Shape Memory Superelastic Poly(isocyanurate-urethane) Aerogels (PIR-PUR) for Deployable Panels and Biomimetic Applications

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Supporting Information

ABSTRACT: Shape memory polymers (SMPs) remember and return to an original shape when triggered by a suitable stimulus, typically a change in temperature. They are pursued as cost-effective, low-density, higher-strength tolerant alternatives to shape memory alloys. Arguably, porous SMPs may offer the near-ultimate refinement in terms of density reduction. To that end, shape memory polymeric aerogels (SMPAs) may offer a viable approach. The necessary condition for SMPs is rubber-like superelasticity, which is introduced via cross-linking. Cross-linking is also a necessary condition for inducing phase separation during solution-phase polymerization of suitable monomers into 3D nanoparticle networks. Such networks form the skeletal frameworks of polymeric aerogels. Those principles were explored here with rigid trifunctional isocyanurate cross-linking nodes between flexible urethane tethers from four short oligomeric derivatives of ethylene glycol: H(OCH2CH2)nOH (1 ≤ n ≤ 4). Formation of self-supporting 3D particle networks depended on the solubility of the developing polymer, which translated into specific combinations of the diol, monomer concentration, and composition of the solvent (CH3CN/acetone mixtures). Those parameters were varied systematically using statistical design-of-experiments methods. The skeletal frameworks of the resulting poly(isocyanurate-urethane) (PIR-PUR) aerogels consisted of micrometer-size particles. Bulk densities were in the 0.2–0.4 g cm⁻³ range, and typical porosities were between 70% and 80% v/v. Glass transition temperatures (Tg) varied from about 30 (n = 4) to 70 °C (n = 1). At and above Tg, all SMPAs showed rubber-like elasticity. They also became stiffer after the first stretching cycle, which was traced to maximization of H-bonding interactions (NH···O= C and NH···O(CH2)n). Below the Tg zone, the elastic modulus of all formulations decreased by about 1000 fold. That property gave rise to a robust shape memory effect (SME), the quality of which was evaluated via several figures of merit that were calculated from tensile stretching data over five temperature cycles between Tg + 10 °C and Tg − 40 °C. All thermomechanical testing was carried out with dynamic mechanical analysis (DMA). The strain fixity was always >98%, pointing to very low creep. After the first cycle, strain recovery (a measure of fatigue) improved from 80–90% to about 100%, and the fill factor, a cumulative index of performance, reached 0.7, which is in the range of fast elastomers. The robust shape memory effect was demonstrated with deployable panels and bionic hands capable of mimicking coordinated muscle function.

1. INTRODUCTION

Shape memory materials (SMMs) remember and return to an original shape. The transition is triggered by light, electric or magnetic fields, but most frequently through a change in temperature. The two main classes of SMMs are shape memory alloys (SMAs) and shape memory polymers (SMPs). Application areas range from aerospace (deployable structures), to biomedical (implantable devices, surgical sutures, drug delivery vehicles), to transportation, construction, electronic, textile and various consumer product industries (e.g., as lightweight actuators). The first SMA was a Au–Cd alloy (1930s). Nitinol (a Ni–Ti alloy), arguably the most well-studied material in that class, was introduced in the 1960s. Nitinol is a superelastic material, meaning that it recovers its shape after extreme deformations, e.g., after bending by 180°. Superelasticity is a necessary condition for the shape memory effect but not sufficient: just so it happens, the martensitic phase of Nitinol, which is brought about by lattice deformation under shear stress, is also stable at lower temperatures. Thus, deformation at a higher temperature followed by cooling “freezes” Nitinol to a temporary shape that is retained even after stress is removed. By raising the temperature, the martensitic phase returns to the normal stress-free austenitic phase of the material and the object recovers its original shape. SMAs develop high recovery
stress, in the range of 50–500 MPa, on the downside though they are heavy and costly and their recoverable transformation strains are low (usually <10%—above that level, deformation causes unrecoverable lattice slippage).\textsuperscript{22}

SMPs are high strain-tolerant, lightweight alternatives to SMAs. The first SMP was disclosed in a 1941 patent and was based on a methacrylic acid ester for dental applications.\textsuperscript{23} The familiar cross-linked polyethylene-based heat-shrinking tubing was introduced in the 1960s,\textsuperscript{24–26} however, systematic research on SMPs started gaining momentum only in the 1990s.\textsuperscript{27–29}

Superelasticity is again a necessary condition for the shape memory effect, but here it is more commonly referred to as “rubber-like elasticity.”\textsuperscript{30} Rubber-like elasticity implies that superelastic polymers are elastomers; thus, their response to tensile stress is associated with rigid covalent cross-linking nodes between extendable (i.e., linear) polymeric strands. However, for such elastic behavior, polymeric strands must be free to move in the first place; therefore, the polymer must be amorphous and above its glass transition temperature. Thereby, in the simplest form, if an elastomer with a glass transition temperature ($T_g$) below room temperature ($T_r$) is cooled below $T_g$, segmental motion of the polymeric chains stops and covalent cross-linking nodes cannot pull the polymer back to its original shape. Raising the temperature back above $T_g$ allows the covalent cross-linking nodes to do their job.

