

Self-Healing Supramolecular Elastomers Based on the Multi-Hydrogen Bonding of Low-Molecular Polydimethylsiloxanes: Synthesis and Characterization

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ABSTRACT: Novel self-healing supramolecular elastomers based on polydimethylsiloxanes (SESi) were synthesized from a mixture of polydimethylsiloxanes derivatives with single, di-, or tri-carboxylic acid groups (PDMS-COOH_x, where $x = 1, 2,$ and $3,$ respectively), diethylene triamine, and urea with a two-stage procedure. The reactions and the final products were tracked, characterized, and confirmed by Fourier transform infrared spectroscopy, ¹H-NMR, differential scanning calorimetry, dynamic mechanical analysis, and gel permeation chromatography. Compared with a supramolecular rubber based on dimer acid (reported previously) with a similar synthesis procedure, the SESi showed a lower glass-transition temperature of about -113°C for the softer chain of polydimethylsiloxane and showed real rubberlike elastic behavior and self-healing properties at room temperature or even lower temperatures. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2435–2442, 2013

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INTRODUCTION

According to the classical theory of elastomers, the large deformation (if not destruction) of crosslinked elastomers, could be completely or approximately recovered in a short time at room temperature or even lower temperatures.^{1,2} The elastomers are consisted long-chain molecular with molecular weights ranging from 5×10^4 to 100×10^4 g/mol, and the long chains are crosslinked by covalent bonding, such as in vulcanizates; glassy or crystalline domains, such as in thermoplastic elastomers;² multiple hydrogen bonds;^{3–6} or ionic bonds.^{7,8} The crosslinking of vulcanizates are nonreversible, and thermoplastic elastomers can mend and be reprocessed by melting. The processing of elastomers associated by hydrogen bonds or ionic bonds is reversible, although all of the previously mentioned elastomers based on long chains cannot be mended at room temperature.

The concepts of supramolecular polymerization and hydrogen bonding between the macromolecules were investigated by Meijer and coworkers.^{9,10} More than a decade ago, the formation of exceptionally stable Donor-Donor-Acceptor-Acceptor (DDAA) dimers of a simple ureidopyrimidinone (UPy) deriva-

tive was reported.^{10,11} These units can be incorporated into a polymer chain by various techniques, such as through the use of a functional initiator or postpolymerization modifications. For example, compared with unfunctionalized poly(ethylene butylene), a UPy end-capped poly(ethylene butylene) macromonomer showed dramatically enhanced mechanical properties in the solid state: the former is a viscous oil at room temperature, whereas the latter can form stand-alone flexible thermoplastic films; this is mainly due to the entanglements of the long chain associated by the UPys and also the aggregation of the UPys groups.^{11–13} Thus far, in bulk, these supramolecular networks flow or partially crystallize and behave like plastic resins or fibers,¹⁴ whereas few rubberlike behaviors have been reported.

Recently, Leibler and coworkers^{15–17} proposed a new and very different strategy for synthesizing supramolecular rubber (SRDA) based on dimer acid, diethylene triamine (DETA), and urea that were not only thermoreversible and processable but also capable of self-healing when cut or torn into pieces without the application of heat or a catalyst. The idea was not to functionalize low glass-transition temperature (T_g) linear or

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star-shaped polymers but to use randomly branched oligomers with multiple functional groups capable of associating via parallel hydrogen bonds.¹⁸

In principle multifunctional molecules with an average functionality higher than 2 are capable of forming directional supramolecular networks and thus behaving like covalent polymer networks, provided the associations of functional groups are directional and robust.^{14,18–20} Unfortunately, strong interactions between molecules favor crystallization,²¹ so the solution of Leibler and his coworkers to prevent crystallization consisted of using mixtures of multifunctional branched oligomers with a controlled distribution of shapes and lengths and equipping them with a variety of strongly associating groups.

The T_g of SRDA is about 28°C,¹⁵ which means that SRDA cannot show rubberlike elastic properties at room temperature. In fact, most of the reported rubberlike properties of SRDA, such as the tensile, creep and stress relaxation properties, have been tested between 60 and 90°C.^{15–17} It was found that when SRDA was immersed in dodecane or water for several days, the T_g of the plasticized product was reduced to about 8 or –15°C,¹⁵ whereas the stability of the small-molecule plasticizer would be another question for SRDA. Compared with commercial vulcanizates, such as natural rubber, styrene–butadiene rubber, or butadiene rubber,^{1,2} a T_g higher than 0°C or even room temperature would not make SRDA a real rubber, especially under room or lower temperature.

It is known that polydimethylsiloxane (PDMS) shows a lower T_g (to –130°C) because of its soft chain.^{1,2} Thus, we might assume that if the carbon chains of dimer acid were replaced by PDMS chains, the T_g of an SRDA based on a single, di-, or tricarboxylic acid terminated PDMS would be significantly reduced, and a real self-healing supramolecular elastomer with rubberlike properties at room temperature or even lower temperatures could be obtained with a similar synthesis procedure.

