C- n , increases with m . More details of this transition are discussed later, together with parameters determined from analyzing the linear viscoelasticity (LVE).

Linear Viscoelasticity

Fig. 3 compares the master curves of linear viscoelastic storage and loss moduli, G' and G'' as functions of angular frequency ω for the precursor TPS-1.1, and TPS-1.1/C-2 and TPS-1.1/C-4 reduced at a reference temperature chosen to be $T_r=60^\circ\text{C}$. To construct the pseudo-master curve, the G' and G'' data are multiplied by an intensity factor of $b_T=T_r/T$, and shifted horizontally to achieve the best superposition. Given that the moduli of samples in this study are mostly in the range of 10^2 – 10^7 Pa and reflect the entropic stress, G' and G'' should be proportional to ρT in principle, where ρ and T are the sample density and absolute temperature, respectively. However, as a change in ρ is usually much smaller than a change of T itself, the vertical shift factor b_T of samples can be safely approximated as $b_T=T_r/T$.

The master curves of all three samples exhibit the typical linear viscoelastic behavior of unentangled chains, where no plateau was observed before the terminal relaxation characterized by $G'\sim\omega^2$ and $G''\sim\omega$. This feature is well predicted because each end moiety contains only about one monomer, and thus the crosslinker having a functionality of 2 can serve as a chain extender. Moreover, n is chosen to be 2 or 4 that is larger than 1.1, the crosslinker is of great excess, and thus only the plasticizing effect is seen.

Fig. 4 (Fig. 5 shows the temperature dependence of shift factor a_T obtained from Fig. 4) and Fig. 6 compare the linear viscoelasticity of the representative TPS-2.8/C- n samples shifted by different methods. The LVE results of TPS-3.5/C- n and TPS-6.4/C- n samples are summarized in Figs. S11 and S12 (in ESI). In Fig. 4, the pseudo-master curves of storage and loss moduli, G' and G'' , are multiplied by $b_T=T_r/T$ and plotted against reduced angular frequency, ωa_T . The horizontal shift factor a_T is chosen to superpose the Rouse regime of the moduli. For $n=0$ and 6 where no plateau is seen, time-temperature superposition holds, and thus a_T can be easily chosen. In comparison, for $n=0.6$ –4, the plateau regime is clearly seen for G' , indicating the formation of the vitrimer network. At this regime, G'' lower than G' first decreases and then increases with decreasing ω , leading to a valley in between. For this case, a_T is chosen to superpose the high- ω side of the G'' valley, which corresponds to the relaxation activated by the thermal motion of the network strands. After this shift, a no-

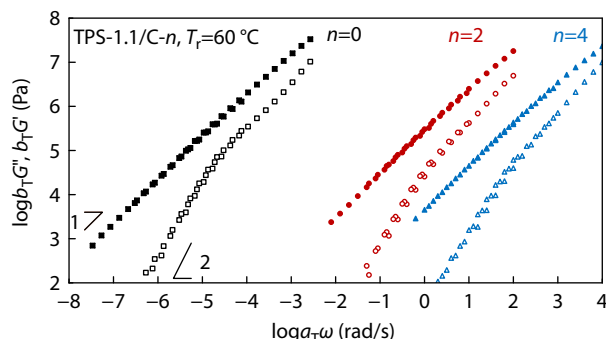


Fig. 3 The storage modulus G' (unfilled symbol) and loss modulus G'' (filled symbol) as a function of angular frequency ω at 60°C for precursor TPS-1.1 and sol-samples TPS-1.1/C-2, TPS-1.1/C-4.

