Crosslinking mechanism of supramolecular elastomers based on linear bifunctional polydimethylsiloxane oligomers

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ABSTRACT: Supramolecular elastomers (SESis) were synthesized via a simplified synthesis route on the basis of a linear bifunctional polydimethylsiloxane. Compared with previous synthesis methods, the structure of the product was much clearer. The ^{1}H-NMR titration results show that the hydrogen-bond associations in SESis were relatively weak. During ^{1}H-NMR reaction monitoring, the viscosity analysis of SESis and the model reactions demonstrated a previously neglected covalent crosslinking reaction not only during the reaction process but also during the postprocess; this led to a hybrid network, that is, covalent crosslinking and hydrogen association, in SESis. This finding explained the poor solubility of the SESis, and it provides us with an important way to controllably synthesize this material and adjust its properties. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43385.

INTRODUCTION

In a traditional vulcanizate, such as natural rubber, macromolecular chains are linked with each other by a covalent network to form a robust crosslinking network that endows elastomers with good mechanical properties.[1] These crosslinking networks are permanent because of the irreversibility of covalent bonds. In recent years, the introduction of hydrogen bonds to the polymer system has been actively used to prepare novel supramolecular elastomers (SESis).[2–7] These SESis usually show some interesting properties, such as self-healing and reprocessability, because of the dynamic nature of the hydrogen bond and the special crosslinking networks, which differ from those in the vulcanizate.

The application of multiple hydrogen-bonding units, such as 2-ureido-4[^{1}H]-pyrimidinone, as associating groups in bifunctional or multifunctional molecules is a highly developed approach to the preparation of SESis.[8–10] Strong hydrogen-bonding interaction between the moieties can effectively link the polymer chains. Additionally, the noncovalent interaction (e.g., π–π stacking) between bonded moieties can result in a crystalline domain or microphase separation; these can act as crosslinks.

Another approach to the generation of SESis was reported by Guan and coworkers.[11–14] In the bulk material, a two-phase morphology, which is similar to that of a thermoplastic elastomer (TPE), was observed. Hydrogen bonds were introduced into the soft segments. As a result, the proper adjustment of the traditional TPEs led to the combination of the TPEs' mechanical properties with the supramolecular material's dynamics and healing capabilities.

Recently, a new kind of SESi with a hybrid crosslinking network was reported.[15–17] This material was prepared via a two-step reaction of fatty acids (a mixture of mono-, di-, and tri-acids), diethylene triamine (DETA), and urea. A variety of urea derivatives was generated; this formed different kinds of hydrogen-bonding interactions between the polymer chains and efficiently prevented crystallization. The fatty acids have a relatively high functionality (>2). Hence, a hybrid network consisting of hydrogen bonds and covalent bonds was constructed. Compared with the two strategies mentioned earlier, the crosslinking network in this material was much closer to that in the vulcanizate. There was no doubt that this system provided us with a novel approach for the design and preparation of SESis. However, because of the complexity of the composition of the fatty acid and the reaction involved, the crosslinking mechanism and the cooperation of covalent crosslinking and hydrogen-bonding crosslinking are still not clear, and the application of this approach is restricted.

Additional Supporting Information may be found in the online version of this article.
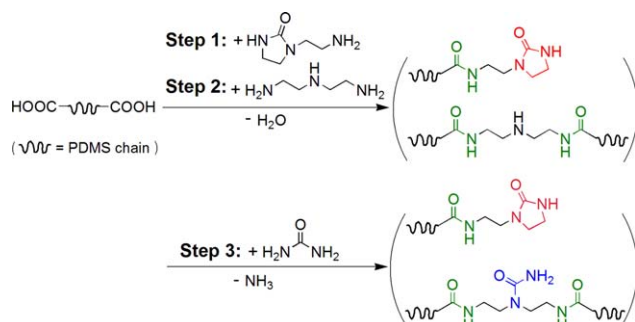
Scheme 1. Reaction of the (A) primary amine and (B) secondary amine with urea. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Scheme 3. Chemical structures of EI, UDETA, and 11DU.