In this study, novel supramolecular elastomers based on mixtures of multi-acid-functional PDMSs were synthesized and characterized.

EXPERIMENTAL

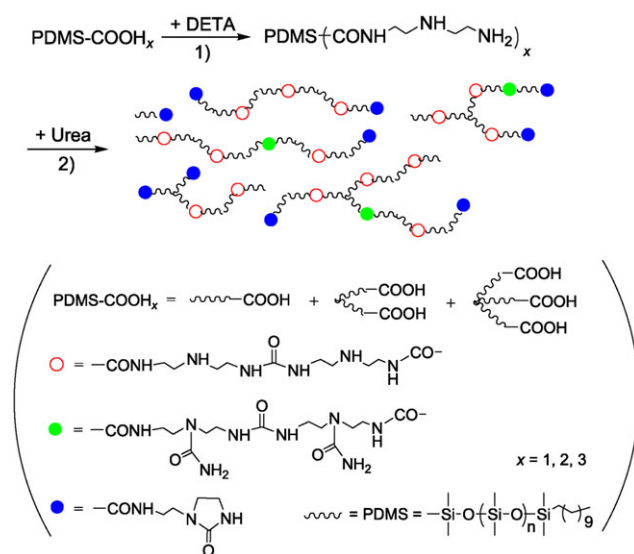
Materials

Low-molecular-weight polydimethylsiloxanes with single, di-, or tri-terminated carboxylic acid groups [PDMS–COOH_x, where $x = 1, 2,$ and $3,$ respectively; the number-average molecular weights (M_n 's) of PDMS–COOH₁, PDMS–COOH₂, and PDMS–COOH₃ measured by gel permeation chromatography (GPC) were 1.07×10^4 , 1.09×10^4 , and 1.18×10^4 g/mol, respectively] were supplied by Bald Silicone Co., Ltd. (Hangzhou, China). DETA (98%) and urea (99%) were used as received without further purification.

Instrumentation

¹H-NMR spectra were recorded in CDCl₃ with a Bruker 600 MHz NMR (Bremen, Germany) spectrometer.

GPC experiments were performed in chloroform (1 mL/min) at room temperature with an Elite EC2000 GPC (Dalian, China) equipped with a single Shodex column (K-804L). The molecular



Scheme 1. Two-step synthesis procedure of SESi. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

weights were obtained with a polystyrene calibration. M_n was also measured by ¹H-NMR (see the Results and Discussion section and the Supporting Information for further details).

Fourier transform infrared (FTIR) spectra were obtained from the KBr disk method at room temperature or at a high temperature with a Bruker V70 spectrometer fitted with a high temperature bracket.

Differential scanning calorimetry (DSC) measurements were carried out with a DSC 204 F1 apparatus (Netzsch Instruments, Selb/Bavaria, Germany). Two heating cycles between –160 and 150°C were recorded at 10°C/min.

Dynamic mechanical analysis (DMA) was performed with a DMA 242 apparatus (Netzsch Instruments) over a wide temperature range from –150 to 50°C at 10 Hz with a heating rate of 5°C/min with a tension clamp; the sample size was $6 \times 1 \times 20$ mm³.

X-ray diffraction analysis was performed with an X'Pert-Pro X-ray diffractometer (PANalytical X'Pert Pro, Almelo, The Netherlands) with a Cu K α radiation monochromatic filter in the 2 θ range of 5–70°.

Capillary viscosity (Nanjing, China) was performed at $30 \pm 0.2^\circ\text{C}$ with an Ubbelohde viscometer (Diameter = 0.45 mm). A solution in chloroform was prepared at least 1 day before the measurements and was filtered on 0.45- μm polytetrafluoroethylene filters.

Synthesis of the Supramolecular Elastomers based on Polydimethylsiloxanes (SESi)

The procedure for the synthesis of SESi was an optimized two-stage reaction^{15,16} according to Scheme 1 and as detailed in Scheme S1 in the Supporting Information.

In the first stage, a mixture of PDMS–COOH, labeled PDMS–COOH_x, containing various contents of PDMS–COOH₁, PDMS–COOH₂, and PDMS–COOH₃, and DETA, as listed in Table I, was added at room temperature to a 500-mL,

Table I. Reaction Formula of SESi

No.	Mixture of PDMS-COOH _x			DF ^a	DETA (mmol)	Urea (mmol)
	PDMS-COOH ₁ (mmol)	PDMS-COOH ₂ (mmol)	PDMS-COOH ₃ (mmol)			
SESi-1	10.5	35.0	5.3	1.90	4.75	3.80
SESi-2	7.8	35.0	8.0	2.00	5.01	4.01
SESi-3	7.3	25.5	10.7	2.08	5.20	4.16

