Soft Materials with Recoverable Shape Factors from Extreme Distortion States

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Bulk soft matter assemblies are of interest for the fabrication of stretchable devices.[1–7] Conformable material platforms for sensors and electronics that display apparent self-healing and recovery from cannulation and other penetrating interconnect processes are desirable.[8] Common natural and synthetic elastomers typically have modest stretchability and recovery (elongations in the range of 100%–800%) and are susceptible to penetration damage and tear propagation, as evidenced by low tear strengths.[9–11] Here, we report a synthetic pathway to a new class of highly deformable polymeric structures which are formally linear polymeric liquids that exhibit shape recovery properties. This development is enabled by a living polymerization that results in heterobifunctional poly(dimethylsiloxane) (PDMS) macromonomers of intermediate molecular weight, which in a second distinct step-growth polymerization, are converted to high molecular weight materials with elastomeric properties. While the homogeneous polymer systems exhibit recovery from very high elongations, elongations significantly greater than any previously reported for an elastomeric material (>5000%) are observed in nanocomposites.[12,13] No cross-linking has been detected by a variety of analytical techniques including the first example of selective gradient suppression NMR applied to a solid material. Elastomeric behavior is observed at temperatures greater than both the $T_g$ and $T_m$ of the polymer, suggesting that topological features associated with constrained interchain or intrachain entanglements, rather than covalent cross-linking or domain formation are operative. The exceptional elastic deformation and recovery of these polymers challenges conventional physical models for polysiloxane elastomeric behavior.

The majority of siloxane polymers is prepared by equilibrium ring-opening polymerization (ROP), which results in polymers with broad molecular weight distributions (polydispersity index (PDI) > 2.5) and curtails their ability to act as precise structural elements. Until now, elastomeric behavior in siloxanes has been induced by cross-linking ROP polymers produced by equilibration, utilizing a variety of techniques.[14] In the course of our earlier work on dendrimers,[15] we noted a low efficiency in generational growth based on hydroxysilylation of structural elements containing silicon–hydride (Si–H) and silicon–vinyl (Si–CH$_2$–CH$_3$) terminations. In general, the lack of efficiency can be attributed to stoichiometric imbalance at the reactive centers due to steric interference, phase separation, or divergent reaction pathways. The most obvious divergent reaction in this system is cyclization. While cyclization reactions are known in general for polymer systems,[16] in siloxane systems they have been studied only under equilibrium ROP conditions.[17]

In order to better understand the limitations of efficient formation of higher order siloxanes by hydroxysilylation, heterobifunctional macromonomers with Si–H and Si–CH$_2$–CH$_3$ at opposite ends of the polymer chain were studied. Linear polymerization of low molecular weight heterobifunctional macromonomers produced by hydrolytic condensation was attempted earlier using a hydrolysilation reaction, but only low molecular weight polymers were achieved.[18] After developing a new synthesis for heterobifunctional macromonomers,[19] we were able to demonstrate that the inability to achieve high molecular weight polymers in earlier reports was a consequence of the inability to generate macromonomers of sufficient purity and degree of polymerization to avoid divergent chain termination and cyclization reactions. Living anionic ring opening polymerization (AROP) of siloxanes has been reported in the development of well-defined monofunctional siloxane macromonomers, utilized, for example, in contact lenses where they satisfy mechanical property, hydration, and oxygen permeability requirements for corneal tissue.[20] We report a further advance in living AROP which allows access to heterobifunctional siloxane macromonomer structures with tunable functionalities that are unachievable by equilibrium and hydrolytic polymerizations (Scheme 1).

These heterobifunctional macromonomers are of satisfactory purity and molecular weight with intrinsic stoichiometric equivalence between reactive end groups. The heterobifunctional macromonomers reported here have number average molecular weights ($M_n$) ranging from 4000–50 000 Da and a PDI near unity. The macromonomers contain a vinyl group and a hydride...
group at the opposite ends of the siloxane, which were confirmed to be in a substantially 1:1 stoichiometric ratio using NMR. With a precise 1:1 stoichiometric ratio of complementary functionalities inherent on each polymer chain, the heterobifunctional macromonomer fits the ideal model for an A-B step-growth linear polymerization. In the presence of a homogeneous catalyst, such as a platinum complex, the vinyl and hydride end groups undergo an efficient intermolecular hydrosilylation reaction and the macromonomer attains an extremely high degree of polymerization (Scheme 2).