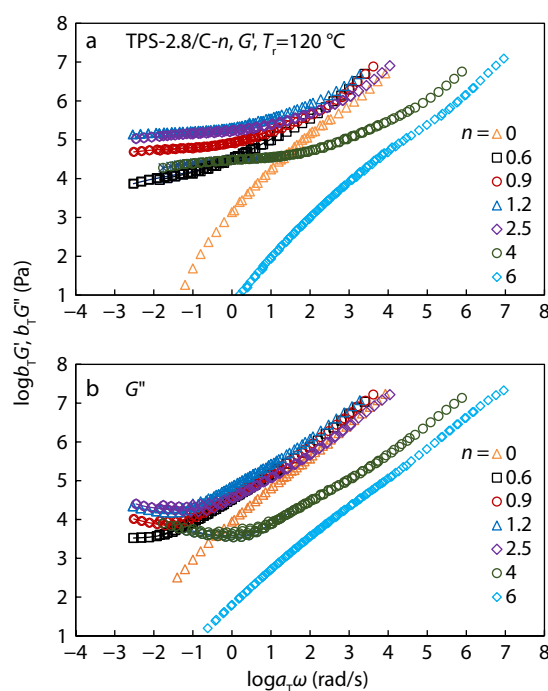


Fig. 4 The storage modulus G' (a) and loss modulus G'' (b) as functions of angular frequency ω reduced at 120°C for the precursor TPS-2.8, and the vitrimer samples TPS-2.8/C-0.6, TPS-2.8/C-0.9, TPS-2.8/C-1.2, TPS-2.8/C-2.5, TPS-2.8/C-4, and TPS-2.8/C-6. The data plots obtained at the same T are connected in line at low ω to show more clearly the failure of time-temperature superposition therein.

table deviation is observed at the low- ω side of the G'' valley, where the modulus is contributed by the network relaxation activated by the exchange reaction (as discussed in more detail in Fig. 6). A sol-to-gel transition is observed upon increasing crosslinker n from 0 to 1.2 in this system, whereas a reentry to the sol regime is seen upon further increase n from 2.5 to 6, where the excess crosslinker molecules open the crosslinking site, *i.e.*, one crosslinker molecule and one crosslinking site react to form two separated sites, each composed of one functional monomer attached by one crosslinker molecule.

The shift factor a_T , obtained from the shift explained above, is plotted against $T - T_r$ in Fig. 5. The temperature dependence of a_T strengthens slightly with increasing n up to 1.2, owing mainly to the increase of T_g therein (*cf.* Fig. 2). Further increase of n up to 6 weakens the temperature dependence of a_T . This change is reminiscent of the T_g change seen earlier in Fig. 2(b).

To test the influence of a change of T_g on a_T , we choose a new iso-frictional temperature $T_{\text{iso}} = T_g + 34^\circ\text{C}$, and shift the $\log a_T$ vertically to ensure that the plots of $\log a_{\text{iso}}$ against $T - T_{\text{iso}}$ go through (0, 0), as shown in Fig. 5(b). A good agreement is found for the plots of all TPS-2.8/C- n samples irrespective of the n value in Fig. 5(b), demonstrating that the T dependence of the moduli obtained at the high- ω side of the G'' valley is indeed governed by a distance of T from T_g . Namely, the change of temperature dependence for the Rouse regime is controlled by the crosslinking effect that increases

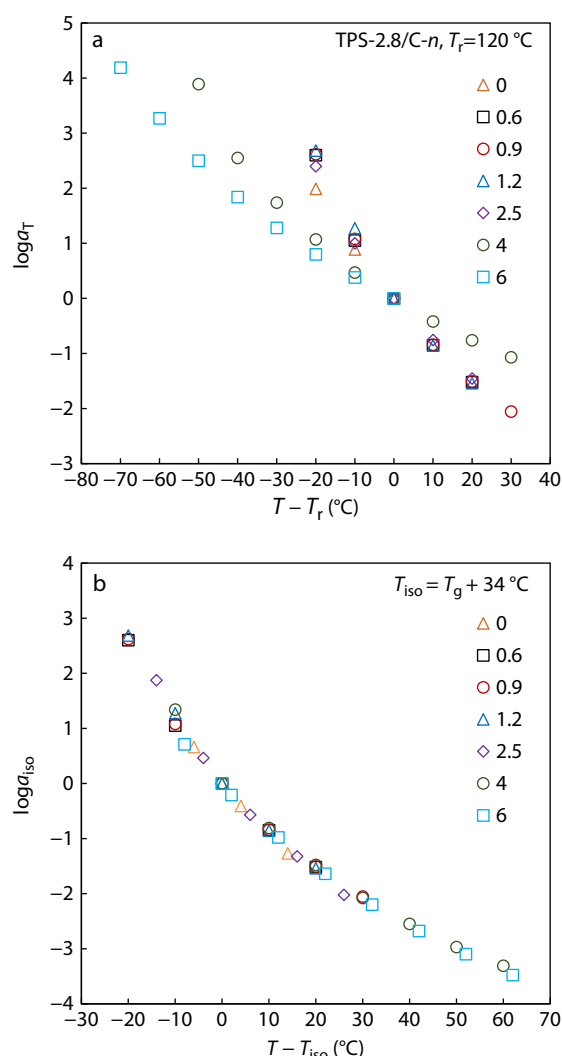


Fig. 5 (a) LVE shift factor a_T obtained in Fig. 4, from superposing the high- ω Rouse part of the modulus, plotted against $T - T_r$ at reference temperature $T_r = 120$ °C, and (b) a_{iso} reevaluated concerning the new reference temperature $T_{iso} = T_g + 34$ °C, plotted against $T - T_{iso}$.