Those principles have been implemented with a wide range of polymers and combinations thereof in blends and in layers, utilizing for the shape memory effect glass transitions but also crystallization phenomena.\textsuperscript{31–33} SMPs include polycrylate copolymers,\textsuperscript{34} segmented polyurethanes,\textsuperscript{35,36} and polyurethane ionomers,\textsuperscript{37} poly(ether ether ketone) ionomers,\textsuperscript{38} epoxy-based polymers,\textsuperscript{39} thio-ene-based polymers,\textsuperscript{40} cross-linked polyyclooctene,\textsuperscript{41} polynorbornene,\textsuperscript{42} cross-linked ethylene-vinyl acetate copolymers,\textsuperscript{43} and various styrene-based polymers.\textsuperscript{44}

Perhaps, the ultimate refinement in terms of weight reduction in SMM may involve porous polymers. A special class of materials in that category is classified as aerogels and is prepared by drying wet-gels under conditions that preserve the volume of the gel into the final dry object. That process typically involves converting the pore-filling liquid into a supercritical fluid (SCF) that is vented of as a gas. In turn, wet-gels are prepared via a sol–gel process that involves solution polymerization of suitable multifunctional monomers in a suitable solvent.\textsuperscript{55,46} For this, covalent cross-linking, in principle similar to what makes polymers elastomeric, renders the growing polymer insoluble in the polymerization medium and induces phase separation of colloidal polymeric nanoparticles that bear active functional groups on their surface. Moving around randomly, eventually, those polymeric nanoparticles find one another and get linked via reaction of their surface functional groups into a 3D network that comprises the skeletal framework of the aerogel. By this discussion so far it may be perceived that shape memory aerogels are mere SMPs in aerogel form. In reality, however, there are conflicting requirements between those two classes of materials. For shape memory elastomers the polymeric strands between cross-linking nodes are typically long by aerogel standards, and if that chemistry is transplanted directly into aerogel synthesis, one will face the fact that longer tethers increase the solubility of the developing polymer. In turn, that causes accumulation of a secondary polymeric layer on the surface of the primary network via reaction of soluble oligomers in the pores with the active functional groups on the nanoparticles.\textsuperscript{47–49} Upon deswelling during drying, that continuous secondary layer of polymer pulls the particle network together, causing collapse into a more or less dense plastic. Clearly, there is a need for a fine balance between the factors that render a polymer superelastic and at the same time sufficiently insoluble and able to form a sturdy aerogel skeletal framework. The unsatisfied quest for that balance is what has rendered shape memory aerogels elusive. A closer look at superelasticity and aerogels is therefore in order.

Superelastic aerogels have been described mostly with silica or silica–organic hybrids.\textsuperscript{50–53} The phenomenon has been associated invariably with a spring-back effect after compression—not tension. We are aware of only one recent example of thiol–ene-based aerogels that went through temperature cycles and showed size fixation upon cooling and recovery upon heating.\textsuperscript{54} Again, those materials were tested only under compression. However, folding/unfolding and other complicated deformations typically associated with the shape memory effect require rubber-like superelasticity under tension. In that context, there are numerous literature reports about flexible polymeric aerogels, most notably polyimides,\textsuperscript{55} and certain isocyanate-derived aerogels based on polyureas\textsuperscript{56} and polyurethanes\textsuperscript{57,58} that could be bent by 180°, but rubber-like elasticity is still lacking: only a small fraction, if any, of that deformation could be recovered after stress was removed. Nevertheless, there is a particular class of isocyanate-derived polymers, polyisocyanurate (PIRs), which warrants special attention. PIRs come from trimerization of isocyanates and, because of their high thermal stability and low flammability, are pursued as insulation foams, coatings, and adhesives.\textsuperscript{59–61} On the down side though, PIRs are friable—they can be easily crumbled. To overcome that issue, commercial PIRs are urethane-modified polymers made by mixing an excess of a diisocyanate with a diol and a suitable catalyst. Reaction of the diisocyanate both with itself and with the diol yields isocyanurate rings linked by urethane tethers. In those poly(isocyanurate-urethane) polymers (PIR-PUR), isocyanurate rings play the role of covalent nodes. PIR-PURs are no longer friable and in many cases elastomeric.\textsuperscript{62,63}

Along the molecular design principles of PIR-PUR, Scheme 1 shows the monomers and the reaction pathway employed in this study toward shape memory aerogels. For closer control of the properties of the polymer, we opted against simultaneous formation of the isocyanurate rings and the polyurethane tethers. Instead, the isocyanurate cross-linking nodes were introduced separately as part of the monomer by using a commercial triisocyanate derivative of aliphatic hexamethylene diisocyanate (N3300A—see Scheme 1), which combines the rigidity of the isocyanurate ring with the flexibility of the $-(\text{CH}_2)_6-$ tethers. The diols were variable-length derivatives of ethylene glycol (EG) and chosen over, for example, hydrocarbon alternatives because of the possibility for H-bonding with the urethane groups of neighboring polymeric branches. Chances for H-bonding, which could be enhanced with longer EG-derived diols, would reduce molecular slippage and macroscopic creep, thus favoring elastic over plastic behavior. On the other hand, though, longer diols would enhance segmental motion of internodal tethers, which could be desirable in terms of lowering glass transition temperatures into a useful range, but they could also increase plasticity. Furthermore, it was also understood that increasing the length of the diol would necessarily increase the solubility of the
developing polymer, which would increase the particle size and consequently decrease surface areas and would compromise thermal conductivity. However, such a departure from typical aerogel properties was deemed acceptable given our objective toward low-density shape memory materials rather than more conventional aerogel applications (e.g., in thermal insulation).