In our previous study, we found that with bifunctional carboxyl-terminated polydimethylsiloxane (PDMS-COOH$_2$), we successfully obtained SESis that exhibited rubberlike properties at room temperature.[18,19] Compared with the use of a mixture of mono-, di-, and tri-acids, the use of bifunctional linear oligomers is a more controllable synthesis route; it could help us to study the reaction mechanism and crosslinking structure in this system. We also studied the relationship between the mechanical, rheological, and self-healing properties of this material and the polydimethylsiloxane (PDMS) chain length in detail; this provided us with guidance for adjusting the properties of the SESis. Moreover, because of the acceptable vapor transition rate and water absorption rate of this material, we attempted to use it as a medical material for wound healing.[20]

Because of the absence of tri-acid, intrinsic covalent crosslinks could be avoided. However, we were not sure as to whether a covalent crosslink could be formed during the synthesis process and what role covalent crosslink would play in this system. In addition, the reaction with urea (Scheme 1) was relatively complex because both the primary amine and secondary amine were present in the product of amidation (excessive DETA was added). The 1,3-dialkyl urea and monoalkyl urea, generated from primary amine, may have caused some difficulties in the analysis of the crosslinking mechanism. To prevent the effect of the primary amine, we investigated a simpler system, in which 1-(2-aminoethyl)−2-imidazolidinone (UDETA) was used to introduce imidazolidone groups, and the stoichiometry of the reagents in amidation was adjusted. We expected that the analysis of this simplified system could help us figure out the crosslinking mechanism of this kind of SESi. We believe, on the
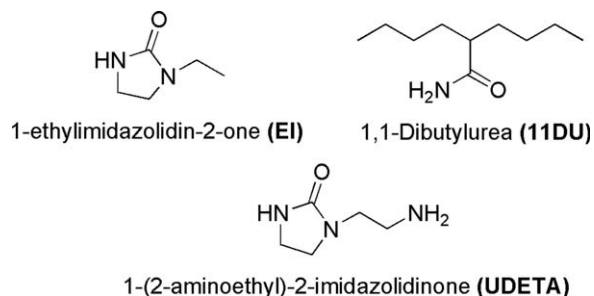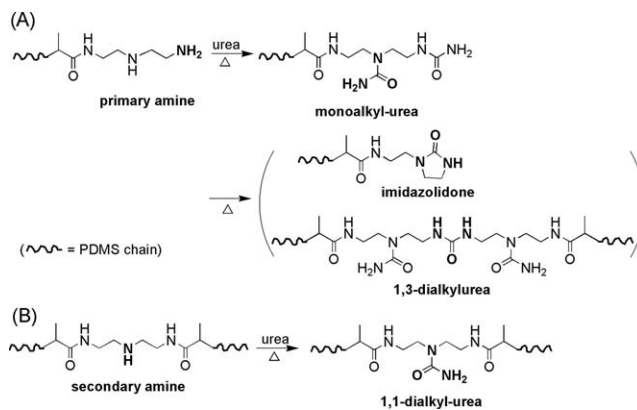
basis of a deeper understanding of the reaction and the crosslinking mechanism, we can synthesize SESi with a more controllable structure and tunable properties and then further develop this kind of SESi.

In this article, we report a three-step synthesis of SESis based on PDMS-COOH$_2$, UDETA, DETA, and urea. (Scheme 2) The bond strength of different hydrogen bonds in this system was measured by ^{1}H-NMR titration. We analyzed the reaction mechanism in detail through the monitoring of the reaction with several methods. Moreover, the dynamic mechanical properties of the samples with different postprocessings were evaluated. On the basis of these results, a more appropriate crosslinking mechanism was proposed.