T_g and the plasticizing effect that lowers T_g .

In Fig. 6, we constructed the pseudo-master curves of G' and G'' obtained at the low- ω side of the G'' valley, corresponding to the network relaxation. The raw G' and G'' data are multiplied by the intensity factor T_r/T and shifted horizontally by a factor a_T' to superpose the modulus at the low- ω side of the G'' valley, which leads to failure of time-temperature superposition at the high- ω side of the G'' valley. In particular, the upturn of G'' obtained at the higher T appears at the higher ω after this shift, indicating that the plateau regime widens with increasing T . This feature was also observed for the random vitrimer samples in our previous study, which reflects the difference in the temperature dependence of the segmental relaxation of the network strands and that of the network relaxation activated by the exchange reaction. Namely, the increase of T accelerates the segmental relaxation more significantly than the exchange reaction, leading to the broader plateau regime at the higher T . As a result, the

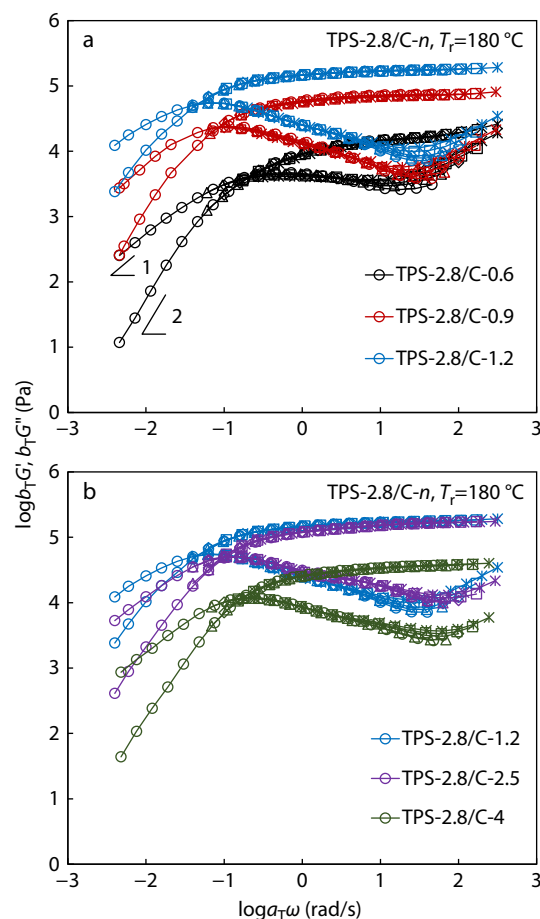


Fig. 6 Pseudo-master curves of the storage modulus G' and loss modulus G'' as functions of angular frequency ω at 180 °C for (a) vitrimer samples TPS-2.8/C-0.6, TPS-2.8/C-0.9, and TPS-2.8/C-1.2, and (b) TPS-2.8/C-1.2, TPS-2.8/C-2.5, and TPS-2.8/C-4. The data plots obtained at the same T are connected in line, to show more clearly the failure of time-temperature superposition at the high- ω side of the G'' valley.

horizontal shift factor a_T' obtained in Fig. 6 exhibits weaker temperature dependence than a_T shown earlier in Fig. 5.

The pseudo-master curves of all vitrimer samples shown in Fig. 6 exhibit typical LVE behavior of gel chains, characterized by a plateau regime followed by the crossing of G' and G'' and subsequently by a terminal relaxation regime characterized by $G' \sim \omega^2$ and $G'' \sim \omega$. The transition between these two regimes, characterized by the characteristic frequency ω_χ where G' and G'' cross, shifts to a lower frequency with increasing n from 0.6 to 1.2 (Fig. 6a). Further increase of n from 1.2 to 2.5 does not change the plateau but accelerates the network relaxation, as indicated by the shift of ω_χ to the higher frequency (Fig. 6b). The same plateau (for $n = 1.2$ and 2.5) means that the degree of gelation is the same. Then, the natural question is, why do the two networks having a similar number density of strands exhibit different relaxation rates?

