

Interplay of Crosslinking Structures and Segmental Dynamics in Solid-Liquid Elastomers

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Electronic Supplementary Information

Abstract There have been significant interests in recent years for incorporating dynamic bonds into polymer materials for achieving multiple functionalities, such as self-healing, recycling, stimuli-responsiveness, and so on. Nevertheless, the impact of dynamic bonds on the polymer dynamics is actually less explored. In this study, we investigate a self-healing solid-liquid elastomer (SLE), which is a dual-crosslinked network made by coupling a permanently crosslinked polydimethylsiloxane (PDMS) network with polyborosiloxane (PBS) via abundant dynamic boron/oxygen dative bonds. Proton double-quantum (DQ) NMR reveals that the crosslinking degree is reduced while the structural heterogeneity of network is enhanced with increasing PBS content, i.e., increasing the content of dynamic boron/oxygen dative bonds. Rheological experiments clearly reveal two chain relaxation modes in the SLE samples with a characteristic relaxation time of around 2.1 s and 11.8 s, corresponding to the relaxation of coupled PBS and PDMS chains, respectively. The master curves obtained from variable-temperature frequency-dependent rheological experiments also reveal enhanced heterogeneity of chain relaxation with increasing PBS content. Finally, the impact of boron/oxygen dative bonds on the Rouse dynamics is further revealed by fast-field-cycling (FFC) NMR experiments, where the spin-lattice relaxation rate (R_1) of all SLE samples follows the same power law of $R_1(\omega) \propto \omega^{-0.33}$. Nevertheless, the incorporation of PBS did slightly increase the energy barrier of Rouse dynamics. Our study well demonstrates a combined use of rheology and solid-state NMR spectroscopy can provide piercing insights into the interplay of crosslinking structures and dynamics of polymer materials.

Keywords Fast-field-cycling NMR; Multiple-quantum NMR; Rheology; Dynamics; Dynamic bonds

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INTRODUCTION

Incorporation of dynamic bonds (H-bonds, entanglements, dynamic covalent bonds, ionic interactions, metal-ligand interactions, etc.)^[1–7] into polymer network (i.e., transient polymer network) has attracted significant attention in recent years. Dynamic bonds can not only help retain the advantageous chemical and physical properties of thermoset/thermoplastic polymers, but also endow polymer materials with variable functionality and adaptability, such as shape memory,

reprocessing and recycling, self-healing, stimuli-response and so on.^[8–14] Despite remarkable progresses have been achieved in the last decade on the polymer synthesis and material fabrication using dynamic bonds, tremendous efforts have been made into understanding the special viscoelastic or chain dynamic behaviors in transient polymer network.^[15–26] For example, it was revealed that the unentangled polymers will exhibit the viscoelastic behaviors of entangled polymers when there are strong hydrogen bonding side groups.^[27] In addition, the functional hydrogen bonding groups on the chain ends will determine the self-healing behaviors and terminal relaxations of polymers, the latter of which show no independence on the molecular weight.^[28,29] Shanbhag *et al.* revealed that the interplay between chain relaxation and cross-link exchange controls linear rheological behaviors for unentangled vitrimer

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melts *via* using two different sticky Rouse models.^[26] Rowan's group found that when the concentration of dynamic bond is beyond 50%, it will form a percolating dynamic network, where its viscoelastic behaviors are determined by the dynamic bonds.^[16] Chen *et al.* also examined the reaction kinetics and chain dynamics of vitrimers based on dioxaborolane metathesis, revealing the substantial influences of bond exchange reaction kinetics on the chain dynamics.^[30,31] Notably, in recent years, there are rising interests in incorporating orthogonal dynamic/permanent bonds into elastomers for tuning physical and chemical properties,^[14,32–39] adopting the structures of interpenetrated or dual-crosslinked network as widely explored in hydrogel systems. Nevertheless, the function of orthogonal chemical bonds in the polymer network is not trivial and remains to be explored, since the role of individual chemical bond may not be independent, and both can affect the final crosslinking structures and segmental dynamics as well as the viscoelastic properties.^[13,40] Besides, there are few systematic studies on the influences of dynamic bonds on the crosslinking structures, segmental dynamics and rheological properties.^[16,31,36,40,41]

Recently, we reported a highly stretchable and self-healing elastomer by coupling polyborosiloxane (PBS) with polydimethylsiloxane (PDMS) *via* dynamic bonds, which shows high elasticity and structural stability as well as strain-rate dependent mechanical behaviors due to the boron/oxygen dative bonds (formed *via* triple and quadruple bonds between boron and oxygen in the Si—O groups).^[42,43] Because such elastomers show both solid and liquid behaviors under different strain rate at room temperature due to the dynamic boron/oxygen dative bonds, they are named as solid-liquid elastomers (SLEs). For understanding the interplay of crosslinking structures and segmental dynamics in SLEs, we further systematically examined the crosslinking structures and segmental dynamics of SLEs with a variable PBS content (*i.e.*, variable content of dynamic boron/oxygen dative bonds). Proton double-quantum (DQ) NMR clearly reveals that increasing PBS content will reduce the crosslinking density of SLEs while increasing the structural heterogeneity of polymer network. Besides, two different relaxation modes are found in SLEs, corresponding to the relaxation of coupled PBS and PDMS chains, respectively. Finally, fast-field-cycling (FFC) re-

vealed that the power law of Rouse dynamics in SLEs does not change with PBS content, while the activation energy of Rouse dynamics is slightly increased with increasing PBS content.