In practice, particle sizes and secondary polymer accumulation on the primary network were controlled not only via the chemical identity of the diol but also via the sol concentration and via the gelation solvent, which was varied from pure acetonitrile to a 1:1 v/v mixture of acetonitrile/acetone.

Materials are described in terms of their chemical composition, micromorphology, and thermomechanical properties. The shape memory effect was quantified with several figures of merit that include the shape fixity ratio, the strain recovery ratio, the strain recovery rate, and the fill factor. Varying the alcohol affected the glass transition temperature, which in the case of TEG translated into shape-recovery activated at room temperature. That accounts for the most dramatic demonstration of the shape memory effect in terms of potential applications in deployable panels and biomimetic devices.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Chemical Identification of Polyisocyanurate Aerogels. The reaction of Scheme 1B was implemented according to the protocol of Scheme 2A. Urethane formation was catalyzed by dibutyltin dilaurate (DBTDL) in a 1:120 mol/mol ratio relative to N3300A, and gelation took place at room temperature. Monomers were used at their stoichiometric amounts (triisocyanate:diol = 2:3 mol/mol). Wet-gels were aged up to 16 h to ensure complete reaction and dried to aerogels by extracting the pore-filling solvent with liquid CO2, which, at the end, was converted to a supercritical fluid (SCF) and vented off as a gas. Solids were prepared in acetonitrile:acetone mixtures from 50:50 v/v to pure CH3CN. The total monomer concentration was varied between 15% and 25% w/w. The ranges of the solvent ratio and the monomer concentration were based on screening experiments with TEG-based PIR-PUR aerogels, in which we looked for low-density materials demonstrating room-temperature rubber-like superelasticity similar to that of alloys, as shown in Figure 1. Such TEG-based samples either above the selected concentration range or prepared in sols consisting of more than 50% v/v acetone seemed to collapse into dense "plastics." Below the selected concentration range, if sols could still form gels, the resulting aerogels did not seem to have the strength to "lift" themselves up as in Figure 1. Samples prepared in pure acetonitrile did not seem to show optimal performance in terms of their recovery time (Figure 1). Since those two exploratory variables, monomer concentration and solvent composition, seemed to have a similar effect in terms of their ability to form low-density rubber-like superelastic materials, it was deemed reasonable that their effects were coupled. Thereby, for the purposes of the protocol of Scheme 2A, sample preparation with each diol was guided by response surface methodology implemented with a central composite

Scheme 1. (A) Reagents (triisocyanate, ethylene glycol-based diols); (B) Reaction Pathway to Isocyanurate Cross-Linking Nodes Linked with Urethane Tethers (PIR-PUR)

Scheme 2. (A) Synthetic Protocol of PIR-PUR Aerogels (ALC-xx); (B) ALC-xx Formulation According to a Central Composite Rotatable Design Model (CCRD)"
rotatable design model (CCRD—see Appendix I in the Supporting Information), in which point selection in the domain of the exploratory variables was carried out using the JMP11 software package, from the perspective of a subsequent quadratic dependence of the derived properties (e.g., density, porosity, modulus, etc.) on the exploratory variables. Individual samples are referred to as ALC-xx, according to their diol (ALC) and their position (−xx) on the rotatable domain. The design space is summarized in Scheme 2B. The exact formulations are tabulated in Tables S.1 and S.2 of Appendix I in the Supporting Information, along with the phenomenological gelation times. Here, in brief, ALC-1/ALC-10 correspond to the middle VCH3CN/Vsol_Total ratio (0.75) and the low/high monomer concentrations, respectively. The central point of the design was repeated twice (ALC-5 and ALC-6). Even-numbered ALC-2, ALC-4, and ALC-8 correspond to higher VCH3CN sols. Odd-numbered ALC-3, ALC-7, and ALC-9 correspond to acetone-rich sols.