To answer this question, we should remember that $n = m$ represents the stoichiometric point. The plateau amplitudes are the highest and the same for TPS-2.8/C-1.2 and TPS-2.8/C-2.5, suggesting that the gelation is saturated at n between 1.2 and 2.5, which is close to the stoichiometric point $n = 2.8$. Us-

ing the same criterion, *i.e.*, the saturation of the plateau modulus as an indication of the highest degree of gelation, we noted that the highest degree of gelation is achieved for TPS-3.5 at $n=4$ and for TPS-6.4 at $n=6$. All these values are quite close to the stoichiometric point. This feature supports the argument that the reentry of the sol regime (after saturation of the degree of gelation) is due to the reaction between the crosslinking sites and the excessive crosslinkers. The differences in terminal relaxation times will be further discussed below through the variations in apparent activation energy E_a of different samples.

Fig. 7 compares the plots of a_T' obtained in Fig. 6 against $1000/T$ for all vitrimer samples. Given that the plots of a_T against $T - T_r$ with fixed T_r are quite different and highly dependent on n (Fig. 5a) owing to a change of T_g with n , the difference in a_T' is much smaller because a_T' is more relevant to the kinetics of the exchange reaction. This contrast is more clearly seen in Fig. S13 in ESI, where the plots of a_T and a_T' are directly compared. Linear fits of these plots allow us to evaluate an apparent activation energy E_a for the network relaxation. E_a is plotted against n in the inset of Fig. 7. In Fig. 7, the temperature dependence of a_T' is consistent for samples with n in a range between 0.6 and 2.5, where the plots almost coincide, whereas the temperature dependence weakens considerably upon further increasing n to 4. The former coincidence means that a change of T_g plays a less significant role in the terminal relaxation if we compare Figs. 5(a) and 7 (direct comparison is given in Fig. S13 in ESI). This difference reflects that the terminal relaxation is governed more by the kinetics of the exchange relaxation of the end moieties than the segmental mobility of the central block. The weakening of the temperature dependence and the decrease of E_a seen in the inset suggests an acceleration of the reaction kinetics by the excessive crosslinker molecules for $n=4$, which is in accordance with the observation in Fig. 6. The decrease of E_a will be discussed later.

Fig. 8 summarizes the glass transition temperature T_g , plateau modulus G_N , and a characteristic time $\tau_X = 1/\omega_X$ obtained at $T_r = 180^\circ\text{C}$, where ω_X is the cross point of G' and G'' at the low- ω end of the plateau, and the apparent activation

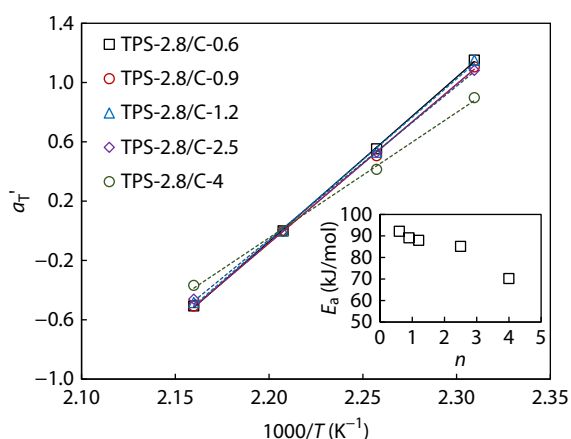


Fig. 7 Shift factor a_T' plotted against $1000/T$ for vitrimer samples TPS-2.8/C-0.6, TPS-2.8/C-0.9, TPS-2.8/C-1.2, TPS-2.8/C-2.5, and TPS-2.8/C-4. The inset shows the plots of the apparent activation energy E_a against n .

