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A Surprise from 1954: Siloxane Equilibration Is a Simple, Robust, and Obvious Polymer Self-Healing Mechanism

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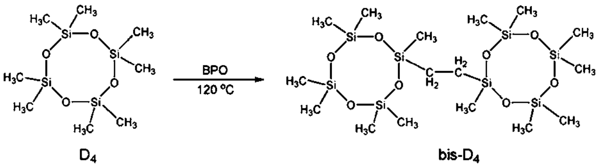
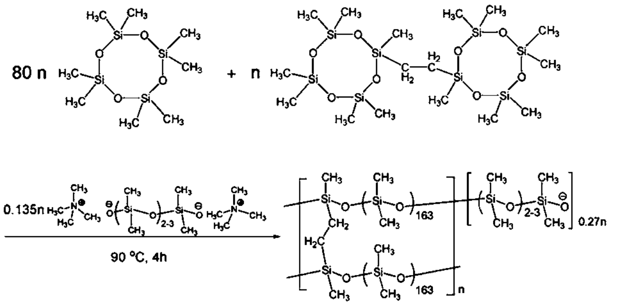
ABSTRACT: Tetramethylammonium silanolate-initiated ring-opening copolymerization of octamethylcyclotetrasiloxane (D_4) and bis(heptamethylcyclotetrasiloxanyl)ethane (bis-D_4) renders cross-linked network polymers that contain ethylene bridges and active silanolate end groups. These "living" reactive anionic species are not neutralized by ambient atmosphere exposure (are stable to water, oxygen, CO_2) and promote thermally activated equilibration among different network isomers and cyclic oligomers. The cross-link density of these living networks can be controlled by the ratio of D_4:bis-D_4, and the density of active chain ends is determined from the initiator:monomer ratio. We report that samples prepared with particular ratios of initiator:D_4:bis-D_4 can be cut with a sharp knife, even into two pieces, and can heal by siloxane equilibration to restore the original strength of the silicone sample. Fracture toughness measurements were carried out and revealed complete (mechanical) healing. Broken and healed samples generally failed in locations other than the initially cracked region. We call attention to publications and patents from the 1950s that suggest that this self-healing behavior was likely obvious 60 years ago.

Self-healing organic polymer materials, which have the structurally incorporated ability to repair damage, are currently subjects of active research.[1−12] The design approaches to materials of this type can be divided into two types: (1) the storage of healing agents in the materials (adhesives) that are released upon damage and (2) the use of a material that contains reversible bonds that can be activated subsequent to damage. Advantages and disadvantages can be ascribed to both approaches.[2,3,7,11] Systems of the first type have been described as "autonomic" and are generally designed for the healing response (release of adhesive) to function a single time at the working conditions of a host material. Those of the second type involve organic or coordination chemistry and reversible addition/elimination or association/dissociation reactions that mediate polymerization/depolymerization events. These systems are designed so that healing of damage can be repeated many times; however, the kinetics of these reactions in solid polymers at use temperatures requires activation of the damaged area with heat or light. Here we report an example of the second type based on the anionic equilibration of cross-linked poly(dimethylsiloxane).

Octamethylcyclotetrasiloxane (D_4) and 2.5 wt% benzoyl peroxide (BPO) were heated together with stirring at 120 °C for 2 h. The resulting yellow solution was passed through alumina to remove BPO-derived byproducts and yield a clear mixture of D_4 and 2.4 wt% bis(heptamethylcyclotetrasiloxanyl)ethane (bis-D_4) (eq 1).[13−16] The anionic polymerization initiator, bis(tetramethylammonium)oligodimethylsiloxanediolate[17] (0.2 wt%), was added to (dissolved in) this monomer/cross-linking agent, and the solution was poured into various shaped molds and heated at 90 °C for 4 h (eq 2). Clear silicone elastomeric monoliths were easily removed from the molds.



(1)



(2)

The product of eq 2 exhibits a crystallization temperature at −76.3 °C, a T_g of −129.5 °C (cooling), a melting endotherm at −44.6 °C,[18] and Young's modulus of 0.389 ± 0.019 MPa.[19] The repeat unit structure shown in eq 2 is based on the ratios of monomer, cross-linking agent, and initiator and is approximate; cyclic oligomers are present as well.[20] This elastomer can be considered a "living polymer network" containing reactive tetramethylammonium dimethylsilanolate end groups that can react with network chains to restructure the cross-links in the network and catalyze the equilibration of cyclic oligomers with the network.