The chemical composition of ALC-xx was confirmed with solid-state CPMAS 13C and 15N NMR (Figure 2). Insight to noncovalent interactions (H-bonding) was obtained with ATR-FTIR and is discussed in section 2.3.2 below in conjunction with the thermomechanical properties of ALC-xx. The N13CO and N15CO resonances of the isocyanate (expected at 122 and 149.8 ppm, respectively) were absent from all 13C and 15N NMR spectra, pointing to complete reaction. The 13CNMR resonances at 61.8 and 70.6 ppm were assigned to the aliphatic carbons of ALC, and the relative intensity of the two resonances changed from 1.8 to 2.5, as expected from the number of internal vs terminal −OCH2CH2− groups sandwiched between two urethane groups. The remaining two peaks in the aliphatic region, at 43.0 and 27.7 ppm, were assigned to the aliphatic carbons of ALC, and the relative intensity of the two resonances changed from EG-xx to TTEG-xx, as expected from the number of internal vs terminal −OCH2CH2− groups sandwiched between two urethane groups. The remaining two peaks in the aliphatic region, at 43.0 and 27.7 ppm, were assigned to the −CH2− groups of N3300A (Scheme 1A). Interestingly, the urethane carbonyl resonance at 157.2 ppm (−NH(−C==O)−) was sharper in EG-xx and DEG-xx and became progressively broader in TEG-xx and TTEG-xx. In the solid-state 13C NMR spectra, the resonance at 149.8 ppm was assigned to the isocyanurate ring and the one at 80.5 ppm to the urethane nitrogen. A resonance was detected in the 50−60 ppm region that could be assigned to −NH2 from hydrolysis of unreacted −NCO. Just like in the solid-state 13C NMR spectra, again, we noted a progressive peak broadening of the −NH(−C==O)− resonance, which became most prevalent in TTEG-xx. Peak broadening in both the 13C and the 15N NMR spectra of the −NH(−C==O)− group signifies that as the length of ALC increased, urethane groups found themselves in more diverse environments and/or H-bonded.

2.2. General Material Properties, Micromorphology, and Growth Mechanism of ALC-xx from an Exploratory Variable Perspective. Relevant material properties of ALC-xx are summarized in Table S.3 of Appendix II in the Supporting Information. Here, in graph form, Figure 3 compares shrinkage, bulk densities, and porosities of all ALC-xx as a function of their position in the domain of the exploratory variables (i.e., the sol composition). For quick reference, that domain is reproduced as a separate frame in Figure 3. Most ALC-xx aerogels shrunk roughly 20−25% in linear dimensions relative to the molds. Samples that stand out are all TTEG-xx aerogels, except TTEG-2 and TTEG-4 (pointed by gray arrows), and TEG-10 (pointed by blue arrows). TTEG-2 and TTEG-4 shrunk less (29% and 31%, respectively) than the other TTEG-xx (40−50%); TEG-7, TEG-9, and TEG-10 shrunk more than the other TEG-xx samples, in fact in the TEG-xx range (40−50%). Importantly, all shrinkage in all samples was observed exclusively during drying: even the collapsed samples of Figure 3 (i.e., those that shrunk excessively) showed no shrinkage during solvent exchange, suggesting that (a) all four polymers were swollen in their wet-
gel state and (b) no major reorganization of the nanostructure took place during solvent exchanges. High shrinkages were accompanied by high bulk densities ($\rho_b$) in some cases >1.0 g cm$^{-3}$—and low porosities ($\Pi$): in most collapsed samples $\Pi < 10\%\ v/v$. At any rate, the vast majority of EG-xx, DEG-xx and TEG-xx were low-density materials ($\rho_b < 0.5\ g\ cm^{-3}$) with high porosities (mostly 70–80% v/v). Within their respective ranges, $\rho_b$ and $\Pi$ followed the general upward and downward trends expected by increasing the sol concentration. Two notable exceptions were EG-1 and DEG-1 (pointed with color-coded arrows, red and yellow): although their densities/porosities were not excessive (high/low, respectively), those two samples did stand out with densities disproportionally higher and porosities disproportionally lower than those of the rest of the EG-xx and DEG-xx. Those two samples were at the lower end of the isocyanate concentration range, and upon closer examination they appeared chalky and could not be machined for mechanical testing, and by looking back at the gelation process it was noticed that the reaction products looked more like loose precipitates (flocs) rather than colloidal gels.

Overall, considering all information above together, longer TTEG generally caused excessive shrinkage, which, in two cases, TTEG-2 and TTEG-4, could be controlled via the two exploratory variables, namely, by keeping the TTEG concentration low in combination with CH$_3$CN-rich sols. Similarly, the three TEG-xx samples that shrunk excessively (TEG-7, TEG-9, and TEG-10) were among those from high TEG concentration sols, in combination with acetone-rich solvent. Clearly, as it has been alluded to already from the preliminary runs (section 2.1), the effects of the monomer concentration and the solvent composition were coupled.

Excluding only EG-1 and DEG-1 (i.e., the two samples that seemingly came from flocs), quadratic fitting of $\rho_b$ to monomer concentration ($X_1$) and solvent ratio ($X_2$) according to eq 1 gave good correlations for all four ALC-xx, as shown in Figure 4 ($0.917 \leq R^2 \leq 0.945$).

$$\rho_b = A(X_1)^2 + B(X_2)^2 + C(X_1)X_2 + D(X_2) + E(X_1) + F$$

Coefficients A–F are cited in Table S.4 of the Supporting Information. It is noteworthy that despite the sudden onset of excessive shrinkage in many samples, density still varied smoothly with $X_1$ and $X_2$ in all four ALC-xx systems. That finding together with the fact that shrinkage was observed always at the drying stage signify that all ALC-xx sols followed similar gelation processes, and the resulting aerogels shared some key microscopic/network characteristics, irrespective of their macroscopic appearance (collapsed or otherwise).