EXPERIMENTAL

Materials and Sample Preparation

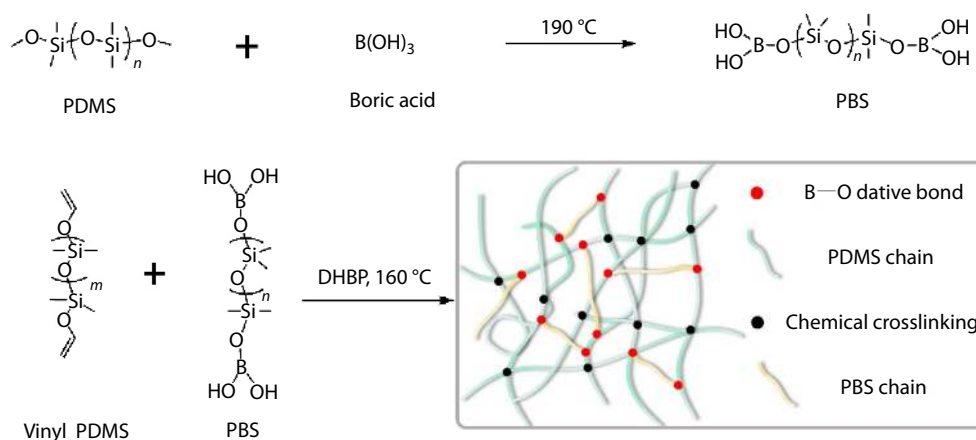
PBS was obtained by heating PDMS (number-averaged molecular weight $M_n \sim 2.5 \times 10^4$ g/mol) and boric acid (BA) at 190 °C for 4 h. The M_n of the obtained PBS is around 2400 g/mol. By roll-milling PBS, vinyl-PDMS ($M_n \sim 5.3 \times 10^5$ g/mol) and DHBP (2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane, 0.5 wt% to PBS/PDMS mixture) at room temperature and further compression molding and vulcanizing at 160 °C for 12 min, the self-healing SLEs can be obtained. By varying the weight ratios between PBS and vinyl PDMS ($n = m_{\text{PBS}}/m_{\text{PDMS}}$), we can obtain a series of SLE samples, denoted as SLE-*n*. As a control sample, a permanently crosslinked PDMS sample was also prepared following the same procedure. More experimental details about the preparation of the SLE samples and the relevant raw materials can be found in the previous publication,^[43] and the schematic synthetic routes are shown in Scheme 1.

Rheology

All experiments were performed with an ARES-G2 (TA Instruments) using a set of 25 mm of diameter parallel plates and a gap around 1 mm. The strain deformation was fixed within the linear region using a strain amplitude of 1%. Frequency-dependent experiments were measured from 100 °C to 25 °C, and 10 min was given at each temperature for thermal equilibrium. The temperature-dependent G'/G'' curves were measured at a strain frequency of 6.28 rad/s in a temperature range of 25–100 °C with a heating rate of 2 °C/min.

Solid-State ^1H DQ NMR Experiments

^1H DQ NMR experiments were performed at a 9.4 T magnetic field on a JEOL JNM-ECZR400R/M1 spectrometer, equipped with a 3.2 mm HXY MAS probe (JEOL RESONANCE Inc., Japan). The ^1H $\pi/2$ pulse length is about 2.2 μs . A well-established offset-compensated Baum-Pine pulse sequence^[44,45] was adapted to excite double-quantum coherences. Detailed account of the principle and data processing procedures can be



Scheme 1 Schematic synthetic routes for the sample preparation.

found in the electronic supplementary information (ESI). In short, from DQ experiments, we can obtain a normalized DQ buildup curve as a function of DQ excitation time (τ_{DQ}), whose signal buildup rate is exclusively depending on the crosslinking density when the experimental temperature is far beyond the glass transition temperature (usually beyond $T_g + 100$ K). Since the DQ excitation relies on the presence of residual dipolar coupling (D_{res}) induced by the crosslinkages, the numerical fitting of the normalized DQ (nDQ) curve will enable the extraction of the distribution curve of D_{res} , which actually reflects the structural heterogeneity of polymer network.

^1H FFC NMR Experiments

Proton T_1 values were measured on a Spin Master FFC-2000 FC NMR relaxometer (Stelar srl, Mede, Italy) at different temperatures. The Larmor frequency range is 0.01–10 MHz. The prepolarized and non-prepolarized pulse sequences^[46,47] were used below and above 4.6 MHz, with a polarizing and detection frequencies of 10 and 7.2 MHz, respectively. A 1.5 ms field switching time and a 90° pulse length of $6.5 \mu\text{s}$ was used. A scan number of 16 was used for all experiments. Stelar ST-VTC variable temperature controller was used to control the sample temperature within $\pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

Based on our previous study,^[43] in the SLE samples, a dynamic network can be formed mainly through boron/oxygen dative bonds between PBS and PDMS chains as well as PBS chain themselves. Therefore, SLE samples are actually composed of two networks, including the permanently crosslinked PDMS network and the dynamic network by PBS as shown in Scheme 1. In this study, we will mainly focus on understanding the effect of dynamic boron/oxygen dative bonds on the structures and segmental dynamics of SLE samples by varying PBS contents in SLE samples. A higher content of PBS implies the presence of a larger amount of boron/oxygen dative bonds.

Crosslinking Structures

The crosslinking structures of SLEs are firstly examined using proton DQ NMR spectroscopy, as shown in Fig. 1. Fig. 1(a) shows the DQ signal intensity as a function of DQ excitation time (τ_{DQ}), where the variation of segmental dynamics will lead to the shift of peak position (τ_{max}). Faster segmental dynamics typically corresponds to a larger value of τ_{max} . In fact, the segmental dynamics is strongly coupled with the crosslinking structures.