^aDF was calculated by the following equation: $DF = (a_1 \times 1 + a_2 \times 2 + a_3 \times 3)/(a_1 + a_2 + a_3)$, where a_1 , a_2 , and a_3 are the molar fractions of PDMS-COOH₁, PDMS-COOH₂, and PDMS-COOH₃, respectively.

three-necked round-bottom flask fitted with a reflux condenser, a stirring system, and a nitrogen inlet, the molar ratio of DETA to carboxylic acid was 2.5:1 for all of the samples. The mixture was first heated to 120°C, then heated to 150°C at a heating rate of 5°C/h, and maintained at 150°C for 24 h under the same nitrogen flow during this stage. The mixture was then cooled to room temperature, solubilized in 250 g of chloroform, and washed five times with a mixture of 300 g of water and 120 g of methanol. The oligoamide was collected as a solution in chloroform; then, chloroform was evaporated first by a rotary evaporator and then a 300 mL/min nitrogen flow at 80°C overnight in the same reactor listed previously.

In the second stage, solid urea was added. The mixture was heated under a 200 mL/min nitrogen flow at 135°C for 2 h, and then the temperature was raised up to 160°C at a heating rate of 5°C/h. After remaining further at 160°C, the mixture became viscoelastic and began to rise up the stirring stem. Once the whole content of the reactor had risen on the stirring stem, the stirring was stopped, and the mixture was cooled to room temperature. The product was elastic and nonsticky and could be easily removed from the flask and stem; it was then cut into fragments about 2 mm thick and washed in water at 50°C for 72 h. Then, the dried material was solubilized in 250 g of chloroform and washed three times with a mixture of 300 g of water and 120 g of methanol. After chloroform was evaporated, the dried material was pressed at 135°C under 10 MPa for at least 20 min and then cooled to room temperature under pressure to obtain the desired SESi.

¹H-NMR (600 MHz, CDCl₃, δ , ppm): 0.08 (m, Si-CH₃), 0.51 (m, Si-CH₂CH₂), 1.27 (m, -CH₂-CH₂- chain), 2.17 [t, CH₂CH₂C(O)NH], 3.25 [m, C(O)NHCH₂CH₂NH], 3.37–3.48 (m, amidoethyl-imidazolidone). FTIR (ν , cm⁻¹): 1650 (ν_{CO} amide), 1609 (ν_{NC} imidazoline), 1546 (δ_{NH}).

Mechanical Tests

All mechanical measurements of the SESi samples were performed after equilibration under an ambient atmosphere for at least 48 h. Tensile measurements were performed with a Zwick 1010 apparatus (Ulm, Germany) on ISO 527-3 (2002) normalized specimens at 500 mm/min.

Stress relaxation experiments were conducted on a Zwick 1010 tensile apparatus at room temperature; a deformation of 100% was applied on the 6.0 × 2.0 × 50 mm³ samples for 240 min. Then, the samples were left to recover for 24 h.

Creep experiments were conducted on a laboratory-made assembly at room temperature. Rectangular SESi samples with dimensions of 25 × 6.0 × 2.0 mm³ were used; two marks with a distance of 10 mm between were labeled on the surface of these samples. A 15-g weight was applied to stretch the samples vertically and supplied a nominal 12.5 kPa of stress. The distances of the marks were recorded.

Healing experiments were performed at 25°C. The samples (6.0 × 2.0 × 50 mm³) were cut with a sharp knife from the middle; then, the broken samples were kept apart for set times (1 min, 30 min, 1 h, 2 h, 6 h, 12 h, and 24 h) before the cut surfaces were brought together. To make sure the cut surface had good contact, a very small force (<0.2 N) was applied for a very short period (<15 s); this supplied a very small pressure of about 20 kPa, as shown in Figure S1 in the Supporting Information. The mended samples were then horizontally set without applied stress for 24 h before the second tensile testing. To describe the healing effect, the factor of healing efficiency was introduced, which was defined as follows:

$$\text{Healing efficiency} = \frac{TS_{\text{healed}}}{TS_{\text{virgin}}} \times 100\% \quad (1)$$

where TS_{virgin} and TS_{healed} are the average tensile strengths of the virgin samples and the healed samples, respectively.

RESULTS AND DISCUSSION

Reaction Mechanism of the Synthesis Processing of SESi

The synthesis of SESi was carried out via a two-step procedure according to Scheme 1 and Scheme S1 in the Supporting Information, and the advancement of the reactions was monitored by FTIR spectra of the samples taken from the mixture, as shown in Figures S2 and S3 in the Supporting Information. In the first step, excessive DETA was reacted with a single/di-/tri-acid mixture of PDMS-COOH_x ($x = 1, 2, \text{ or } 3$) to ensure that each terminal carboxylic acid group was transferred to the -C(O)-NH-CH₂-CH₂-NH₂ group, as shown in Table I and Scheme 1. At the end of the stage I, excessive DETA was washed away via extraction processing with water/methanol/chloroform.