The micromorphology of ALC-xx was investigated with SEM (Figure 5). All noncollapsed samples consisted of networks of large micrometer-size spherical particles (see xx = 2 column of Figure 5). The contact area around the interparticle neck zones of EG-xx was narrow. The particle size first increased in DEG-xx relative to EG-xx and then decreased (in TEG-xx and TTEG-xx), while the interparticle neck zones became wider, in essence fusing particles together. The two TTEG-xx samples that did not collapse (TTEG-2 and TTEG-4) and the three TEG-xx samples that did collapse (TEG-7, TEG-9, and TEG-10) became the experimental and conceptual link between the nanostructures of collapsed and noncollapsed samples. Noncollapsed TTEG-2 consisted of smaller particles than the other ALC-2 samples, with enhanced merging at the necks. Noncollapsed TTEG-4 seemed to consist of even smaller particles shrouded by a layer of polymer thicker than the...
particles themselves. Importantly, the latter was also the common appearance of all TEG-xx samples that did collapse (see, for example, TEG-7 in Figure 5 as well as TEG-9 and TEG-10 in Figure S.3 of the Supporting Information). To recast and summarize, remnants of particles were still discernible in all collapsed samples, but they were smaller and coated with a thick layer of polymer. 

Albeit at different length scales (about 100× smaller than what we are dealing with here), particle fusion at higher sol concentrations, just like what we have been able to visualize in Figure 5, has been inferred previously with numerous other polymeric aerogels by comparing particle sizes calculated based on small-angle X-ray scattering and gas sorption data. A universally consistent hypothesis that explains both the previous systems and the morphological evolution noted in Figure 5 involves formation of a primary network of connected spherical particles, followed by accumulation of a secondary polymer layer, preferably at the points of negative curvature— the interparticle necks. That secondary accumulation of polymer takes place via reaction of soluble oligomers or yet unreacted monomer remaining in the pores of the primary network with functional groups on the surface of the particles of the primary network. Clearly, that monomer/oligomer-to-network growth mechanism depends on how fast the primary network is formed, hence on the monomer concentration, and the solubility of the developing polymer. The solubility of the developing polymer depends on the solvent system and the freedom for segmental motion of the polymer chains. In ALC-xx the relevant polymeric segments are the $-(\text{CH}_2)_k-\text{NH}(-\text{COOCH}_2\text{CH}_2)_n-\text{O}(-\text{CO})\text{NH}-(\text{CH}_2)_k- \text{tethers} (1 \leq n \leq 4)$ connecting the isocyanurate nodes and consist of two fixed-length aliphatic moieties $-(\text{CH}_2)_k-$ and one variable-length ether moiety sandwiched in between. The longer the tether, the more soluble the developing polymer, and secondary polymer accumulation was favored. Similarly, secondary polymer accumulation was enhanced with sols richer in stronger H-bonding acetone, which favors solubilization of the developing polymer. Now, it was also observed that the more secondary polymer accumulation, the higher the chances for excessive shrinkage. Given that all samples, no exceptions, shrank only during drying, it is reasonable that deswelling of particles was uniform and preserved the morphology and porous structure of the particle network. On the other hand, deswelling of the polymeric layer from secondary accumulation pulled the particle network together causing collapse. Thereby, success in the synthesis of porous PIR-PUR networks is predicated upon the strength of the primary particle network to support itself and resist stresses developing by deswelling of the secondary polymer layer. Overall, a viable aerogel network requires synthetic parameters that reach a balance between particle size and thickness of the polymeric layer from secondary accumulation.

2.3. Thermomechanical Characterization. That was carried out with emphasis on data related to shape memory effects.

2.3.1. Glass Transitions. Glass transitions were determined with temperature scans using dynamic mechanical analysis (DMA) in a tensile test configuration as described in the Experimental Section. Only lower density, noncollapsed samples were considered. That excludes EG-1, DEG-1, TEG-
7, TEG-9, TEG-10, and all TTEG-xx samples except TTEG-2 and TTEG-4. Typical DMA data are exemplified with TEG-8 in Figure 6A. At lower temperatures, all materials were stiff with elastic moduli, $G'$, about 10 times higher than the loss moduli, $G''$. As temperature increased, both $G'$ and $G''$ started decreasing, crossed one another twice, and eventually got again stabilized at higher temperatures. The final values of both $G'$ and $G''$ were about 1000 times lower than their respective low-temperature values, but again $G'$ was approximately 10 times higher than $G''$. Results from repetitive scans of the same samples were practically identical. The glass transition temperatures reported, $T_g$, are the maxima of tan $\delta$ ($=G''/G'$). $T_g$ values varied randomly by a few degrees within each ALC-xx. As shown in Figure 6B, the average $T_g$ values of the four ALC-xx followed the order $(T_g)_{EG-xx} > (T_g)_{DEG-xx} > (T_g)_{TEG-xx} > (T_g)_{TTEG-xx}$, and were spaced approximately 10–20 °C apart from one another (for the primary data refer to Table S.5 in the Supporting Information). The glass transition zones were generally narrow. For instance, all full widths at half maxima (fwhm, Table S.5) of all tan $\delta$ plots for all ALC-xx were in the range of 12.0–17.7 °C. As the onset of segmental motion in polymers is typically considered the maximum in the $G''$ curve (indicated with an arrow in Figure 6A). Those maxima were generally 10–13 °C lower than the tan $\delta$ maxima (see Table S.5 and Figure S.8 in the Supporting Information) and may be considered either as the upper temperature limits for fixing the shape of the polymer or loosely as the onset of shape recovery.