EXPERIMENTAL

Materials
1-Ethylethylene diamine, N-methyl propionamide (MA), potassium cyanate, urea, di-n-butyl amine, and DETA were supplied by Aladdin Reagent Co., Ltd. (Shanghai, China).
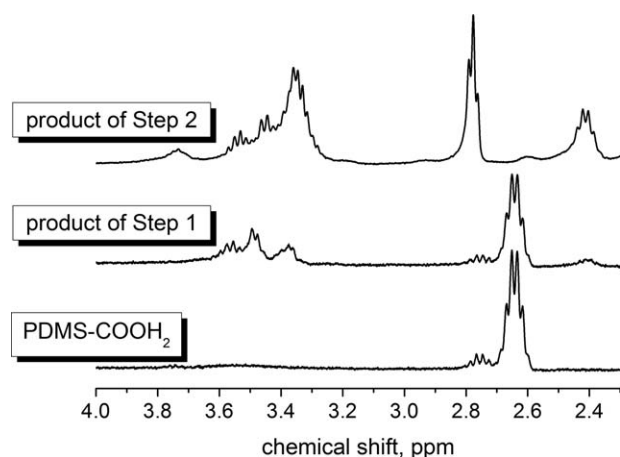
Synthesis Procedures
Linear PDMS-COOH$_2$ was prepared as previously described.[19] An SESi was synthesized via a three-step synthesis process, as presented in Scheme 2; this was similar to the route reported by Leibler et al.[16] Briefly, PDMS-COOH$_2$ reacted with UDETA in step 1 to introduce imidazolidone groups and were then reacted with DETA in step 2 to introduce secondary amines and increase the molecular weight. In step 3, 1,1-dialkyl urea was formed as a result of the reaction between amine and urea. The detailed synthesis process of SESi, 1-ethylimidazolidin-2-one (EI), UDETA, and 1,1-dibutyl urea (11DU), as shown in Scheme 3, can be found in the Supporting Information.

Characterization
IR spectra were recorded with a Bruker Vertex 70 Fourier transform infrared spectrometer. High-resolution mass spectrometry was performed on an Agilent 1290/maXis Impact instrument (Bruker, Germany) with methanol as the solvent. ^{1}H-NMR spectra were collected with a Bruker Avance III-400 (400-MHz) spectrometer with CDCl$_3$ as the solvent.

The association constant of self-association (K_{AA}) and the association constant heteroassociation of hydrogen bonds were

1-ethylimidazolidin-2-one (EI)   1,1-Dibutylurea (11DU)

1-(2-aminoethyl)-2-imidazolidinone (UDETA)

Scheme 2. Synthesis and structure of SESi.

Figure 1. ^{1}H-NMR spectra of the PDMS-COOH$_2$ and the products of steps 1 and 2.

Figure 2. (A) ^{1}H-NMR spectra at 25 °C of 11DU (from 0.1 to 1.1 mol/L). (B) Fitted plot of the chemical shift change of —NH$_2$ in 11DU.

determined by concentration-based NMR titration. CDCl$_3$ was used as the solvent. The data were analyzed by least square fitting methods. Different fitting formulas were used for different hydrogen-bonding couples. All titration experiments were processed at 25 °C.

Gel permeation chromatography (GPC) was performed with a Waters 515 HPLC pump (Waters) equipped with a Shodex K-G guard column and a Shodex K-804L chromatographic column. Detection was achieved with a Waters 2414 refraction index detector, and the samples were analyzed at 30 °C with chloroform as the eluent at a flow rate of 1 mL/min. The instrument was calibrated with low-polydispersed polystyrene standards.

An RPA 2000 rubber process analyzer (Alfa Technologies) was used for rheological temperature sweeps (30–160 °C). The dynamic temperature sweep was performed at a strain amplitude of 3% and a frequency of 1 Hz.

RESULTS AND DISCUSSION

Synthesis of the SESis

In our previous work,[19,20] we reported a two-step process to prepare SESis. First, PDMS-COOH$_2$ was reacted with an excess of DETA, with both secondary amine (—NH—) and primary amine (—NH$_2$) groups present in the oligoamide. Second, the —NH$_2$ group reacted with the urea to form monoalkyl urea, and at higher temperature, monoalkyl-urea was transformed into imidazolidone derivatives and a small amount of 1,3-dialkyl urea derivatives [Scheme 1(A)]. The —NH— groups reacted with urea to form 1,1-dialkyl urea [Scheme 1(B)].