Figure 1a shows a sample of living silicone rubber that was prepared as described using a 20 mL scintillation vial as a mold. The diameter of the cylindrical sample is 2.35 cm, and the length is ~1 cm. This sample was cut in half using a razor blade (Figure 1b) and rejoined by wrapping the perimeter with Teflon plumbing tape. This assembly was heated in an oven at

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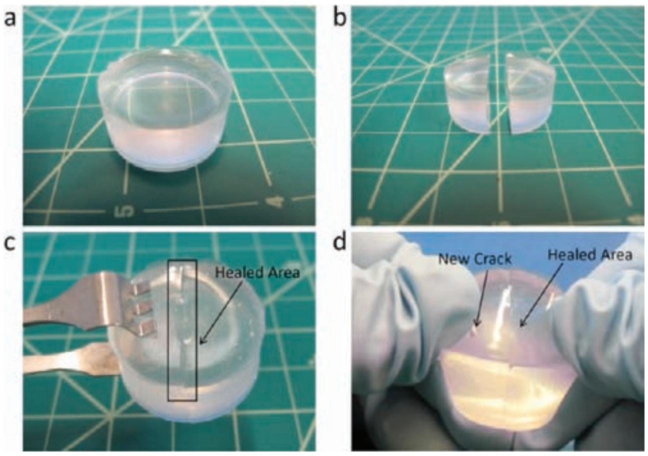


Figure 1. The original cylindrical sample (a) was cut in half using a razor blade (b). Twenty-four hours after healing at 90 °C (c), the healed sample was deformed by hand, and cracking occurred at a place other than the healed area (d).

90 °C for 24 h,[21] the healed sample (Figure 1c) was subjected to bending by hand until it split—in a different location than the initial razor blade cut (Figure 1d). Many repeated experiments with different shaped objects revealed the same qualitative result: that the healed interface had strength comparable to the cohesive strength of the undamaged elastomer.

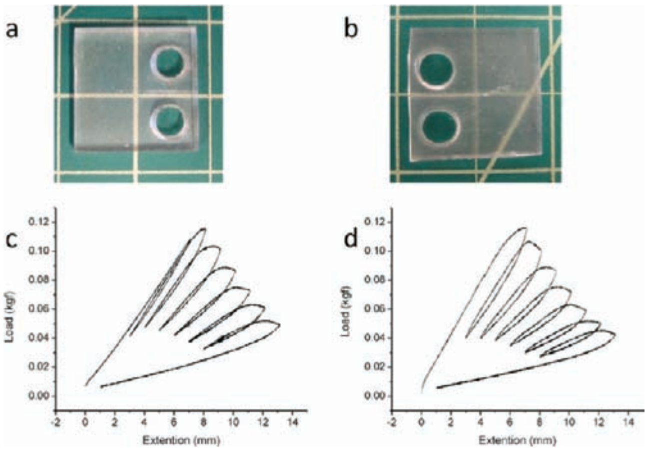


Figure 2. Photographs indicating the geometry of the original (a) and the cracked-and-healed sample (b) used for fracture toughness measurements. Load versus extension data for the original (c) and the cracked-and-healed sample (d).

Fracture toughness measurements[22] were carried out in an attempt to quantify differences between original and healed samples. Figure 2 shows photographs of an original and a cracked-and-healed sample as well as load versus extension data for two samples. Fracture toughness data (G_{IC}, the energy per unit area of crack surface or critical strain energy release rate) for the two samples are indistinguishable ($G_{IC} = 61 \pm 14$ J/m^2 for the original sample and 70 ± 12 J/m^2 for the cracked-and-healed sample). Close examination of the new failed surface of the cracked-and-healed sample reveals that fracture did not occur along the healed seam. The experiment described in Figure 3 was carried out with the objective of offering exceptionally strong qualitative evidence of self-healing. A dog bone-shaped sample was cut into pieces and remolded into the shape of a dog. The thermoplastic nature of this living cross-linked elastomer is obvious.