When practiced experimentally for a series of heterobifunctional macromers, the step-growth hydrosilylation polymerization unexpectedly yielded elastomeric bodies, despite the lack of an obvious cross-linking mechanism during the linear polymerization. Mechanical testing revealed that these polymer systems have high elongations in the range of 800–2500% (dependent on macromonomer molecular weight), good elastic recovery, while maintaining tensile strengths (0.2–0.3 MPa) characteristic of unreinforced siloxane elastomers (Figure 1). Dynamic mechanical analysis (DMA) of the polymers showed the transitions expected from a linear siloxane and did not suggest a cross-linked system.

These polymers were not amenable to direct methods of molecular weight determination. To investigate the minimum molecular weight requirements for elastomeric behavior of these polymers, a monofunctional reagent, vinylpentamethyldisiloxane, was added in different concentrations to the macromonomer polymerization to create a stoichiometric imbalance of reactive groups. This, at once, allowed for molecular weight control in linear A-B step-growth polymerizations and provided a basis for estimating the molecular weight at high conversions of macromonomer. The degree of polymerization, $D_p$, is described by the Carother’s equation: $D_p = \frac{1}{(1 - p)}$, where $p$ is the extent of polymerization.

| Siloxane Macromonomer ($M_w$) | Elastic Elongation (%) | Strain Recovery (1 Cycle; %) | Tensile Strength (MPa) |
|-------------------------------|-----------------------|----------------------------|------------------------|
| 3,700                         | 800                   | 100                        | 0.2                    |
| 14,800                        | 1150                  | 100                        | 0.3                    |
| 29,600                        | 2500                  | 100                        | 0.2                    |

Figure 1. Mechanical property measurements showed that the unfilled macromonomer systems yielded low strength polymers with elongations on the upper end of reported values for elastomeric materials. Strain recovery was measured by comparing the change in specimen length after stretching the polymers to 50% of their elongations at break for 10 min followed by 10 min of rest. The polymers showed excellent strain recovery under these conditions (see Figure SE, Supporting Information).

Figure 2. Step-growth polymerization of monodisperse heterobifunctional polysiloxane macromonomers. Molecular weight of a 15 000 Da macromonomer step-growth polymerization was measured directly by GPC up to the elastomeric behavior crossover point showing the dependency on end group stoichiometry. Polymer $D_p$ at end group stoichiometric ratios approaching the crossover point correlates closely with the theoretical $D_p$ values calculated from the modified Carothers equation: $D_p = \frac{1 + r}{1 - r}$.
conversion of end groups. The stoichiometric ratio of end groups is defined as 
\[ r = \frac{N_{PDMS_{hydride}}}{N_{PDMS_{vinyl}} + 2N_{vinylpentamethyldisiloxane}} \]
for A-B step-growth monomers. At \( p \) values near 100%, 
\[ D_r = \frac{(1+r)}{(1-r)} \]
which allows for specific molecular weights to be targeted. At an \( r \) value of 0.7 for a 15 000 Da macromonomer, a crossover between a high molecular weight material with negligible elastic recovery and an elastomer occurred. GPC \( M_n \) and \( M_w \) characterization of polymers with stoichiometric ratios approaching the crossover point show polydisperse materials with weight average molecular weight fractions exceeding 1 000 000 (Figure 2). Polymers above the crossover point merely swell in solvent and cannot be characterized by GPC.

As anticipated, cold-crystallization exotherms associated with traditional polysiloxanes were not appropriate for estimating step-growth polymer molecular weight or \( M_c \), since the ethylene bridges formed during step-growth polymerization resulted in segmental isolation and in fact narrowed the temperature range of the thermal transitions. Using a modification of the WATERGATE solvent suppression \(^1\)H-NMR technique (which achieves high sensitivity through selective suppression of the dominant methyl backbone signal) on \( r = 1.0 \) polymers swollen in \( d_8 \)-toluene, to the limits of detection (2 ppm), we observed no cross-linking which would have been evidenced by incomplete conversion of starting macromonomer end groups or formation of tertiary carbon species associated with the addition reactions of unsaturated species (Figure 3). Evidence of trace amounts of ethenyl linkages between silicon atoms formed from the dehydrogenative coupling of end groups was observed due to increased sensitivity of detection, but is a known minor hydrosilylation byproduct. Dehydrogenative coupling is a chain-extension process analogous to the principal hydrosilylation pathway. We were able to determine from the NMR analysis that the \( p \) for the A-B step-growth monomer is \( >0.995 \) and to extrapolate the number average molecular weight of the polymer to be at least 3 000 000 Da for the 15 000 Da macromonomer.