The strengthening of the $\nu_{C=O}$ amide signal at 1647 cm⁻¹ and the shift of δ_{NH} from 1570 to 1550 cm⁻¹ confirmed the amidation of PDMS-COOH_x in stage I, as shown in Figure S2 in the Supporting Information. The disappearance of ν_{asNH} at 3300–3500 cm⁻¹ and the appearance of the $\nu_{C=O}$ imidazolidone cycle

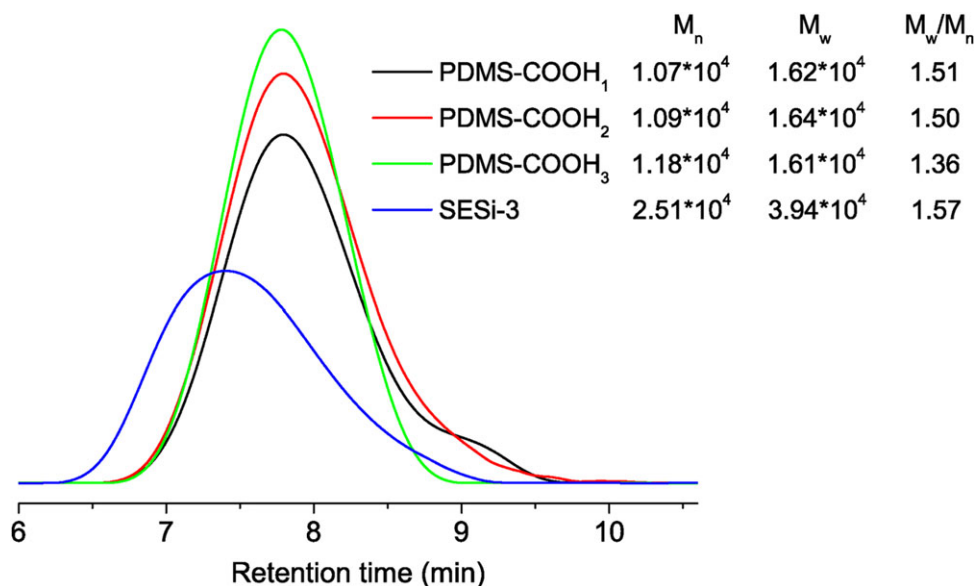


Figure 1. GPC elution curve of SESi-3 and PDMS-COOH_x in CDCl₃ (M_w = weight-average molecular weight). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

at 1654 cm^{-1} confirmed the reaction of urea with primary amines leading to 1,3-dialkyl-ureas and with secondary amines leading to 1,1-dialkyl urea or else with the whole $-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ group leading to an imidazolidone cycle, as shown in Figure S3 in the Supporting Information. Thus, after the two-stage reaction, we were expecting in the final product the presence of several species: imidazolidone, pending urea (1,1-dialkyl urea), and bridging urea (1,3-dialkyl urea), as shown in Scheme 1 and in Figure S4 in the Supporting Information.

Molecular Weight of SESi

Figure 1 clearly illustrates that the average molecular weight of SESi increased compared with PDMS-COOH_x. We also observed that according to the reaction mechanism of the two-step synthesis of SESi, the urea added in the second stage could react with two primary amines to extend the PDMS chains and yield a long-chain product. Finally, it could also react with the terminal DETA group to yield an imidazolidone end group and thus end the chain, as shown in Scheme 1. So, it was possible to estimate the average molecular weight of the final product, that is, SESi, through a comparison of the integration of hydrogen in the terminal imidazolidone group and the methylene near amide, as shown in Figure S5 in the Supporting Information. The dotted arrows in Figure S5 indicate the signals of amidoethylimidazolidone end groups ($\delta = 3.48 \text{ ppm}$), whereas the solid arrow indicates the signal of the methylene group in the α position of the amide groups ($\delta = 2.17 \text{ ppm}$). The ratio of end imidazolidone groups per fatty amide unit, determined as the ratio of $\delta = 3.48 \text{ ppm}$ to $\delta = 2.17 \text{ ppm}$ signals, was $(2.41 \times 0.205/1.205)/1.00 = 0.41$, which, with the branching neglected, yielded the number-average oligomerization index of 2.4; this matched well with the molecular weight results measured by GPC. Both the GPC results and the $^1\text{H-NMR}$ signals revealed that SESi was made of the oligomers.