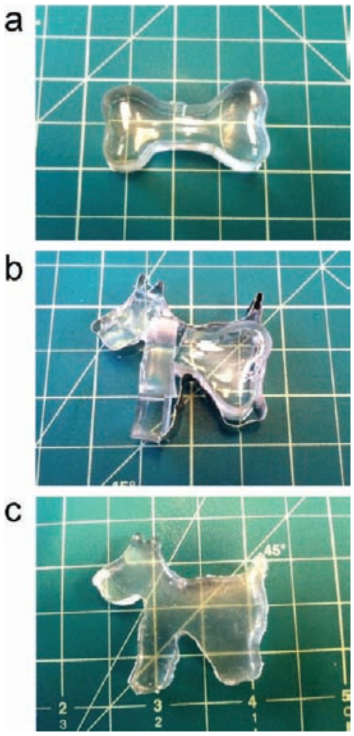
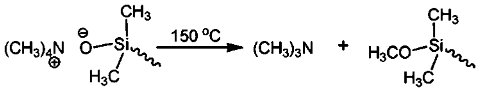


Figure 3. A dog bone-shaped sample (a) was cut into pieces (b) and remolded into the shape of a dog (c).

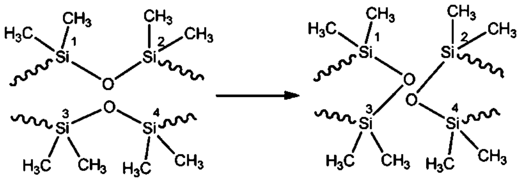
Several points concerning the chemistry of this self-healing silicone network warrant discussion. (1) We emphasize that it is not new. In fact, publications and patents from the 1950s suggest that this behavior would have been obvious at that time and that the experiments described here are simple extensions of reported work. The radical cross-linking of methylsilicones was used during World War II and was among the first preparative reactions using organic free radicals.[23,24] The α-silyl methyl radicals combine in good yield (eq 1) because they contain no β-C−H or β-C−C bonds; thus, disproportionation and fragmentation reactions do not compete. (2) The mechanism of the anionic polymerization of D_4 (which was also used during World War II) was detailed in a 1954 publication,[25] and copolymerizations of D_4 and bis-D_4 were described in 1959.[20] (3) The living nature of the polymerizations was well appreciated, as this was identified as the cause of poor thermal stability of silicone materials prepared by this method. Tetramethylammonium silanolates were devised as initiators because the living chain ends can be "decatalyzed" at 150 °C (eq 3), rendering the volatile base, trimethylamine.[20](4)



$$(CH_3)_4\overset{\oplus}{N}\ \overset{\ominus}{O}-\underset{H_3C}{\overset{CH_3}{Si}}\sim \xrightarrow{150\ ^\circ C} (CH_3)_3N + H_3CO-\underset{H_3C}{\overset{CH_3}{Si}}\sim \quad (3)$$

Any cross-linked dimethylsilicone elastomer could, in principle, be converted to a living one by the addition of basic catalysts, and there are many possible routes to a variety of networks. We chose the D_4/bis-D_4/silanolate system for multiple reasons: the ethylene bridges give hydrolytic stability, the cross-link density is easily controlled, there are no residual functional groups or catalyst, there is no excess of one or another functional group, the monomer is inexpensive, and the network is intrinsically living and at equilibrium upon polymerization.

A paper[26] published in 1954 with the title, "Chemical Stress-Relaxation of Polydimethylsiloxane Elastomers", tacitly predicts the results that we report here. The authors placed silicone networks under stress and measured the rates of stress relaxation. They showed that either acid[27] or base catalyzes stress relaxation and that a sample with no catalyst (one cross-linked by electron beam irradiation) did not relax its stress.[26] Those authors proposed a "catalyzed chain exchange reaction" as "a possible basis for a theoretical interpretation of this process" and attributed this proposal (eq 4) to "a private communication" with D. T. Hurd in April 1952.[28]



(4)

We have carried out various other types of "chemical stress relaxation" studies that are best described as reversible reshaping experiments. Figure 4a shows a disc-shaped sample of living D_4/bis-D_4 that was subsequently molded against an 1879 U.S. Liberty silver dollar (Figure 4b). A portion of this surface was remolded using a 1979 Susan B. Anthony dollar (Figure 4c). We emphasize that this reversible reshaping is due to chemical stress relaxation of a living network. If the sample is decatalyzed at 150 °C, these impressions are not made.