To improve the elastomer strength, surface-passivated silica nanoparticles were compounded into the macromonomers at loadings of 30 wt% followed by the platinum catalyzed step-growth polymerization. The nanocomposites formed have increased tensile strengths, in the range of 5–11 MPa, and unprecedented elastic elongations, exceeding 5000%, as macromonomer molecular weight increases to 15 000 Da or greater. These nanocomposites exceed the highest reported elongations of any elastomeric materials (Figure 4).

While a number of models can account for the elongation of these uncross-linked polymer systems, there appear to be none that can satisfactorily account for the recovery to original dimensions. Elastic recovery is usually associated with the entropy generated by the release of strain-induced crystallization or cross-linking restraints. Neither mechanism is available for these materials, suggesting that they are not “classical” elastomers. Cross-linking below the level of detection reported here is unlikely to account for the behavior of these materials.

There is a lively debate surrounding the role of knotting and entanglement on the nonlinear behavior of polymers. This investigation was not initiated to enter the debate, but...
Figure 4. Recovery from extreme distortion. a) When the macromonomers were reinforced with silica nanoparticles, the resulting nanocomposites displayed unprecedented elongations. Strain recovery was measured by comparing the change in specimen length after stretching the nanocomposites to 80% of their elongation at break for 10 min followed by 10 min of rest. This tensile set determination procedure (ASTM Standard D412) was performed on the nanocomposites for one and ten recovery cycles. Stress decay was determined by observing the change in stress after 1 min of stretching the nanocomposites to 80% of their elongation at break. b) The stress–strain curves for the nanocomposites. c) A red-dyed sample (left) extended to 4000% elongation (center) and recovery compared to a blue-dyed specimen of original dimensions (right).
computational studies on knotting in polymers\cite{31,32} as well as entanglement measurements\cite{31} suggest that the behavior of these high molecular weight polymers must consider these phenomena. We remark that in NMR studies of the elastomers reported here, the line broadening typically observed in conventionally cross-linked, solvent swollen macromolecular polymer networks was not observed and the spectral linewidths approach those of linear polymeric species in solution. These observations suggest that there are highly localized regions of consistent interactions within a given polymer chain at all concentrations and similarly at all elongations. Furthermore, swelling experiments for the elastomers reported here have calculated molecular weights between virtual restriction points of $\geq 40\,000\,\text{Da}$, exceeding the molecular weight of entanglement ($M_e$) of $12\,000–24\,000\,\text{Da}$ reported for polysiloxanes. These results appear consistent with permanent chain interchain and intrachain entanglement, rather than chemical cross-linking or chain entanglement trapped by cross-linking. It is also noteworthy for the discussion that a previous report of a relatively high elongation polysiloxane system was cross-linked in a solvent, reducing the opportunity for chain entanglement\cite{34}.

The new materials reported here are specifically polysiloxanes, derived from high molecular weight uncross-linked polymeric liquids that when formed into nanocomposites demonstrate exceptional elongations. These materials are readily manufactured and satisfy the structural requirements for long-term stretchable and implantable devices with integrated fluidics and electronics in soft tissue (Figure 5). The general principles of synthesis can be applied to other systems and invite further investigation.