In this study, we used UDETA to introduce imidazolidone derivatives. The stoichiometry of carboxyl acids (—COOH) and primary amine (—NH$_2$ in UDETA and DETA) was 1:1. Carboxyl acids were shown not to have reacted with secondary amine (—NH—).[15] According to the ^{1}H-NMR spectra (Figure 1), at the end of step 2, the amount of unreacted carboxyl acids was very small, and no peak for —CH_2—NH$_2$ (2.67 ppm) was observed. We inferred that the primary amine was barely present in the product of step 2. As illustrated in Scheme 1, the reaction between the primary amine and urea was much more
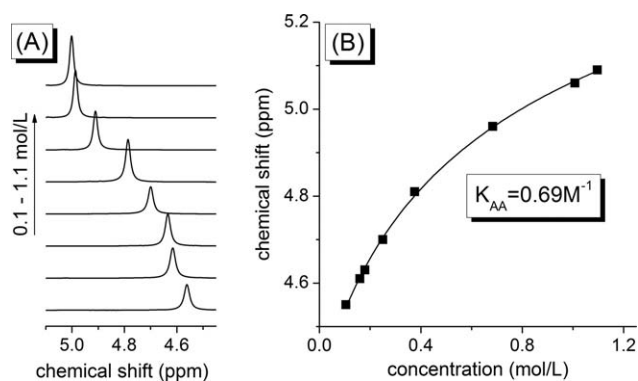
complex than that between the secondary amine and urea. Therefore, the reaction in step 3 was simplified here: urea decomposed into ammonia and isocyanic acid, and these reacted with a secondary amine to form 1,1-dialkyl urea. The formation of monoalkyl-urea and 1,3-dialkyl urea was neglected.

When we adjusted the UDETA fraction (x) and DETA fraction (y; $x/2 + y = 1$) in the reaction, the properties of the final product varied significantly. When $x = 2$ and $y = 0$, the final product was still liquid, with a viscosity that was higher than that with PDMS-COOH$_2$. When $x = 0$ and $y = 1$, the final product was an elastomer with weak stickiness. According to our previous work, x always needs to be equal to 0.15 to yield a final product with the appropriate properties.

Strength of the Hydrogen Bonds

The strength of the hydrogen bonds in the SESi matrix was characterized via ^{1}H-NMR titration. The chemical shifts of the protons implicated in the hydrogen bonds showed a concentration dependence. The observed chemical shift in the rapid-change system was a weighted average between the chemical shift of the free-state and that of the associated-state.

In the SESi reported here, three basic hydrogen-bonding moieties were present, namely, the amide group, 1,1-dialkyl urea, and imidazolidone. The characterization of a particular type of hydrogen-bonding interaction in the SESi matrix appeared to be difficult because of the complexity of the hydrogen-bonding interaction. To address this problem, three compounds, EI, 11DU (Scheme 3), and MA, were used as model systems for hydrogen bonding in the SESis.

All titration experiments were performed in CDCl$_3$, a nonpolar solvent. Figure 2(A) shows the change in the chemical shift of
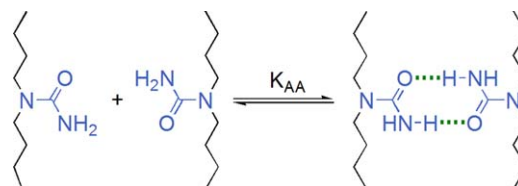
Scheme 4. Self-association of 11DU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Association Constant (M^{-1}) in CDCl$_3$ on the Basis of ^{1}H-NMR Titration

|	MA	11DU	EI
MA	0.24	—	—
11DU	—^{a}	0.69	—
EI	—^{a}	7.39	3.88

11DU. As the species concentration increased from 0.1 to 1.1M, the proton peak of —NH— shifted to a lower field (from 4.55 to 5.09 ppm); this indicated the transformation of free —NH$_2$ to hydrogen-bonded —NH$_2$ (Scheme 4). After we fitted the titration curve, K_{AA} of 11DU in CDCl$_3$ was determined to be 0.69 M^{-1}. More association constant testing results are listed in Table I, and the titration curves are shown in the Supporting Information (Figures S7–S11). The association constants of all of the hydrogen bonds ranged from 0.1 to 10 M^{-1}. The hydrogen bonds between MA and EI/11DU were very weak; this might have been because the imidazolidone groups or 1,1-dialkyl urea groups preferred to form bivalent hydrogen bonds with themselves rather than form monovalent hydrogen bonds with amide groups.