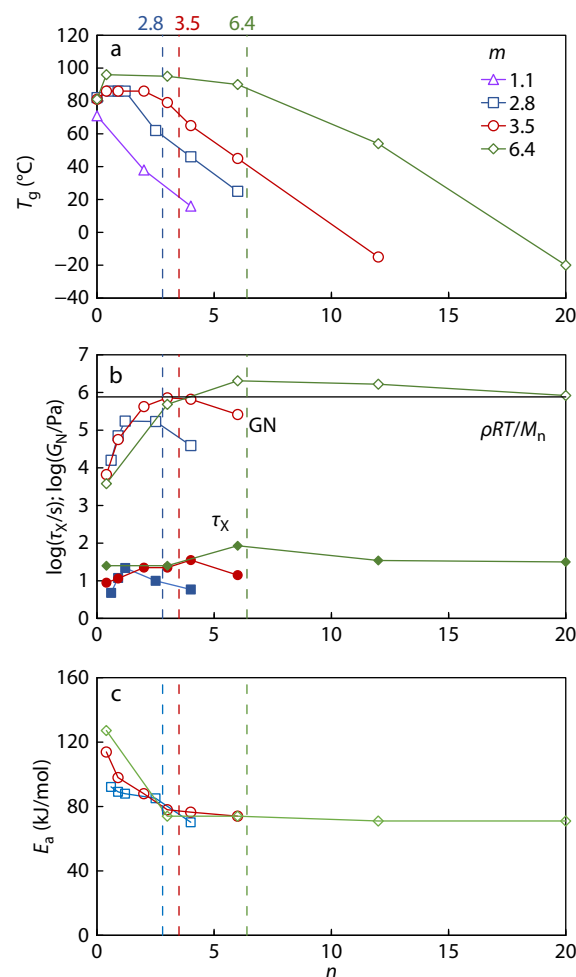


Fig. 8 Comparison of (a) glass transition temperature T_g , (b) plateau modulus G_N and a characteristic time $\tau_X = 1/\omega_X$ obtained at reference $T_r = 180^\circ\text{C}$, and (c) apparent activation energy. These parameters are plotted against n for all vitrimer samples in this study, where ω_X is the cross point of G' and G'' at the low- ω end of the plateau.

energy, as functions of both m and n . The vertical lines indicate $n = m$, which can be regarded as an indication of the stoichiometric point. The plots of the $m = 1.1$ samples are only shown in Panel a but not Panels b and c because these samples exhibit neither the plateau nor ω_X (*cf.* Fig. 3). As explained earlier in Fig. 2, T_g decreases continuously with increasing n for the $m=1.1$ samples, owing to the plasticizing effect of the crosslinker molecules. In comparison, a slight increase of T_g at low n , followed by a significant decrease of T_g at low n is seen for the higher m samples.

In Panel b, we see that G_N and τ_X increase with n for the low n values and decrease with increasing n at sufficiently high n values. The transition point is quite close to the stoichiometric point $n = m$ as indicated in the dashed line, supporting the argument that the excessive crosslinker molecules open the crosslinking sites. For $m = 2.8, 3.5$, or 6.4 , the transition points of G_N and τ_X appear to be closer to the stoichiometric point (indicated in a dashed line) than T_g , whose transition occurs considerably lower than the stoichiometric point, indicating that G_N and τ_X serve as a better indication of the stoichiomet-

ric point.

Panel c shows that the activation E_a , determined by a_T^{-1} (cf. Fig. 7), decreases with increasing n for all samples with varied m . When the crosslinker becomes excessive, i.e., $n > m$, the decrease of E_a weakens greatly. The decrease of E_a with increasing n probably reflects the influence of the number of available exchanging sites on the exchange reaction kinetics: For the associative-type vitrimer in this study, the activation energy E_a is controlled by both the activation energy for chain diffusion and that for the exchange reaction. In other words, the two reaction sites should first “associate” *via* diffusion, and the activation energy for this process may decrease with increasing n and accordingly the number density of the exchanging sites. In relation to this argument, we may attribute the same plateau amplitudes for TPS-2.8/C-1.2 and TPS-2.8/C-2.5, but the faster relaxation of TPS-2.8/C-2.5 to its more exchanging sites (with higher n) given that their degree of gelation are the same (as indicated by the same plateau). In addition, the change of the type of exchanging sites, from sites attached to polymer to free sites (crosslinkers) may also contribute to the decrease of E_a .