Thus, for eliminating the influences of segmental dynamics, the DQ curves were further normalized by utilizing the reference signals as discussed in ESI (Fig. 1b). As a result, the nDQ curve only contains the structural information, as the experiments were performed at a temperature around $T_g + 155$ K (Fig. S1 in ESI), and thus the signal buildup rate is proportional to the crosslinking density of polymer network. It is clearly seen that with the incorporation of PBS in the sample, the crosslinking density of SLEs is significantly reduced compared to permanently crosslinked PDMS sample. Particularly, the crosslinking density is decreased with increasing PBS content. This is further revealed by the D_{res} distribution curves shown in Fig. 1(c), where the median value (D_{med}) of the distribution curves decreases with increasing PBS content. In fact, the structural changes can be ascribed to two aspects. On one hand, the PBS may influence the chemical crosslinking of PDMS chains, as the dynamic boron/oxygen dative bonds between PBS and PDMS chains may impose constraints on the motion of PDMS chains during chemical crosslinking reactions, as compared to the neat PDMS sample. On the other hand, there may be condensation polymerization between PBS chains, leading to the increase of PBS molecular weight, namely increased molecular weight between the dynamic crosslinkages formed via boron/oxygen dative bonds between PBS and PDMS chains. From Fig. 1(c), it is also revealed that the network is becoming more heterogeneous with increasing PBS content, as indicated by the broadening of D_{res} distribution curve. Therefore, experimental results in Fig. 1 clearly revealed that the chemical crosslinking and the dynamic boron/oxygen dative bond exchange are not independent in the last synthetic step (Scheme 1), and their cooperative impacts determine the final crosslinking structures.

Chain Relaxation

The rheological experiments are typically performed with a shear frequency range from 0.1 Hz to 100 Hz, and thus can directly reveal chain dynamics around 0.01 s to 10 s. This time scale can usually indicate the chain dynamics of polymers, giving a clue for the characteristic time of the flow of polymer chains, which is critical for the self-healing and reprocessing of polymer materials with dynamic bonds. The temperature-dependent G'/G'' curves are shown in Fig. 2, where G' is always larger than G'' , indicating an elastic behavior at the probed temperature range from 25°C to 100°C for all samples except PBS. Indeed, the increased temperature will enhance the dissociation of dative boron/oxygen dative bonds in PBS as

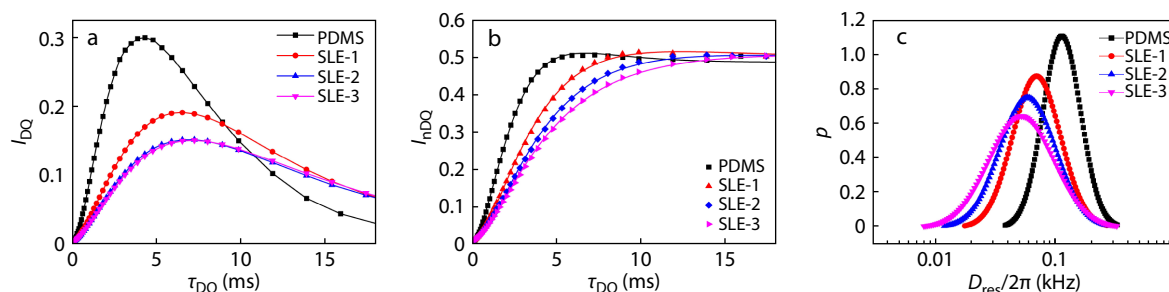


Fig. 1 (a) DQ signal intensity as a function of DQ excitation time for SLE samples as obtained from the proton DQ NMR experiment; (b) Normalized DQ (nDQ) curves as a function of DQ excitation time. The solid lines indicate the numerical integration results using Eq. (S6) (in ESI). (c) D_{res} distribution curve obtained by numerically fitting nDQ curves. All experiments were performed at a temperature of 29°C .

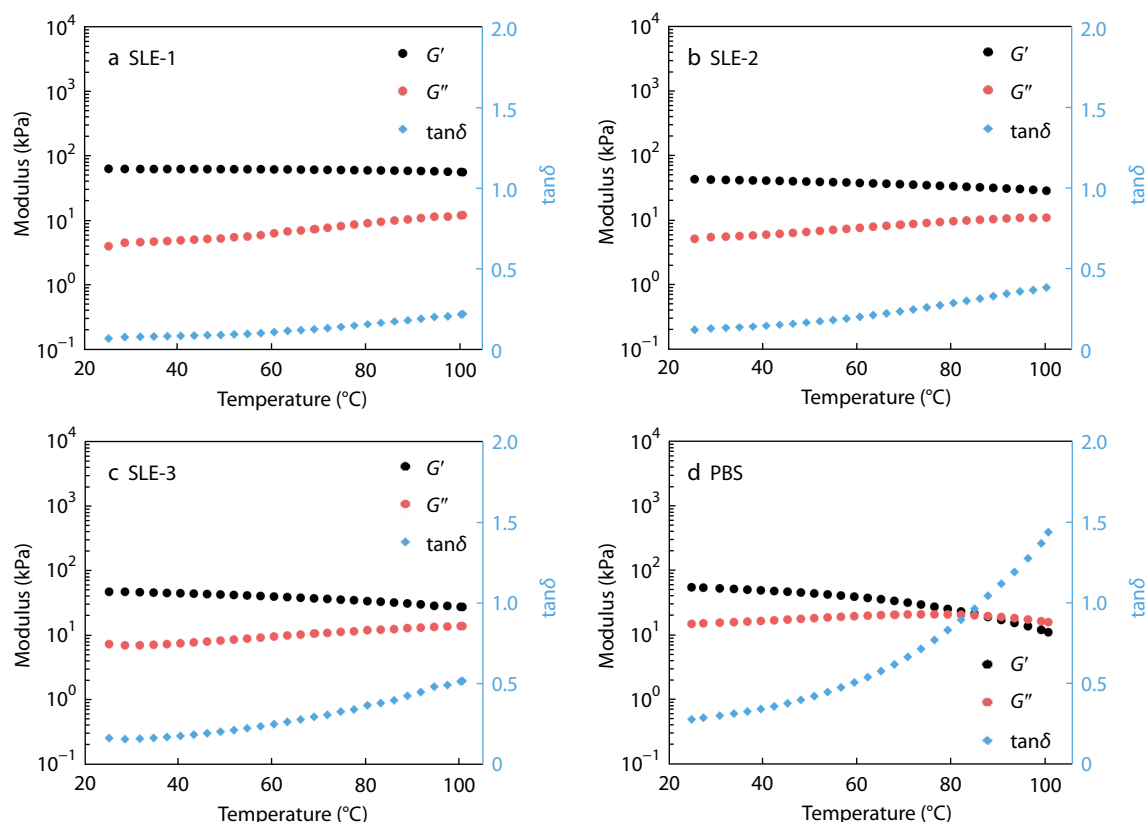


Fig. 2 Storage (loss) moduli (G' , black, G'' , red) and loss factor ($\tan\delta$, blue) for the SLE samples as a function of the temperature. The heating rate is set as $2\text{ }^{\circ}\text{C}/\text{min}$, and the strain rate (ω) and amplitude is set as 6.28 rad/s and 1% , respectively.