### 2.3.2. Elastic Properties of ALC-xx under Tension: Strain Recovery, Creep, and Stress Relaxation as a Function of $T_g$

As a preamble to the shape memory effect, this section investigates the elastic properties of ALC-xx relative to $T_g$. It confirms that ALC-xx can store and keep energy (essential for shape recovery), and explores whether they can do that repetitively. This section offers also an insight into the molecular rearrangements associated with settling after the first stretching cycle and in some cases some minor creep afterward. Those results become important in rationalizing differences in shape recovery rates among the various ALC-xx.

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**Figure 5.** SEM of specific ALC-xx samples selected from the domain of the exploratory variables (see lower right frame) for discussion of the growth mechanism of the solid framework (SEMs of all EG-xx, DEG-xx, and TEG-xx samples are shown in Appendix IV of the Supporting Information).
For those purposes, two randomly selected samples, DEG-4 and TEG-8, were tested under tension at three different temperatures, \( T_g + 40 \, ^\circ C \), \( T_g \), and \( T_g - 40 \, ^\circ C \). That range ensures conditions from well above to well below the glass transition zone (see previous section). Fresh, as-prepared samples were loaded and unloaded five times with constant force ramp rates to predetermined strain values; at the end of the fifth loading cycle, samples were step reloaded to the last strain value, which was maintained while the stress was monitored as a function of time. The ultimate strains at each temperature were set just below the respective failure (snapping) points and chosen (based on preliminary runs) in a way that would accommodate all five cycles (i.e., accounting for creep). The behavior of both DEG-4 and TEG-8 was very similar in all aspects. The results with TEG-8 are shown in Figure 7 (for the results with DEG-4 see Figure S.9 of Appendix VII in the Supporting Information). Referring to TEG-8 and Figure 7, at both \( T_g \) and \( T_g + 40 \, ^\circ C \) (40 and 80 \( ^\circ C \), respectively), samples were essentially linearly elastic. Overall, at \( T_{el} \) samples were about twice as stiff as at \( T_g + 40 \, ^\circ C \). At both temperatures, samples became stiffer at the second loading cycle and beyond (the stress–strain slope increased). Beyond the second cycle, stress–strain curves were superimposable at \( T_g + 40 \, ^\circ C \). At \( T_g \), we noticed a small drift toward larger strains with repetitive cycling (yellow arrow pointing to the right), indicating a small amount of creep. Below the glass transition range (\( T_g - 40 \, ^\circ C = 0 \, ^\circ C \)), samples were much stiffer (notice the narrow strain range) and repetitive stretching led to accumulation of unrecoverable strains. At \( T_g + 40 \, ^\circ C \) samples could store and keep >98% of the energy spent for stretching (last frame of Figure 7). That energy was available for recovery of the original dimensions after stress was released. Energy was progressively lost from the stretched state as the temperature was decreased: already at \( T_g \) TEG-8 lost about 9% of the energy stored. Below the glass transition range (again at \( T_g - 40 \, ^\circ C \)), the energy lost was about 65% and kept on increasing even after 20 min of constant strain. Energy loss notwithstanding, stress relaxation was fast at or above \( T_g \) and much slower below the glass transition zone (note the different time scales in the last frame of Figure 7).