For some compounds, the association constants of self-association and hetero-association were close; this affected the accuracy of the measurement. Nevertheless, our results still show that compared with the multiple hydrogen bonds introduced into supramolecular materials, all of the hydrogen bonds we measured were weak, even too weak to be detected. Although the synergistic effect of two or more hydrogen-bonding groups may lead to stronger interactions in the SESi matrix, a large number of hydrogen bonds will form a supramolecular network. We still doubt that the supramolecular network based on these hydrogen bonds is strong enough to endow the material with good elasticity. That is, we can reasonably assume that covalent crosslinks also exist in SESis based on a bifunctional oligomer.

Covalent Crosslinking during Synthesis

As mentioned earlier, after a complete reaction between the carboxyl acids and primary amine (—CH$_2$—CH$_2$—NH$_2$), the secondary amine (—CH$_2$—CH$_2$—NH—CH$_2$—CH$_2$—) became the major reactive group in the reaction system. We believe that the reaction between the secondary amine and urea led to a covalent crosslinking structure.

To verify our hypothesis that some type of covalent crosslinking structure was formed in the SESis, a model reaction under
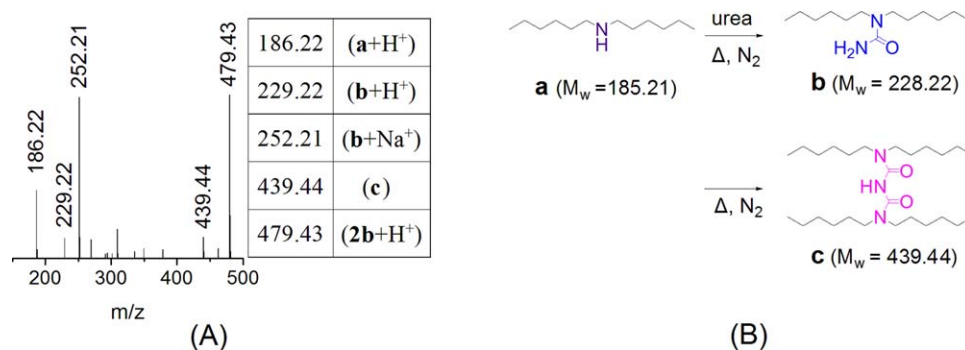

Figure 3. (A) High-resolution mass spectrum for the product of the model reaction. (B) Structure and molecular weight of 1,1-dihexyl urea and biuret. Δ = heating, the reaction carried out at 160 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
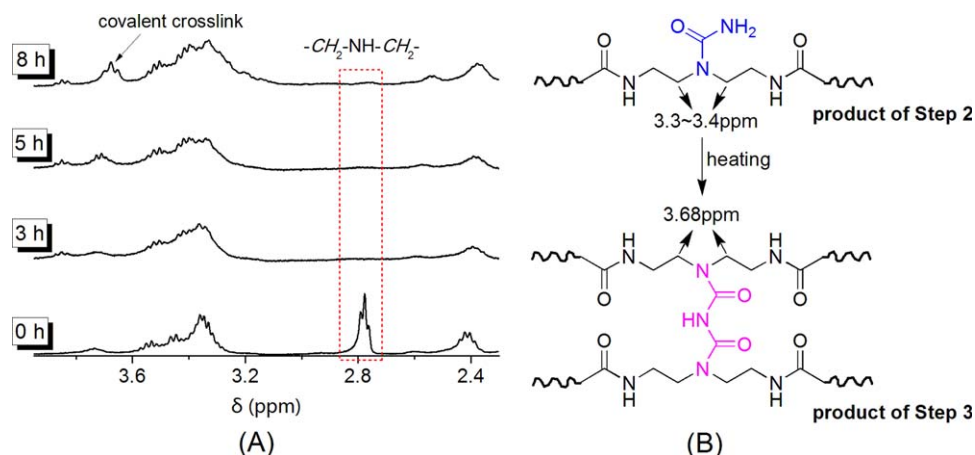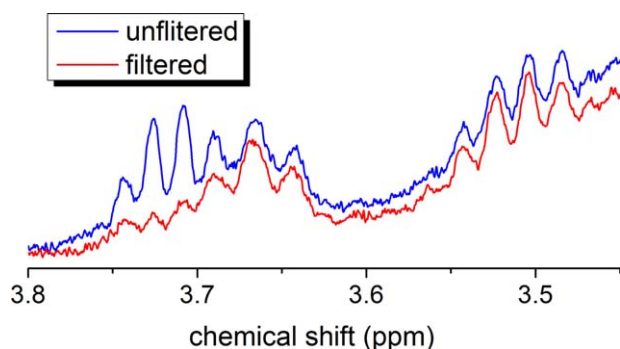