well as the hydrogen bonds, leading to obvious decrease of storage modulus and increase of loss modulus. Instead, the storage modulus of SLE samples are much less affected by the temperature due to the presence of permanent crosslinked PDMS network. Notably, due to the enhanced dissociation of boron/oxygen dative bonds, the capability of energy dissipation is enhanced with increasing the temperature, and thus the loss moduli increase as well as the loss factor. Therefore, the SLE samples can basically retain the structural integrity with increasing the temperature due to the presence of permanently crosslinked PDMS network, while the presence of dynamic boron/oxygen dative bonds can actually lead to efficient energy dissipation and thus enhanced tensile stretchability and self-healing performances.

To further understand the impact of dynamic boron/oxygen dative bonds on the linear viscoelasticity, frequency sweep experiments were performed at a temperature range between 25 and $100\text{ }^{\circ}\text{C}$, and the master curve as obtained using the time-temperature superposition (TTS) principle is shown in Fig. 3. TTS principle typically assumes that the effect of time and temperature on the viscoelastic behaviors are equivalent. Thus, the viscoelastic curves at different temperatures can be horizontally shifted (and slightly vertically shifted as well considering the potential changes of sample density with temperature) relative to the curve at a specific temperature to superimpose into a master curve. It is clearly observed that TTS applies well for the SLE samples, implying a stable chemical structure within the specified temperature

range, even though the dissociation of boron/oxygen dative bonds are enhanced, *i.e.*, basically only the chain relaxation is affected by the temperature.^[48] This is actually partially confirmed by the temperature-dependent IR spectra, as shown in Fig. S2 (in ESI), where the IR spectra do not change with increasing the temperature to $100\text{ }^{\circ}\text{C}$. From Fig. 3, as is clearly observed, the characteristic relaxation time, *i.e.*, the G'/G'' crossover point at the low frequency (ω_d), increases with increasing PBS content from 0.0075 rad/s (SLE-1) to 0.165 rad/s (SLE-3), *i.e.*, τ_d equals to 133.3 s , 9.3 s , 6.1 s for SLE-1, SLE-2, and SLE-3 sample, respectively, while the ω_d is 1.44 rad/s (*i.e.*, $\tau_d=0.69\text{ s}$) for the PBS sample due to the fast reversible association/dissociation of the boron/oxygen dative bonds.^[42,49] The characteristic relaxation time for each sample is summarized in Table 1. Note that all the samples have a glass transition temperature around $-126\text{ }^{\circ}\text{C}$ (Fig. S1 in ESI), and thus the influence of glass transition on the G'/G'' crossover point can be ignored. Therefore, including PBS into PDMS network can significantly enhance the chain relaxation and thus self-healing performance as previously demonstrated.^[43]

According to viscoelastic master curves constructed with a reference temperature of $25\text{ }^{\circ}\text{C}$, the average molecular weight between crosslinks (M_c), *i.e.*, inverse of the crosslinking density, of each sample is further calculated (see ESI) and summarized in Table 1. Note that M_c of PBS is much higher than the nominal molecular weight of PBS, indicating the condensation polymerization between PBS chains during sample preparation due to the abundant presence of free boron hy-