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For those purposes, two randomly selected samples, DEG-4 and TEG-8, were tested under tension at three different temperatures, \( T_g + 40 \, ^\circ C \), \( T_g \), and \( T_g - 40 \, ^\circ C \). That range ensures conditions from well above to well below the glass transition zone (see previous section). Fresh, as-prepared samples were loaded and unloaded five times with constant force ramp rates to predetermined strain values; at the end of the fifth loading cycle, samples were step reloaded to the last strain value, which was maintained while the stress was monitored as a function of time. The ultimate strains at each temperature were set just below the respective failure (snapping) points and chosen (based on preliminary runs) in a way that would accommodate all five cycles (i.e., accounting for creep). The behavior of both DEG-4 and TEG-8 was very similar in all aspects. The results with TEG-8 are shown in Figure 7 (for the results with DEG-4 see Figure S.9 of Appendix VII in the Supporting Information). Referring to TEG-8 and Figure 7, at both \( T_g \) and \( T_g + 40 \, ^\circ C \) (40 and 80 \( ^\circ C \), respectively), samples were essentially linearly elastic. Overall, at \( T_{el} \) samples were about twice as stiff as at \( T_g + 40 \, ^\circ C \). At both temperatures, samples became stiffer at the second loading cycle and beyond (the stress–strain slope increased). Beyond the second cycle, stress–strain curves were superimposable at \( T_g + 40 \, ^\circ C \). At \( T_g \), we noticed a small drift toward larger strains with repetitive cycling (yellow arrow pointing to the right), indicating a small amount of creep. Below the glass transition range (\( T_g - 40 \, ^\circ C = 0 \, ^\circ C \)), samples were much stiffer (notice the narrow strain range) and repetitive stretching led to accumulation of unrecoverable strains. At \( T_g + 40 \, ^\circ C \) samples could store and keep >98% of the energy spent for stretching (last frame of Figure 7). That energy was available for recovery of the original dimensions after stress was released. Energy was progressively lost from the stretched state as the temperature was decreased: already at \( T_g \) TEG-8 lost about 9% of the energy stored. Below the glass transition range (again at \( T_g - 40 \, ^\circ C \)), the energy lost was about 65% and kept on increasing even after 20 min of constant strain. Energy loss notwithstanding, stress relaxation was fast at or above \( T_g \) and much slower below the glass transition zone (note the different time scales in the last frame of Figure 7).
There are two possible contributors to settling after the first stretching cycle at \( T_g \) and \( T_g + 40 \, ^\circ C \) or the subsequent creep at \( T_g \); heating, stretching, or both. Insight was obtained with ATR-FTIR of several random ALC-xx samples. Spectra of a representative sample (TEG-2) are shown in Figure 8 (for the others refer to Appendix V in the Supporting Information). Data relevant to this discussion are summarized in Table 1. All spectra were dominated by the isocyanurate carbonyl stretch near 1680 cm\(^{-1}\). The 2300–2000 cm\(^{-1}\) region was clean of any unreacted N=C=O stretch, in agreement with the solid-state NMR data (Figure 2). The free urethane carbonyl stretch was observed at 1729 cm\(^{-1}\) as a shoulder to the intense isocyanurate absorption. Possible absorptions of H-bonded urethane carbonyl groups would appear at lower energies, but they were masked by the intense isocyanurate absorption. The N–H bending coupled to C–N stretching gave an absorption at 1529 cm\(^{-1}\). The absorptions at 1240, 1129, and 1049 cm\(^{-1}\) were attributed to the ethylene glycol and urethane asymmetric and symmetric C–O–C stretches.\(^{74,75}\) Using flat baselines from 3050 to 3800 cm\(^{-1}\), the N–H stretch region of all the ALC-xx tested was deconvoluted into three absorptions (Figure 8B): one in the 3423–3545 cm\(^{-1}\) range (free NH);\(^{76,77}\) a second one, typically the most intense absorption, in the 3331–3341 cm\(^{-1}\) range (NH bonded to carbonyl: NH···O(CH\(_2\))\(_2\));\(^{77,78}\) and a

![Figure 8. Room-temperature ATR-FTIR spectra of ALC-xx taken under different conditions. (A) Entire spectrum of a representative as-prepared TEG-2 sample. (B) 3000–3800 cm\(^{-1}\) range of frame A, deconvoluted for H-bonding. (C) Same sample as in A and B, heated at \( T_g + 10 \, ^\circ C \) for 15 min, and then cooled back to room temperature. (D) Same sample as in A–C, heated again at \( T_g + 10 \, ^\circ C \) for 15 min, and stretched to about 60% strain; then the stretching force was released, and the sample was let cool back to room temperature (Similar spectra for DEG-2, DEG-4, TEG-2, TEG-8, and TTEG-2 are shown in Appendix V of the Supporting Information. H-bonding data for all samples are summarized in Table 1.).](image)

<table>
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<th>sample</th>
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<th>[free NH] 3423–3545 cm(^{-1})</th>
<th>[NH···O=O] 3331–3341 cm(^{-1})</th>
<th>[NH···O(CH(_2))(_2)] 3204–3234 cm(^{-1})</th>
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<td></td>
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<td>7.1</td>
<td>1.3</td>
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<td>1.2</td>
<td>0.0</td>
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<tr>
<td></td>
<td>heated-cooled(^b)</td>
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<td>7.6</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
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<td>8.6</td>
<td>1.4</td>
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<tr>
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<td></td>
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<td>heated-stretched-cooled(^c)</td>
<td>8.6</td>
<td>1.7</td>
<td>1.5</td>
</tr>
</tbody>
</table>

\(^a\)All spectra were taken at room temperature. Data from spectra shown in Figure 8 and Figures S.4-S.7 in the Supporting Information.\(^b\)Heated at \( T_g + 40 \, ^\circ C \), cooled to room temperature.\(^c\)Heated at \( T_g + 40 \, ^\circ C \), stretched at that temperature, left to relax, and cooled back to room temperature.
third weaker absorption in the 3204−3234 cm$^{-1}$ range assigned to NH···O(CH$_2$)$_2$ (NH stretch, H-bonded to glycol groups). Following the same trend with the progressive broadening of the −NH(C=O)O− resonance in the $^{13}$C NMR spectra and the −NH(C=O)O− resonance in the $^{15}$N NMR spectra, it is noted that by going from DEG-2 to TEG-2 to TTEG-2, the absorption intensity ratio of [free NH]:[NH···O]=1.0, showing, albeit only qualitatively, an increase of H-bonded NH at the expense of free NH as the length of the ALC increased.