Figure 4. (A) ^{1}H-NMR spectra of the samples collected in step 3. (B) Transformation from 1,1-dialkyl urea to biuret and the chemical shift of —CH$_2$—N—CH$_2$— in these structures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
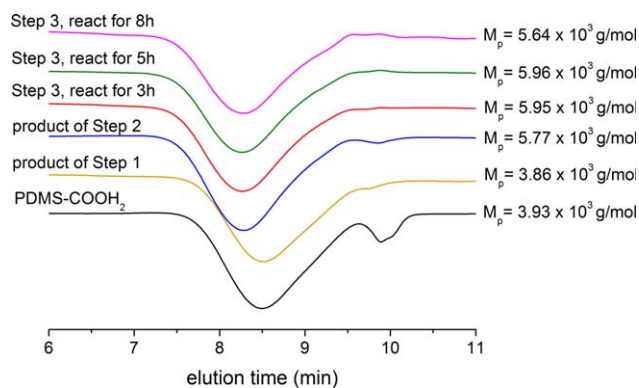
Figure 5. Molecular weight distribution of the PDMS-COOH$_2$ (black), the product of Step 1 (yellow), the product of Step 2 (blue), and the sample collected in step 3 at 3 h (red), 5 h (green), and 8 h (pink). M_p = peak molecular weight. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. ^{1}H-NMR spectra of the sample collected in step 3, unfiltered (blue) and filtered (red). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

similar conditions was constructed. Therefore, 1 mol of dihexylamine was reacted with 2 mol of urea at 160 °C under nitrogen for 5 h. The crude product was analyzed by high-resolution mass spectrometry [Figure 3(A)]. A biuret compound [illustrated in Figure 3(B)] with a weight-average molecular weight (M_w) of 439 was detected; this indicated that a covalent link between two dihexylamine formed under such conditions. We

Table II. Postprocess Conditions of the Different SESi Samples

|	Temperature (°C)	Time (h)	Atmosphere
SESi-1	50	24	Vacuum
SESi-2	100	24	Air
SESi-3	120	24	Air
SESi-4	120	48	Air

also noted that the main component of the crude product was 1,1-dihexyl urea (M_w = 228); this indicated that even when the reaction forming the biuret occurred, its extent was insignificant. As we determined earlier, a high-temperature reaction for a long period of time was necessary to obtain a material with acceptable mechanical properties.

Moreover, to monitor the development of the crosslinking network, the samples were collected from the flask at different times during step 3. The ^{1}H-NMR spectra [Figure 4(A)] showed that the secondary amine completely reacted at an early stage of the reaction (the peak at 2.78 ppm disappeared), at which time the product still flowed slowly. As the time progressed and the temperature increased, the fluidity of the product decreased, such that after 8 h, a sticky elastic material was obtained. Meanwhile, the peak for the biuret (ca. 3.70 ppm) was augmented, and the peak for 1,1-dialkyl urea (3.3–3.4 ppm) was weakened; this indicated the transformation from 1,1-dialkyl urea to biuret [Figure 4(B)]. Therefore, a higher temperature and a longer reaction time led to a higher crosslinking density, which was necessary to yield a stable elastic material.