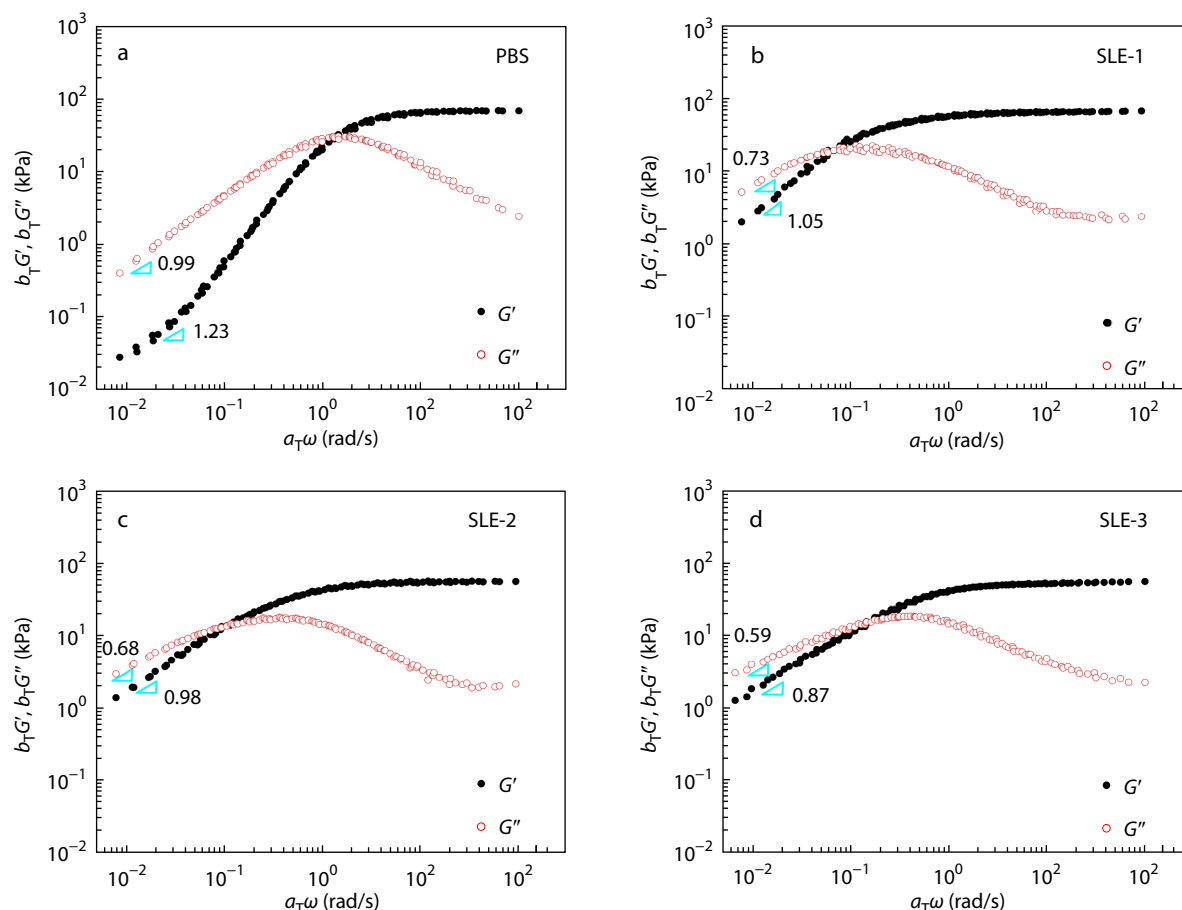


Fig. 3 Linear rheological master curves obtained by shifting the frequency sweep curves at different temperatures for (a) PBS, (b) SLE-1, (c) SLE-2, and (d) SLE-3 samples with a reference temperature of 25 °C.

Table 1 Relaxation time (τ_d) determined from the G'/G'' crossover frequency as well as the averaged molecular weight between crosslinks (M_c) determined at $T=25$ °C.

Samples	Relaxation time (τ_d) (s)	M_c (kg/mol)
PBS	0.69	34.8
SLE-1	133.3	35.7
SLE-2	9.3	46.8
SLE-3	6.1	44.0
PDMS	/	30.9

droxyl groups. Note that the crosslinking density, $1/M_c$, of SLE-3 is slightly larger than SLE-2, which seems to be in contradiction with the DQ NMR results shown in Fig. 1. However, it should be pointed out that the storage modulus in rheologic experiments is significantly affected by the presence of network defects, which are actually not considered in the theoretical models. Thus, DQ NMR is actually a more robust method to reveal the actual crosslinking density of polymer network by eliminating the influence of network defects. Power-law fits to G' and G'' are also made at the terminal relaxation region as shown in Fig. 3. According to the Maxwell model, the power-law exponent should be 1 and 2 for the G'' and G' curves for an entangled linear polymer sample, respectively.^[50] However, the entanglement molecular weight of PDMS is around 10^4 g/mol,^[51] which are much larger than

the molecular weight of used PBS here. Thus, the characteristic relaxation time, τ_{dr} , is actually determined by the reversible boron/oxygen dative bonds. Therefore, it is not surprising to see G' (and G'') curve has a power-law exponent of around 1 due to the coupling of PDMS and PBS via boron/oxygen dative bonds. When PBS is incorporated into PDMS network, the power-law exponents of G'' and G' curves both decrease with increasing PBS content. The smaller exponent typically implies a more heterogeneous relaxation dynamics, which is actually caused by the enhanced structure heterogeneity with increasing PBS content, as well proved by the proton DQ NMR results shown in Fig. 1. Furthermore, from the shift factor as a function of temperature, the activation energy for chain relaxation can be extracted as shown in Fig. 4(a). Notably, SLE-3 sample shows a slightly higher E_a than others, implying stronger constraints on the chain relaxation. This may be ascribed to the larger amount of oxygen/boron dative bonds between PDMS and PBS chains, leading to higher energy barrier for the terminal flow of polymer chains. Note that this activation energy cannot be simply ascribed to that of boron/oxygen dative bond exchange, since it is strongly coupled with and dependent on the polymer chain dynamics. Thus, it is well expected that such activation energy determined from rheology is typically larger than that of the exchange reactions using small molecules as model compounds.^[26]

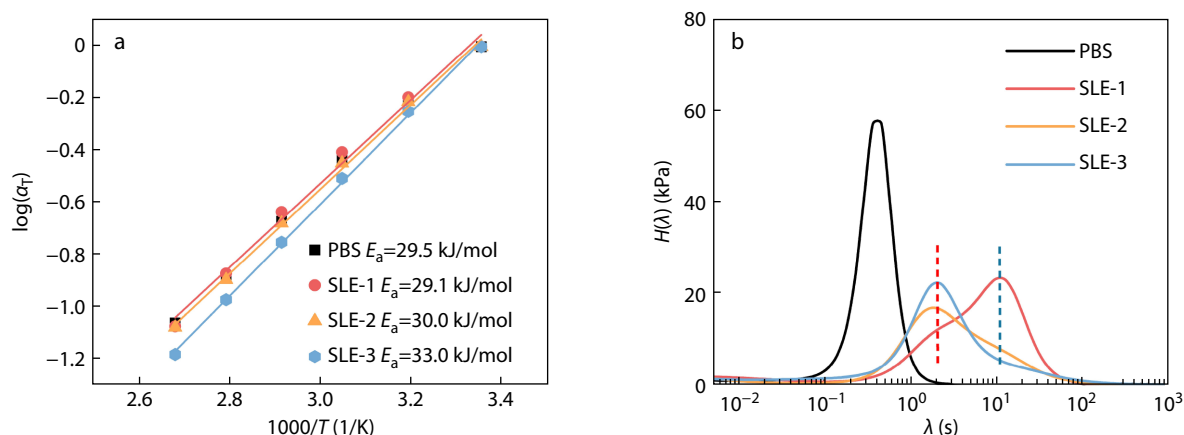


Fig. 4 (a) Arrhenius plots of the horizontal shift factor, a_T , as a function of the experimental temperature. The reference temperature is 25 °C. (b) Relaxation time spectra determined via iterative fitting of master curves shown in Fig. 3 via Eqs. (2) and (3). The red and blue dash lines indicate two characteristic relaxation time, corresponding to the relaxation of coupled PBS and PDMS chains, respectively.