**Experimental Section**

**Synthesis of Heterobifunctional Macromonomers:** An exemplary synthesis of monovinyl, monohydride terminated poly(dimethylsiloxane) with 50 repeat units is provided. Other molecular weight asymmetric heterobifunctional siloxane macromonomers were synthesized in an analogous manner by adjusting monomer to initiator ratios to control polymer chain length. Lithium vinyl(dimethylsilanol) (0.321 mol) in hexane (25 mL) was synthesized in situ from the reaction of methyl lithium and trivinyl-dimethyldisiloxane in a method analogous to previous work.\cite{15,35} (For the tagging experiments utilized in the NMR analysis, lithium butylvinylmethyldimethyldisiloxane was substituted.) Hexamethyldisiloxane catalyst (D$_2$) (16 g, 0.072 mol) was added to the reaction mixture, followed by the addition of DMF or THF (5 mL) to the solution as polymerization promoter. Upon $\sim 95\%$ conversion of monomer, the polymer was terminated with a slight excess dimethylchlorosilane (30 g, 0.328 mol). The solution was stirred overnight and washed three times with deionized water. The organic layer was dried with MgSO$_4$ and concentrated under vacuum (1 mm Hg) at 80 °C.

**Step-Growth Polymerization of Heterobifunctional Macromers:** A representative procedure of the step-growth polymerization of a 3700 Da monovinyl, monohydride terminated PDMS is provided. The heterobifunctional macromonomer (10 g, 0.01 mol) and platinum-divinyltetramethyldisiloxane catalyst (2 wt% Pt) solution in xylene (2 drops) were added to a scintillation vial and the mixture was mixed vigorously by shaking for 5 min. The mixture was poured into an aluminum pan and placed into an oven set at 80 °C for 1 h. Compounding and Sample Fabrication: In reinforced systems, 30 wt% of hexamethyldisilazane-passivated silica nanoparticles (20 nm) and platinum-divinyltetramethyldisiloxane catalyst were compounded in separate steps into the heterofunctional macromonomer using a FlackTek DAC 600.1 VAC programmable speedmixer at 2200 rpm for 5 min. The mixture was poured into a mold and heat cure in an oven at 80 °C for 1 h.

**Gel Permeation Chromatography (GPC):** Gel permeation chromatography (GPC) analyses. GPC data were collected in THF at 35 °C. Data were analyzed with a refractive index detector using a calibration made with polystyrene standards.

**Thermal Analysis:** Modulated differential scanning calorimetry (DSC) was performed using a TA Instruments Discovery DSC. Heating and cooling rates were 10 °C min$^{-1}$ over a range −150 to 200 °C.

**NMR:** All $^1$H solution state NMR analyses were carried out using a Bruker Avance III NMR spectrometer operating at 600 MHz. GPC data were collected on TopSpin 3.2 software. 10 mg samples of the elastomeric silicones were massed into precision 5 mm Wilmad probe and operating on TopSpin 3.2 software. All spectra were acquired at 298 K. 1D $^1$H NMR spectra were collected with using a gradient based “solvent” suppression technique, optimized to selectively suppress the methyl proton backbone signal and allow high-resolution spectra of low molar content species to be collected without receiver saturation from the otherwise dominant methyl proton backbone signal. The sequence used was a modification of the WATERGATE-W5$^{[16]}$ suppression sequence; Shaped PRESSaturation WATER suppression by Graident-Tailored Excitation using optimized WS pulse trains (SPR-WS-WATERGATE) developed by Lam and Simpson.$^{[17]}$ 2040 scans were collected with a total acquisition time (aq) of $\approx 2$ h per sample. 2 Hz exponential line broadening was applied to the Fourier transformed data sets.

**Mechanical Property Measurements:** Tensile and elongation testing of the samples was conducted at 20–22 °C according to ASTM D-412-80 test method using dumbbell configured specimens according to ASTM D-638 Type V (width: 3.18 mm; length: 9.53 mm; thickness: 2 mm) at a crosshead speed of 500 mm min$^{-1}$ using an Instron Universal Testing Machine model 3345. DMA of the samples was performed using a TA Instruments DMA Q800 at a frequency of 1 Hz and a strain amplitude of 10 μm. Heating rates were 3 °C min$^{-1}$ over a range −150 to 50 °C. Stress relaxation experiments were run under conditions comparable to those previously described.$^{[18,19]}$

**Swelling Experiments:** Swelling experiments of the unfilled polymers were performed in heptane at 20 °C for 48 h. Using the Flory–Rehner model, a γ polymer–solvent interaction parameter of 0.45 was used for
the calculation of molecular weight between cross-links in the siloxane polymers. $M_c$ was calculated to be 40,000 for the 3700 Da unfilled polymer and 57,000 for the 14,800 Da unfilled polymer.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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