Figure 5 shows that in step 3 of the synthesis process, the molecular weight measured by GPC first increased and then decreased. We interpreted this trend as evidence for the development of a covalent crosslinking network. At an early stage of the reaction, only a small amount of the covalent crosslinking structure formed, and the polymer chain propagated but was still soluble in chloroform. A rise in M_w could be detected at this stage. At the later stage, a more complete network formed; the crosslinked portion of the sample only swelled in chloroform and was filtered out before the GPC test. What we detected here was the M_w for the noncrosslinked part. This
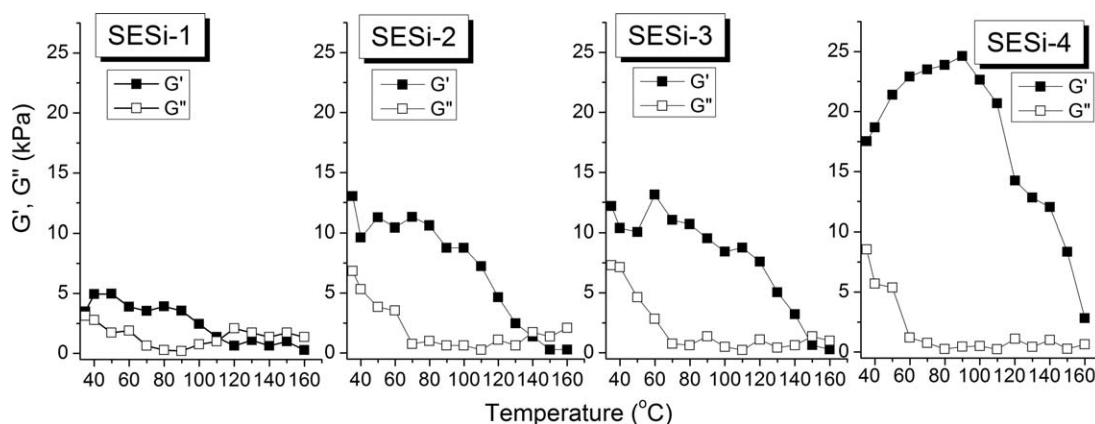
Figure 7. Temperature dependence of G' and G'' for the SESi samples (SESi-1–SESi-4) dried under different conditions.
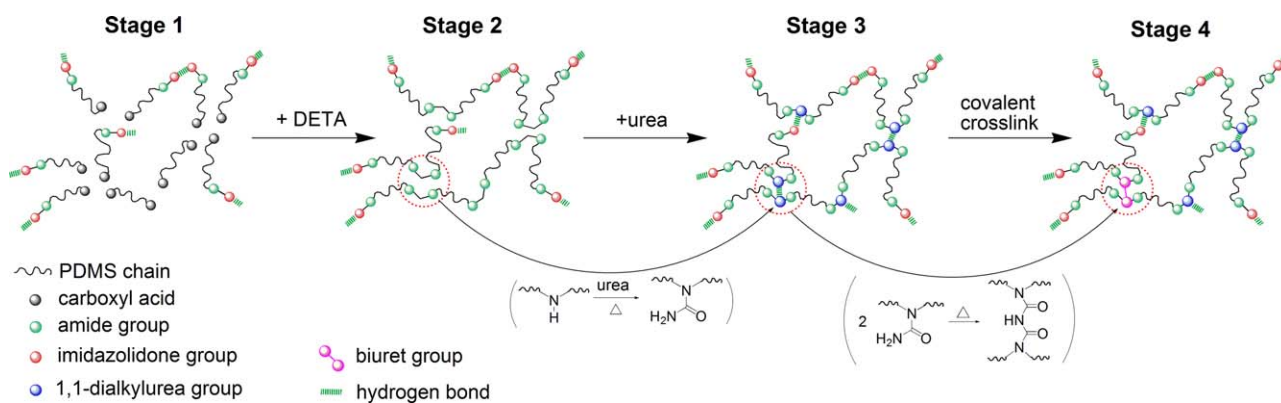
Figure 8. Development of a crosslinking network in SESi. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interpretation was also supported by ^{1}H-NMR spectroscopy (Figure 6).

Covalent Crosslinking during the Postprocess

The drying time and temperature also affected the final properties of the SESis. Here, we showed that the change in the viscoelastic properties to emphasize that the reaction between groups on the polymer chains caused the covalent crosslinks. The viscoelastic properties of the different SESi samples according to the conditions listed in Table II were measured to evaluate the development of a covalent crosslinking network during the postprocess. For SESi-1, this product was dried in a vacuum oven at a low temperature to ensure that water was removed. Figure 7 shows the evolution of the storage modulus (G') and loss modulus (G'') with increasing temperature. For all of the specimens, G' was greater than G'' at low temperature; this showed that this material exhibited an elastomer behavior. When the temperature was higher than a certain value, G' became less than G''; this showed that at a high temperature, this material behaved more like a viscous substance. Moreover, a higher drying temperature and longer time led to a higher transition temperature. For SESi-1, the transition temperature was approximately 110 °C, but for SESi-4, G' was still greater than G'' at 160 °C.