To further reveal the complex relaxation behavior of SLE samples, the frequency-dependent modulus (G' and G'') can be converted into a distinct material function of relaxation times, namely relaxation spectrum, $H(\lambda)$ by solving following Eqs. (1) and (2):

$$G'(\omega) = \int_{-\infty}^{+\infty} H(\lambda) \frac{\omega^2 \lambda^2}{1 + \omega^2 \lambda^2} d\ln(\lambda) \quad (1)$$

$$G''(\omega) = \int_{-\infty}^{+\infty} H(\lambda) \frac{\omega \lambda}{1 + \omega^2 \lambda^2} d\ln(\lambda) \quad (2)$$

The above strategy assumes that each relaxation mode within the material can be well described by the Maxwell element, with a characteristic frequency given by $1/\lambda$. The obtained relaxation spectrum $H(\lambda)$ is shown in Fig. 4(b). PBS only shows a characteristic relaxation time peak due to the dynamic boron/oxygen dative bonds.^[42] Instead, for SLE samples, two relaxation peaks can be observed. The peak indicated by the red dash line at round 2.1 s can be ascribed to relaxation of PBS chains, since its amplitude increases with PBS content. Note that this relaxation is slowed down by the coupling with PDMS via boron/oxygen dative bonds, as compared to pure PBS sample. Similarly, the peak indicated by the blue dash line at around 11.8 s can be reasonably ascribed to the relaxation of PDMS chains that are coupled with PBS via boron/oxygen dative bonds, showing a much slower chain relaxation behavior than PBS due to the strong entanglement of PDMS chains and permanent chemical crosslinking. It is also worth noting that the relaxation spectrum of SLE samples is much wider than that of PBS, implying much more heterogeneous structures in SLE sample as also confirmed by the proton DQ spectroscopy (Fig. 1). Such wide relaxation spectrum can well explain why SLE samples can show strain-rate-dependent mechanical behaviors,^[43] as the chains can relax at a broad time scale from about 0.1 s to 100 s at a reference temperature of 25 °C. Therefore, from the rheological experiments, the dynamic boron/oxygen dative bonds actually determine the terminal relaxation time of SLE samples. In the meantime, the relaxation behaviors (i.e., power law between G'/G'' and ω) at the terminal relaxation region are significantly affected by the heterogeneous crosslinking structures, leading to enhanced dynamics heterogeneity with increasing PBS content.

Rouse Dynamics

Variable temperature FFC NMR experiments were performed to probe the Rouse dynamics of SLE samples. From FFC NMR experiments, we can obtain the nuclear magnetic relaxation dispersion (NMRD) curves, i.e., proton spin-lattice relaxation rate, $R_1 = 1/T_1$, as a function of proton Larmor frequency, ω , as shown in Fig. S3 (in ESI). Since the dipolar couplings among intramolecular/intermolecular proton spin pairs are modulated by the translations and reorientations of polymer segments, NMRD curves can actually reflect the motions of proton spins in the sample due to the dependence of T_1 on the fluctuation of the ^1H - ^1H dipolar interactions. Indeed, proton spin-lattice relaxation rate, R_1 , is related to the spectral density, $J(\omega)$, of the orientational dynamics of monomers via the Bloembergen-Purcell-Pound (BPP) equation,^[52–54]

$$\omega R_1(\omega) = k [\chi''(\omega) + 2\chi''(2\omega)] = k\chi''_{\text{NMR}}(\omega) \quad (3)$$

where k is the NMR coupling constant, and the susceptibility is presented as:^[55]

$$\chi''(\omega) = \omega J(\omega) \quad (4)$$

Note that the spectral density, $J(\omega)$, is the Fourier transform of the rotational/translational correlation function, $C(t)$. Herein, using Eq. (4), the master NMR susceptibility curve, $\chi''_{\text{NMR}}(\omega)$, can be constructed by further applying frequency-temperature superposition (FTS) principle, namely horizontally shifting $\chi''_{\text{NMR}}(\omega)$ curve at different temperatures into a merged curve. The constructed master curves for each sample are shown in Fig. 5, which are obtained by horizontally shifting the $\chi''_{\text{NMR}}(\omega)$ curve at high temperatures with respect to the $\chi''_{\text{NMR}}(\omega)$ curve at 30 °C. As a result, the shifting factor, which is also called scaling factor here, is defined as 1.0 for the $\chi''_{\text{NMR}}(\omega)$ curve at 30 °C as shown in Fig. 6. Such procedure is exactly the same as that applied in constructing master curves of linear viscoelastic rheologic curves in Fig. 3. From Fig. 5, it is noted that all the master curves show an apparent power law regime with $\chi''_{\text{NMR}}(\omega) \propto \omega^{0.67}$, i.e., a power law of $R_1(\omega) \propto \omega^{-0.33}$. This regime is typically ascribed to a constrained Rouse regime (regime II) according to the renormalized Rouse formalism.^[56,57] It is noted from Fig. 5 that the incorporation of PBS into the PDMS network does not change