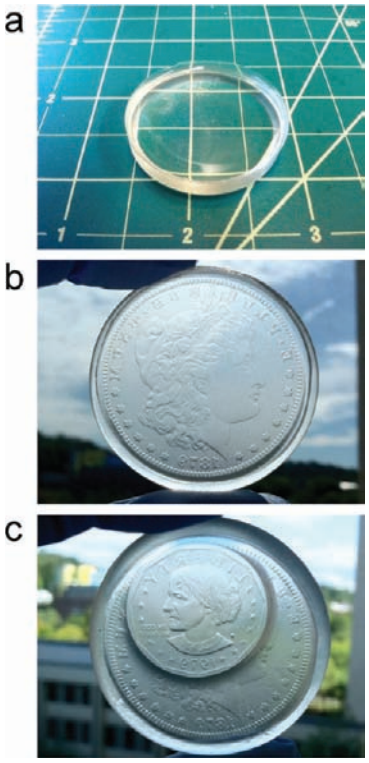


Figure 4. A disk-shape sample (a) was remolded with an 1879 silver dollar (b) and subsequently partially remolded with a 1979 dollar (c).

We conclude with three comments: (1) Our two previous publications[29,30] that have titles beginning with the words, "Rediscovering Silicones", point out that this broad and deep field of chemistry, materials science, and technology has been forgotten and is not part of current curricula. The simple (and old) chemistry used here to prepare truly self-healing materials emphasizes this point. (2) The remarkable and variable properties of silicones as well as their broad use as materials suggest that this simple self-healing mechanism will be broadly applicable. (3) In a sealed environment (the volatility of cyclic oligomers would require a barrier) at a high enough use temperature, this system would behave as an "autonomic" self-healing material.

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Notes

The authors declare no competing financial interest.

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(13) This ratio was determined using ^{1}H NMR (Bruker DPX 300 MHz) and assuming constant densities for D_4 and bis-D_4. The preparation of bis-D_4 and anionic polymerizations of mixtures of D_4 and bis-D_4 is described in several 1950s patents.[14−16]

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(17) Bis(tetramethylammonium)oligodimethylsiloxanediolate was obtained from Gelest. We also conducted experiments using tetramethylammonium hydroxide (Aldrich) that exhibited indistinguishable results.

(18) Differential scanning calorimetry was conducted using a TA DSC Q200 instrument. The sample was first heated to 60 °C, then

cooled to −150 °C, and finally heated to 60 °C again at a rate of 10 °C/min.

(19) Young's modulus was determined using ASTM D638 type V samples with a thickness of 1.46 mm (tensile tests). The living network was first cured and then punched into dog bone-shaped samples. Dimensions were measured using calipers. An Instron 5800 R fitted with a 50 N load cell was used. Five samples were tested at a constant cross-head speed of 10 mm/min at room temperature. An average Young's modulus of 0.389 ± 0.019 (standard deviation) MPa was obtained from linear slopes of the stress−strain curves within 10% strain. We note that the strain at break for the samples of this material is ~235%.

(20) Gilbert, A. R.; Kantor, S. W. *J. Polym. Sci.* **1959**, *40*, 35−58. This paper reports that 13−15 wt% cyclics are an equilibrium component of anionically polymerized D_4. This equilibration is discussed in detail in a book chapter on cyclic siloxane polymerization.[31]

(21) We have not carefully studied the conditions required for complete rehealing. Small incisions heal after 40 min at 90 °C. Samples heated at 105 °C healed smoothly and cleanly at a greater rate. The catalyst begins to decompose at 130 °C.

(22) Fracture toughness measurements were conducted using compact tension geometry according to ASTM D5045-99 at room temperature. The specimens were prepared by curing D_4 and bis-D_4 in the presence of catalyst in a custom-made glass mold with two tubes in the middle. An initial crack was made using a razor blade. The specimen dimensions, for example a width of 30.6 mm (W) and a thickness of 9.01 mm (B), were measured using calipers. An Instron 5800 R fitted with a 50 N load cell was used. The test method involved cyclic loading (at a cross-head speed of 1 mm/min) and unloading (at a cross-head speed of 1 mm/min) with an increase of 1 mm in extension for successive cycles, so that each cycle can be interpreted independently. Initial crack lengths (a) were determined using a camera at the beginning of each cycle. The values of a/W (should be greater than 0.2 and less than 0.8) were calculated to ensure the validity of the measurements. The cracked sample was put back into the mold with a thin piece of Teflon tape in the initial crack area and healed at 90 °C for 24 h. The fracture toughness G_{IC} (energy per unit area of crack surface or critical strain energy release rate) was determined by the ratio of the stored energy (the integration between the loading and the unloading curve) versus the propagated crack area. During the first cycle of the experiment for the original sample (see Figure 2c), the crack did not propagate. The data for cycles 3−7 of original sample and for cycles 2−7 of the cracked-and-healed sample were used to calculate the G_{IC} values reported in the text.

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