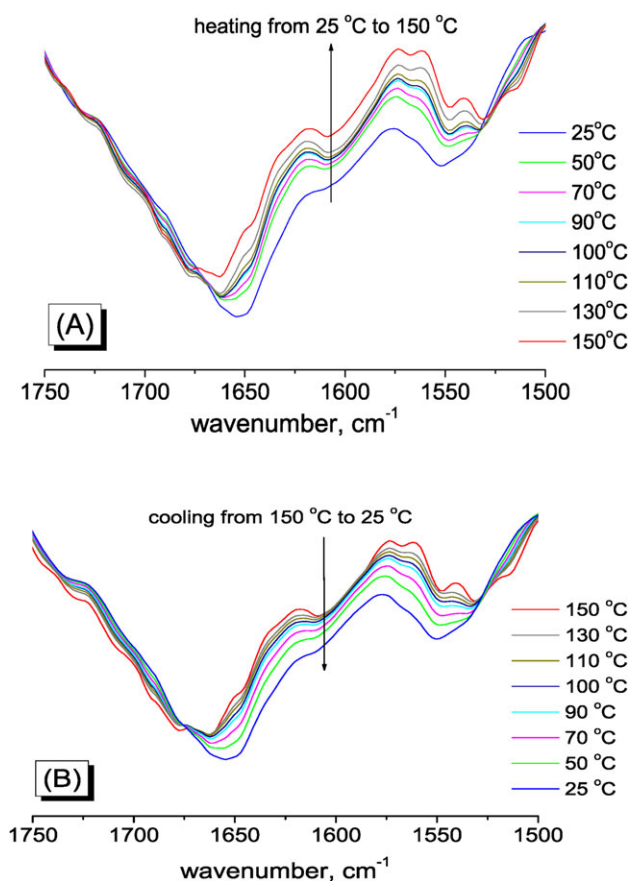


Figure 2. FTIR spectra of SESi-3 upon (A) melting and (B) subsequent cooling. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

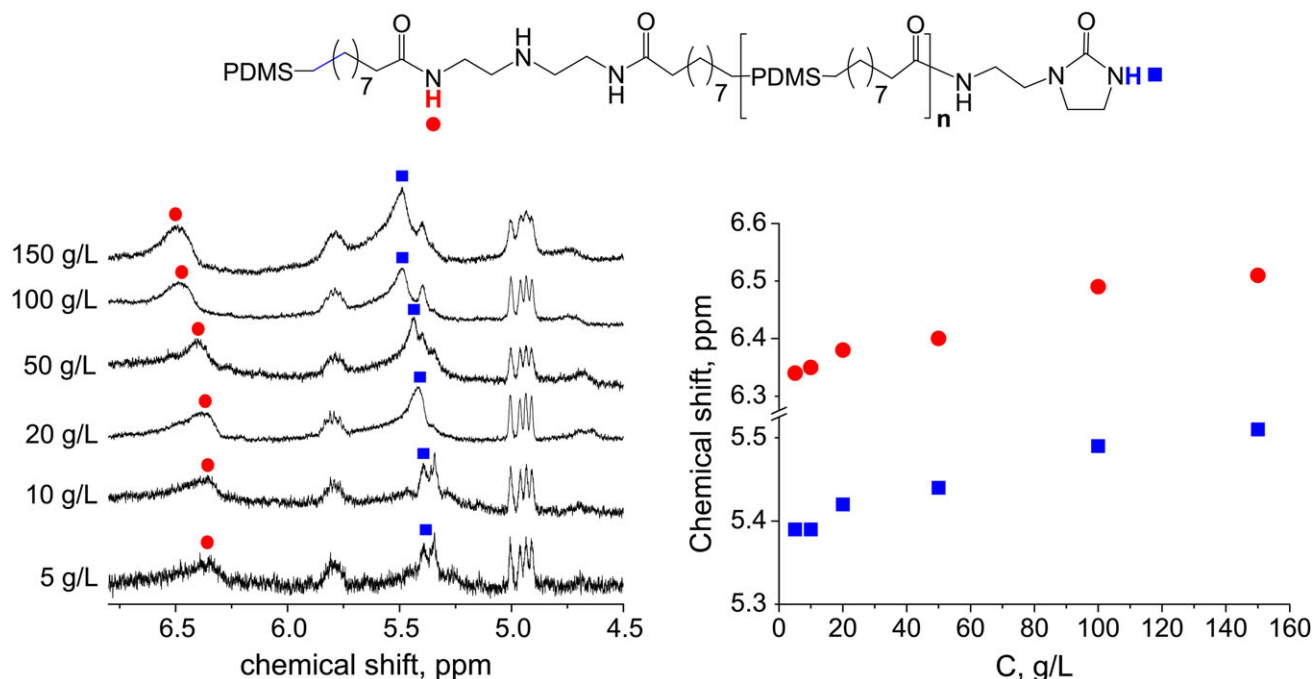


Figure 3. (A) Partial ¹H-NMR spectra of SESi-3 in CDCl₃ at increasing concentrations (Cs). (B) Plot of the chemical shift of the NH signals (red circle and blue rectangle in the online figure) at each concentration (C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of the Hydrogen-Bond Association