Compared with a covalent bond, the hydrogen bonds were much weaker and were much more sensitive to temperature. For the hybrid crosslinking network that consisted of covalent bonds and hydrogen bonds, heating resulted in the destruction of the crosslinking network. At the gelation point, which corresponded to the transition from a material without permanent elasticity to a material with permanent elasticity, G' and G'' were identical.[21] Because the number of crosslinking points, including both covalent crosslinking and noncovalent crosslinking points, was fixed, increasing the degree of covalent crosslink made the network more stable at a high temperature and resulted in a higher transition temperature. The solubility in chloroform of different samples also reflected the development of the covalent crosslinks (Figure S12, Supporting Information).

Hence, we believe that the temperature dependence of the transition temperature and modulus of the SESis was due to the evolution of covalent crosslinking. That is, drying the product at a high temperature promoted the further development of a

covalent crosslinking network. The viscoelastic properties reported here are different from those reported in ref. 19. Compared with our previous work, we intentionally shortened the reaction time of step 3 to control the development of a covalent network during the synthesis process. Thus, the development during the postprocess became prominent, and this influenced the mechanical and viscoelastic properties.

On the basis of our analysis of the results, the construction of a crosslinking network in the SESis was a four-stage process (Figure 8). In stage 1, a small quantity of hydrogen-bonding moieties, that is, amide groups and imidazolidone groups, were grafted to the PDMS chain; the molecular weight and functionality were still unchanged, and the viscosity increased slightly. In stage 2, the reaction between the oligomers and DETA led to a rise in both the molecular weight and functionality after a complete amidation, and the viscosity rose significantly. In stage 3, the secondary amine reacted with urea and turned into 1,1-diakyl urea, and a sticky viscoelastic solid with poor flowability was obtained. In stage 4, part of 1,1-diakyl urea further reacted to form a biuret structure that acted as a covalent crosslink. Finally, a hybrid crosslinking network, which consisted of association of hydrogen bonds and covalent crosslinking, was constructed, and a stable elastic material was formed.

It is necessary to state that, although we found the covalent crosslinking structure generated during synthesis and postprocessing, it was difficult to control the covalent crosslinking degree precisely. (We could only avoid or imprecisely control covalent crosslinking through the adjustment of the reaction time and temperature) Actually, we believe that the generation of covalent crosslinking at high temperature should be avoided because of the uncertainty of the reaction degree. To systematically analyze the relationship between the covalent crosslinking and the properties of this material, we need to find a better way to control the covalent crosslink, which is the issue we will study next.

CONCLUSIONS

We have presented a detailed investigation on the crosslinking mechanism and hydrogen-bonding interactions of novel SESis. A simplified and easily controlled synthesis route was used.

Because of the absence of primary amine, the formation of monoalkyl urea and 1,3-dialkyl urea was avoided.

We believe that three types of basic hydrogen-bonding moieties existed in this system, namely, 1,1-dialkyl urea, amide group, and imidazolidone group. As revealed by the ^{1}H-NMR titration experiment on three well-selected compounds used to simulate the hydrogen-bonding interactions, the hydrogen bonds in this system were relatively weak and were, thus, incapable of constructing a stable crosslinking network.

^{1}H-NMR spectroscopy and GPC were used to monitor the synthesis process and revealed that a covalent crosslinking structure was formed in this material. A model reaction with dihexylamine and urea as model compounds defined the structure of the covalent crosslinking, that is, the organic biuret. The viscoelastic properties of the SESi specimens with different heat-treatment histories indicated that the reaction between the groups on the polymer chains went on to increase the degree of covalent crosslinking.

In conclusion, we found that the reaction between the polymer chains, not mentioned in previous work, could produce covalent crosslinks. Hence, a hybrid crosslinking network existed in this material. We believe that controlling the ratio of hydrogen bonds and covalent bonds in this network is an important method for balancing the mechanical properties and self-healing properties of this material.

ACKNOWLEDGMENTS

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