The amplitude for the saturated G_N increases with m . This feature is probably due to two mechanisms. First, the functional monomers are not uniformly attached to each chain end, and there should be considerable distributions of the number of functional monomers per chain end. This distribution can be evaluated by assuming all chain ends have the same reactivity during the synthesis of the end moieties. For an average number of function monomers per chain end of m , the number fraction of chain ends having x ($= 0, 1, 2, 3, \dots$) monomers can be obtained from the Poisson distribution as:

$$P(x) = e^{-m} m^x / x! \quad (1)$$

The chains that can be effectively crosslinked should have at least two functional chain ends: the chain has no functional end and one functional end can only serve as solvent and dangling chains, respectively. Then, the number fraction precursor chains potentially elastically active becomes $[1 - P(0)]^2 = 0.4, 0.67, 0.80$, and 0.98 for $m = 1.1, 2.8, 3.5$, and 6.4 , respectively. (The square in the superscript is because each chain contains two ends.) This difference should be one reason for the increase of the saturated modulus with m .

Meanwhile, we can estimate a characteristic modulus by assuming all chains are elastically active as:

$$G_c = \rho RT / M_n \quad (2)$$

where $\rho = 0.97 \text{ g/cm}^3$ is the density of polystyrene and R is the gas constant.^[41] Inputting $M_n = 4.8\text{--}7.2 \text{ kg/mol}$ of TPS gives $G_c = 10^{5.7}\text{--}10^{5.9} \text{ Pa}$. The solid line in Fig. 8(b) shows the highest limit $10^{5.9} \text{ Pa}$ based on this evaluation. In comparison, the samples based on TPS-6.4 exhibit a saturated modulus higher than this limit. This result suggests that the crosslinker molecules may also somehow bear the stress in the network. The molar mass of the crosslinker $M = 526 \text{ g/mol}$ is considerably larger than $M_k = 168 \text{ g/mol}$ for polyethylene, thus the crosslinker at the crosslinking sites may also serve as the stress-bearing unit.

The final comment is on the relaxation time. Most of the well-established networks in the study exhibit a relaxation time in 10 and 100 s. This feature is again in sharp contrast to the relaxation behavior of ABA-type ionomers in our previous

studies,^[43,44] where the A block contains a few numbers of connected ionic groups. We found that the plateau modulus widens and the terminal relaxation time increased significantly with increasing the number of connected ions. For example, the width of the plateau almost doubled if the average number of connected ionic groups changed from 1 to 2. Nevertheless, the relaxation time increases much weaker with an increase of m from 2.8 to 6.4 in this study. This feature indicates an important difference between the relaxation mechanisms of the physical network and the chemically adaptive network. Relaxation of the ionomer network relies on the hopping of ion groups from one aggregate to another.^[45] As a result, the connected ions should hop together in a coupled way, and thus the apparent activation energy is proportional to the number of the connected ions m . As a result, the relaxation time of ABA-type ionomers increases exponentially with m . However, the relaxation rate of the current vitrimer samples depends on the kinetics of the associative exchange reaction. The reaction may occur through the more independent association-dissociation for each crosslinking site.

CONCLUSIONS

In this study, we present a series of ABA-type vitrimers that were synthesized by crosslinking A moieties of the ABA precursor using a bifunctional crosslinker. By tuning the functionality per end moiety m and a molar ratio n of the crosslinker and the precursor, we found: (1) No gel network is formed when m is 1.1, whereas a gel network is formed when m reaches 2.8 or higher. (2) For the precursor samples with an average of 2.8 functional groups at the ends, a sol-to-gel transition followed by a gel-to-sol transition is seen upon increasing n . The latter reentry into the sol regime is owing to the opening of the crosslinking site upon reaction with excessive crosslinker molecules. (3) With an increase of $m \geq 2.8$, the saturated plateau modulus G_N increases with m , which is attributed partly to an increase in functionality of the precursor chains, and partly to the stress contribution of the oligomeric crosslinker. Surprisingly, the relaxation time obtained at the saturated G_N does not increase significantly with m . This result is in sharp contrast to those seen for the ABA-type ionomers in our previous studies, where the relaxation time increases exponentially with the number of connected ions at the chain end. This difference indicates that the relaxation mechanism of ABA-type vitrimer is distinct from that of ABA-type ionomers. Dynamic details of the exchange reaction at the crosslinking sites have yet to be clarified.

Conflict of Interests

Quan Chen is an editorial board member for *Chinese Journal of Polymer Science* and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-024-3184-7>.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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