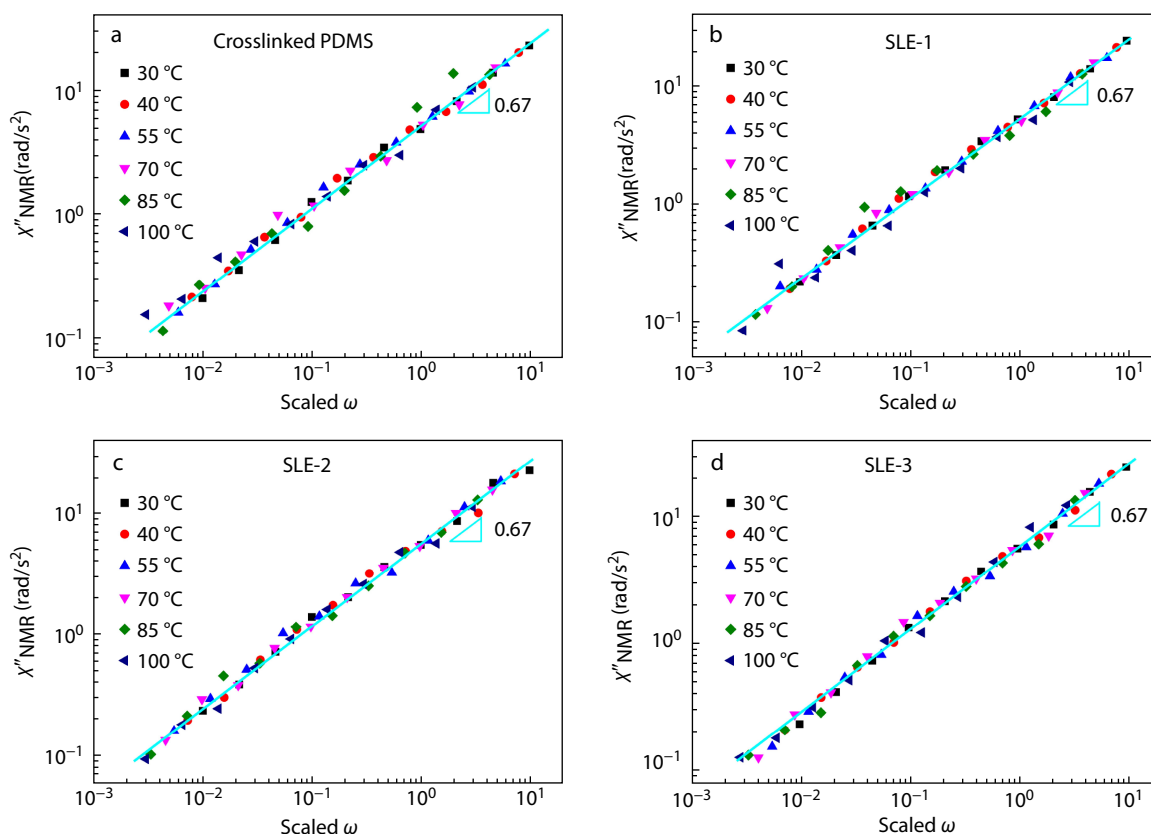


Fig. 5 $\chi''_{\text{NMR}}(\omega)$ master curves for (a) permanently crosslinked PDMS, (b) SLE-1, (c) SLE-2, and (d) SLE-3 samples. All the master curves show the same power law, $\chi''_{\text{NMR}}(\omega) \propto \omega^{0.67}$.

the power law at all, i.e., the exponential index $\gamma \approx 0.67$ is the same for all the samples. This result is not surprising, since regime II is mainly contributed by the segmental reorientations instead of coherent chain motions, while changing the crosslinking density has little influence on the segmental fluctuations,^[58] unless the crosslinking density is very high.^[59] Similar results were also found in the crosslinked rubbers, where chemical crosslinking has no influences on the power law in the frequency region specified for region II.^[58]

It is worth mentioning that the construction of master curves $\chi''_{\text{NMR}}(\omega)$ here is different from the conventional approach.^[60,61] In the conventional approach, the $\chi''_{\text{NMR}}(\omega)$ curve at a specific temperature (T_s) lower than the glass transition temperature (T_g), where the maxima and the high-frequency branch of $\chi''_{\text{NMR}}(\omega)$ curve are both observed, is typically fitted by the Cole-Davidson (CD) function,

$$J_{\text{CD}}(\omega) = \frac{\sin[\beta_{\text{CD}} \times \arctan(\omega\tau_{\text{CD}})]}{\omega[1 + (\omega\tau_{\text{CD}})^2]^{\frac{\beta_{\text{CD}}}{2}}} \quad (5)$$

where $0 < \beta_{\text{CD}} \leq 1$, and τ_{CD} is related to the glassy chain relaxation time τ_s at the specific temperature T_s by the expression:

$$\tau_s = \beta_{\text{CD}}\tau_{\text{CD}} \quad (6)$$

Therefore, using the FTS principle, the relaxation time of chains at different temperatures can be calculated by multiplying τ_s with the corresponding scaling factor for horizontally shifting the $\chi''_{\text{NMR}}(\omega)$ curve at different temperatures with

respect to the reference temperature T_s . However, in current study, all the FFC experiments are performed at a temperature beyond $T_g + 150$ K (Fig. S1 in ESI), and thus the relaxation time of the glassy dynamics cannot be extracted at this moment. Nevertheless, the scaling factor can still be used to calculate the activation energy as shown in Fig. 6. The scaling factor is defined as 1 for all the samples at 30 °C, and the scaling factor as a function of temperature can be simply fitted using the Arrhenius function,

$$f = f_0 e^{E_a/RT} \quad (7)$$

It is noted from Fig. 6 that the activation energy is slightly increased with increasing the PBS content, implying that the boron/oxygen dative bonds between PDMS and PBS actually increase the energy barrier for the constrained Rouse dynamics. Therefore, from FFC experiments, it is noted that the Rouse dynamic behaviors will not be affected by the boron/oxygen dative bonds, while the activation energy is slightly increased. It should also be pointed out that all SLE samples have basically the same T_g around -126 °C (Fig. S1 in ESI). Therefore, the influence of glass transition on Rouse dynamics can be safely ignored. Because FFC NMR here probes the dynamics on the length scale of Rouse segments, while the rheological experiments reveal the relaxation of polymer chains, it is not surprising to observe that the activation energy of terminal flow obtained from rheological experiments is much higher than that of Rouse dynamics obtained from FFC NMR experiments.