The association of hydrogen bonds was demonstrated by the FTIR spectra of SESi at various temperatures (Figure 2), the viscosity curves (Figure S6 in the Supporting Information), and the ¹H-NMR spectra of SESi at various concentrations (Figure 3).^{22–24} With increasing temperature, the C=O stretching signals of amide (1652 cm⁻¹) shifted toward higher wave numbers (1662 cm⁻¹), whereas the N–H bending signals (1560 cm⁻¹) shifted toward lower wave numbers (1540 cm⁻¹). Both these shifts indicated the dissociation of multi-hydrogen bonds between N–H and C=O species, as shown in Scheme S2, when the temperature was increased. When the sample was subsequently cooled to room temperature, its FTIR spectrum was almost identical to that before heating, as shown in

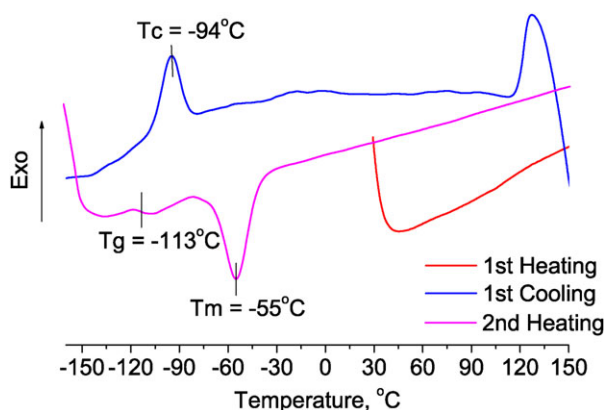


Figure 4. DSC curves of SESi-3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2(A,B). Also, with increasing concentration of SESi in chloroform, both a sharply increased reduced viscosity and shifts in the N–H signals to higher values were observed, as shown in Figure S6 in the Supporting Information and in Figure 3, respectively.

Thermal Properties of SESi

Figure 4 shows the DSC curves of SESi-3. Similar to unfunctionalized linear PDMS, SESi showed a *T_g* of -113°C; this value was much lower than that of SRDA.¹⁵ SESi also showed a crystallization temperature (*T_m*) at -94°C and then subsequent melting at -55°C [melting temperature (*T_m*)]. The DMA curve of SESi in Figure 5 shows that both the *T_g* (-112.7°C) and *T_m* (-52.4°C) matched well with the DSC testing and clearly explained why no crystalline peaks could be found in the X-ray diffraction pattern of SESi, as shown in Figure S7 in the Supporting Information. This confirmed that SESi was not crystalline at room temperature. The lower *T_g* and *T_m* values made the supramolecular real elastomers at room temperature or even at lower temperatures.

Mechanical and Self-Healing Properties of SESi

Although the supramolecular elastomers were associated by hydrogen bonds, they showed similar rubberlike properties to those of covalent-bond-crosslinked elastomers. Figures 6 and 7 show the creep deformation curves and stress relaxation curves of SESi. Most of the deformations were recovered in several seconds after the release of stress, and the residual deformation came to nearly zero after 9 h of the release of stress, when the average degree of functionality (DF) of the SESi samples was larger than 2 for SESi-3, whereas residual deformations of 32 and 11% were found for SESi-1 and SESi-2, respectively, when

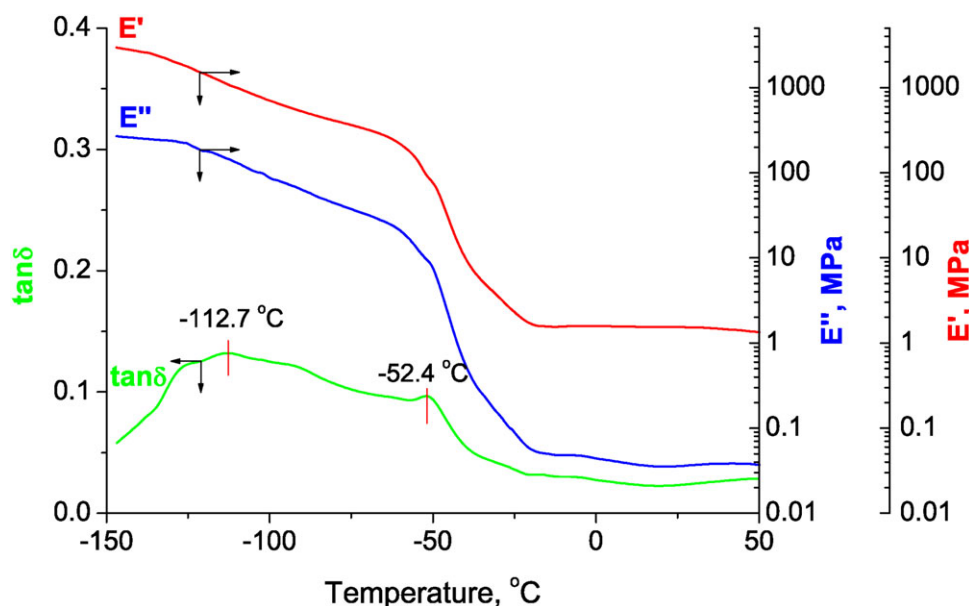


Figure 5. DMA curves of SESi-3 (E' = storage modulus). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the DFs were less than 2. Also, the higher DF was, the larger the equilibrium stress was of the SESi samples after a long time stress relaxation.