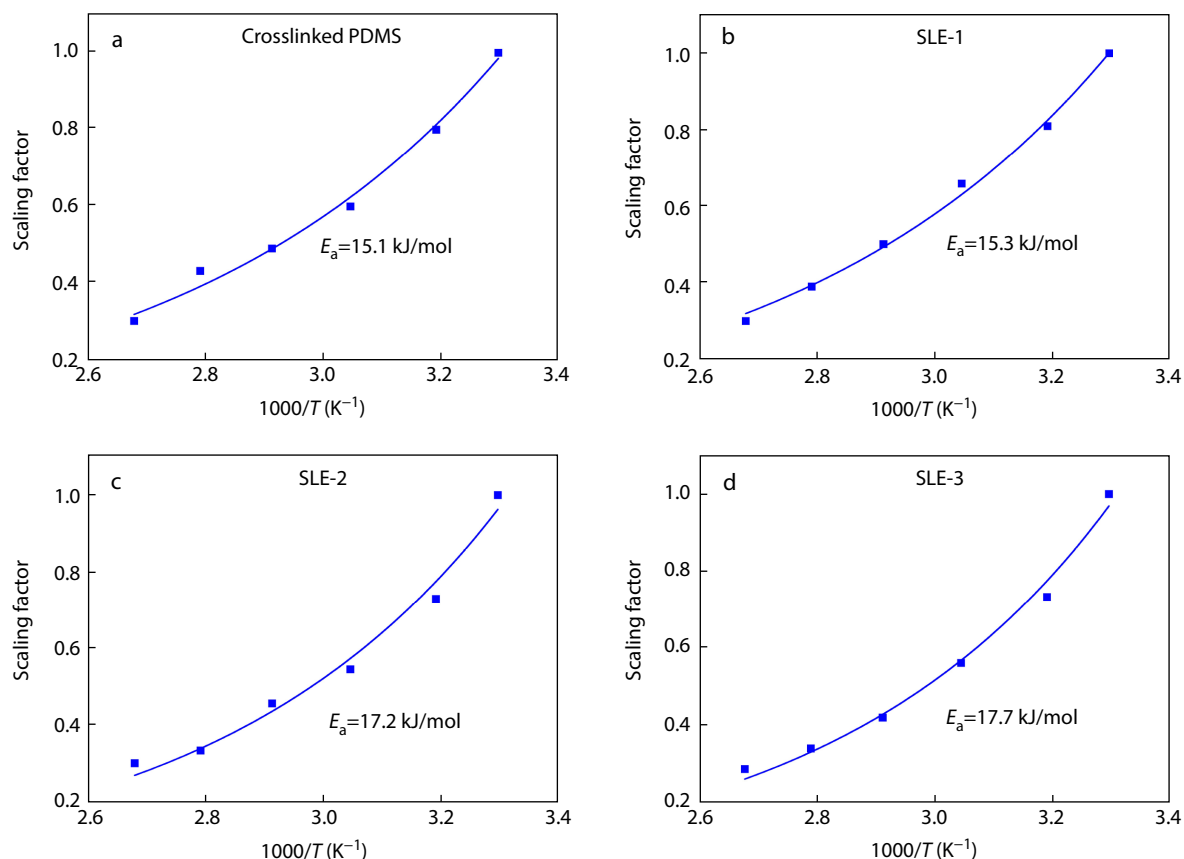


Fig. 6 Scaling factors as a function of temperature for (a) permanently crosslinked PDMS, (b) SLE-1, (c) SLE-2, and (d) SLE-3 samples. The scaling factors were obtained by making the $\chi''_{\text{NMR}}(\omega)$ curve at 30 °C fixed while horizontally shifting the $\chi''_{\text{NMR}}(\omega)$ curve at other temperatures into a master curve. All experimental data were fitted with a simple Arrhenius function, and the corresponding activation energy values were indicated in each figure as well.

It should be mentioned here that FFC NMR and rheology are sensitive to molecular motions at different time scales. FFC NMR usually probes the molecular motions at a time scale inversely proportional to the magnetic field, namely around 0.1 μ s to 0.1 ms in our current experimental setup. Instead, rheology typically probes the motions at a time scale of about 10 ms to 10 s, corresponding to a shear frequency of 100 Hz to 0.1 Hz, respectively. Thus, a combined experimental approach of using FFC NMR and rheology can typically examine the molecular motions in a broad time scale range of around nanoseconds to around tens of seconds with the further use of time-temperature or frequency-temperature superposition principles. Considering that the structure and dynamics are typically coupled with each other, the motions in such a broad time scale can further provide insights into the structures of polymers at a different length scale. This is well demonstrated in current study, where rheology and FFC NMR reveal the chain relaxation and Rouse dynamics, respectively. Besides, the proton DQ NMR spectroscopy can quantitatively reveal the structural heterogeneity of polymer network. Therefore, a combination of proton DQ NMR, rheology and FFC NMR enables understanding the interplay of crosslinking structures and segmental dynamics in polymers, and thus to reveal the molecular origin of viscoelastic properties of SLEs.

CONCLUSIONS

In summary, the crosslinking structures and hierarchical dynamics in the solid-liquid elastomers have been investigated using proton DQ NMR, rheology and FFC NMR techniques. For the solid-liquid elastomers made by interpenetrating PBS with PDMS, the boron/oxygen dative bonds will significantly affect the final obtained crosslinking structures and segmental dynamics. It is noted that with increasing PBS content, namely increasing the content of dynamic boron/oxygen dative bonds, the crosslinking degree of SLE samples will be reduced, while at the meantime the structure heterogeneity of network is enhanced. Rheological experiments further revealed two different chain relaxation processes in the SLE samples with a characteristic time of 2.1 s and 11.8 s, corresponding to the relaxation of coupled PBS and PDMS chains, respectively. Finally, FFC experiments revealed the Rouse dynamics of SLEs, where all the samples follow the same power-law, implying little influences on the Rouse relaxation behaviors by the dynamic boron/oxygen dative bonds. Nevertheless, the activation energy of Rouse dynamics in SLEs is slightly increased due to the increased content of PBS, which are much smaller than the activation energy of terminal flow as obtained from rheology experiments.

NOTES

The authors declare no competing financial interest.

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/s10118-022-2742-0>.

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