Stress–strain curves of SESi under stretching could also be used to evaluate the association strength of the hydrogen bonding among the functioned PDMS oligomers. Figure 8 shows the stress–strain curves of the SESi samples with various DFs before and after the cutting–waiting–mending procedure, in which the cut parts were brought into contact after being cut and apart for 1 min, 30 min, 1 h, 2 h, 6 h, 12 h, and 24 h, respectively, and the mending was performed at 25 °C for 24 h without additional stress. For the SESi-1 and SESi-2 samples with DFs less than or equal to 2, as shown in Figure 8(A,B), the elongations were less than 30%; this made the SESi-1 and SESi-2 samples more likely brittle and soft thermoplastics than the crosslinked

elastomer. When DF was larger than 2, the SESi-3 samples had an elongation larger than 400%, and the stress–strain curves showed a typical rubberlike stress-softening behavior at an elongation higher than 200%, as shown in Figure 8(C).

Because the supramolecular elastomers were associated by self-complementary and complementary multi-hydrogen-bond units, when they were cut, the hydrogen-bond units on the cutting section were broken and eager to find a new partner nearby. Thus, when the two freshly cut sections were brought together, part of the unassociated hydrogen-bond units associates again and, thus, mended the samples. So, the healing efficiency relied on the ratio of free and nonassociated groups, and it could be

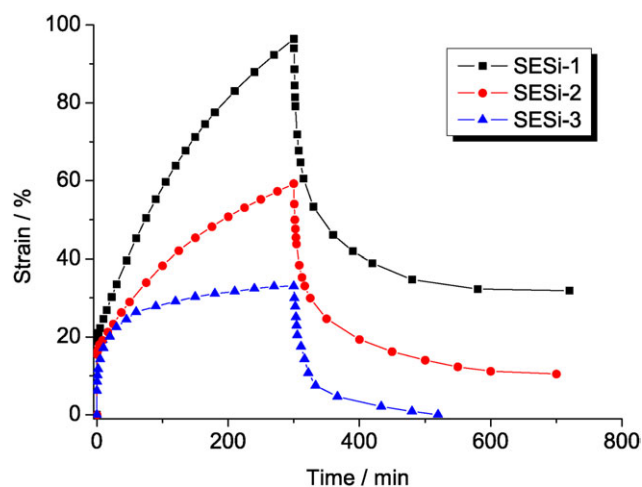


Figure 6. Creep deformation curves of the SESi samples at room temperature. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

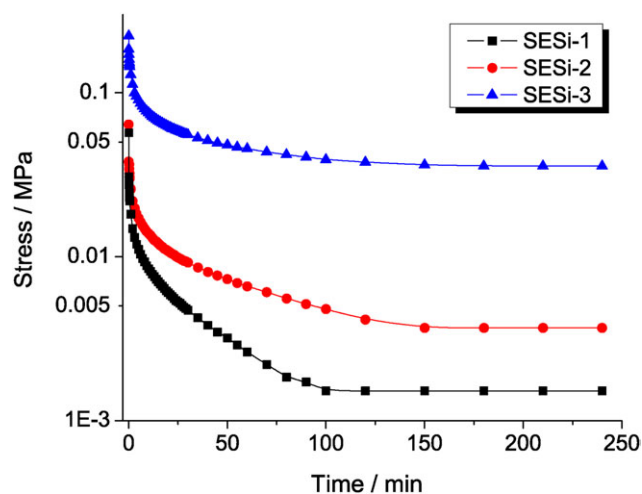


Figure 7. Stress relaxation curves of the SESi samples at room temperature. We observed that the residual stress of SESi-1 was about 0.00152 MPa (supplied by about 0.018 N on a $6 \times 2 \text{ mm}^2$ cross section); it reached the lower detection limit of the stress sensor. Thus, the residual stress of SESi-1 was regarded as zero. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

understood that the longer the waiting time before the mending was, the more associated groups were in the broken part, and the less free and nonassociated groups remained available for the partner. That is, the longer the waiting time was before mending, the lower were the strength and elongation of the samples after mending, and thus, the lower the healing efficiency was, as shown in Figure 8.

It is difficult to obtain direct spectroscopic evidence of an excess of nonassociated hydrogen bonds on a freshly cut surface because even reflectance infrared techniques probe and average over a depth comparable to the radiation wavelength, that is, a few micrometers.¹⁵ Nevertheless, the dynamics of hydrogen-

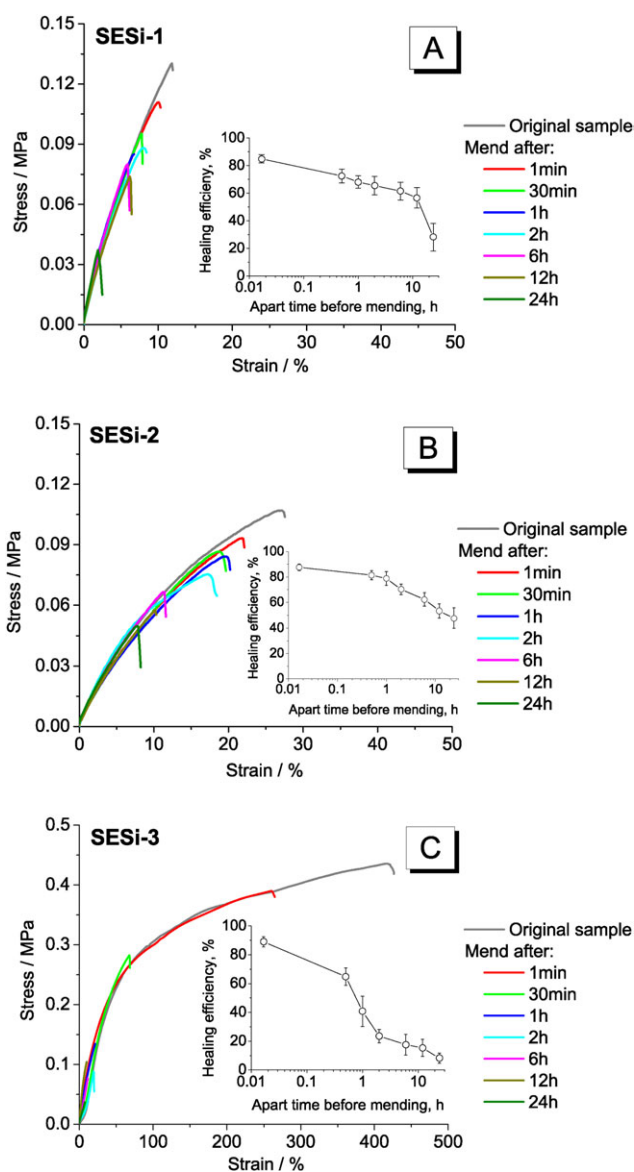


Figure 8. Stress–strain curves of the SESi samples: (A) SESi-1, (B) SESi-2, and (C) SESi-3 before (original sample, without cutting) and after cutting–mending (cut parts were brought into contact after being cut for 1 min, 30 min, 1 h, 2 h, 6 h, 12 h, and 24 h, respectively, and the mending was performed at 25°C for 24 h). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

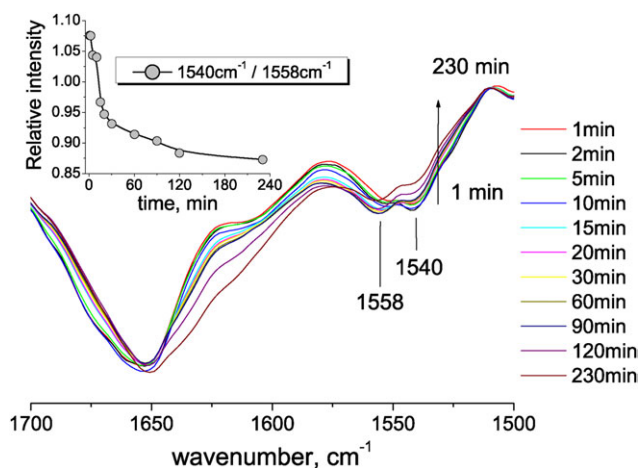


Figure 9. FTIR spectra of SESi-3 upon quenching from 130 to 25°C and the corresponding relative intensity of 1540/1558 cm⁻¹. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bond reassociation in the cut surface could be indirectly confirmed with a temperature-jump experiment (Figure 9). The SESi-3 sample was heated at 130°C for 20 min and was then quickly cooled down to 25°C, and the evolution of the infrared spectrum was observed. Figure 9 shows that the intensity ratio of free N–H (1540 cm⁻¹) and associated N–H (1558 cm⁻¹) decreased with increasing time and became stable slowly after about 6 h. This explained that when excess free hydrogen groups were created by cutting or heating, they associated slowly, and the association times were compatible with the times during which healing was possible.

CONCLUSIONS

In summary, a novel strategy was proposed in this article to obtain supramolecular elastomers associated by self-complementary and complementary multi-hydrogen bonds based on linearly and branched carboxylic-terminated PDMSs. SESi showed a real rubberlike viscosity and elastic properties and also self-healing properties at room temperature; this was mainly due to the multi-hydrogen-bond association and the soft chain of the PDMS.

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