Now, as demonstrated in Figure 8C, a heating cycle above $T_g$ followed by cooling back to room temperature increased the fraction of H-bonded NH. As summarized in Table 1, the new intensity ratio of [free NH]:[NH···O]=1.0, moved in favor of NH···O=C, at the expense of free NH, becoming 1.6/7.1/1.3, 0.8/8.4/0.8, and 0.0/8.2/1.8, in DEG-2, TEG-2, and TTEG-2, respectively. Next, we investigated the effect of heating above $T_g$ stretching at that temperature, and cooling back to room temperature (Figure 8D). That cycle had a similar effect to just heating and cooling; the difference was that a higher portion of free NH would survive the cycle as the ALC became longer (i.e., from DEG to TTEG). The ratio of [free NH]:[NH···O=C]:[NH···O(CH$_2$)$_2$] for the three DEG-2, TEG-2, and TTEG-2 moved to 0.8/7.4/1.8, 1.3/7.7/1.0, and 1.1/7.6/1.3, respectively (Table 1). Similar trends were observed for DEG-4 and TEG-8 (data also included in Table 1). In summary, ATR-FTIR data have shown that as-prepared ALC-xx were in a metastable state. Both heating and stretching were responsible for settling at energy minima that maximized H-bonding interactions. That provides a satisfactory reason for the stiffness increase noted during the first cycle of tensile testing and the small amount of creep afterward.

2.3.3. Shape Memory Effect (SME). The SME of ALC-xx was demonstrated as shown in Figure 9 with a panel similar to the one used in Figure 1 (TEG-8). The strain imposed during bending in Figure 1 was about 25% (calculated from the radius of curvature, $R$, and the thickness of the specimen, $d$, via $d/2R$). In order to force strains closer to the ultimate strain of that kind of samples (about 60%; see Figure 7), the sample was folded to the tighter radius of curvature as shown in Figure 9. Thus, first, the panel was heated in an oven at $T_g + 40$ °C; then it was folded quickly into the spiral form of Figure 9, and that shape was fixed by dipping the folded object in liquid N$_2$. As the spiral form was let to warm up to ambient temperature, it unfolded to its original shape.

The SME was quantified formally for all noncollapsed DEG-xx and TEG-xx samples as well as TTEG-2 and TTEG-4 via three individual figures of merit (the strain fixity, the strain recovery, and the strain recovery rate) and a cumulative one...
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4471

from the perspective of Figure 10B of one full random cycle to cycles. Figure 11C is the direct projection (no time unfolding) pointing to a robust SME.

Appendix VIII in the Supporting Information. In graph form, samples over all cycles are summarized in Table S.6 of

curve is uniquely de

strain

strain

stress

equivalently to the rear plane of Figure 10B. Figure 11A shows the strain along a random temperature cycle (after the first), while Figure 11B shows the strain during the first two cycles. Figure 11C is the direct projection (no time unfolding) from the perspective of Figure 10B of one full random cycle to the strain−temperature (rear) plane. All figures of merit of all samples over all cycles are summarized in Table S.6 of Appendix VIII in the Supporting Information. In graph form, results from the first and fifth cycles are shown in Figure 12.

The strain fixity ratio, \( R_f(N) \), quantifies creep during Stage 2 (i.e., during cooling under constant stress) and was calculated for each cycle, \( N \), from the data like those of Figure 11A via eq 2.

\[
R_f(N) = \frac{\epsilon_u(N)}{\epsilon_m(N)} \times 100
\]  

(The definitions of the two strain values, \( \epsilon_u \) and \( \epsilon_m \) are given directly in Figure 11A.) In agreement with Figure 7, whereas above \( T_g \) there is virtually no creep, by and large, strain fixity in all cycles, including the first one, was always >98% (Table S.6.1). The strain recovery ratio, \( R_r(N) \), quantifies fatigue from repetitive cycling, and just like \( R_f(N) \), it was also calculated from the data of Figure 11A using eq 3.

\[
R_r(N) = \frac{\epsilon_m(N) - \epsilon_u(N)}{\epsilon_m(N)} \times 100
\]  

Reflecting the increase in stiffness observed after the first cycle, all strain recovery values started lower in the first cycle (80−90%), increasing and stabilizing thereafter to values 98%. (The increase of \( R_r(N) \) beyond the first cycle is already evident from the data shown in Figure 12 but for the near-stabilization just after \( N \geq 2 \), refer to Table S.6.2.)

The strain recovery rate, \( R_t(N) \), is an index introduced in this study in order to quantify and compare the relative speed of strain recovery at the heating Stage 4 among different samples and cycles. \( R_t(N) \) is defined via eq 4 as the maximum slope of the strain vs time curve during heating in Stage 4 (refer to the red line in Figure 11B).

\[
R_t(N) = \max \left[ -\frac{\Delta \text{strain}}{\Delta t} \right]
\]  

Since the strain recovery of Stage 4 did not take place at the natural warm-up rate of the material but instead was driven by the imposed heating rate, it was deemed necessary to repeat the experiment at different heating rates (using fresh samples each time) and observe the effect on the rate of recovery (Figure 13). Thus, it is noted that during all cycles, \( R_t(N) \) followed a near-linear relationship with a heating rate up to 5 °C min\(^{-1}\); therefore, different \( R_t(N) \) values reflected steeper recovery
curves or equivalently more narrow temperature windows of recovery. The obvious place to look for supporting evidence for that conclusion was the width of the tan δ plots, but we were unable to find any meaningful correlation between $R_t(N)$ (from Table S.6.3) and the fwhm of tan δ (from Table S.5). Thereby, we concluded that the stretched, frozen starting point of the shape recovery (Stage 4) represented a different state of ALC-xx from the as-prepared samples. According to Table 1, that state was most probably characterized by an enhanced amount of H-bonding relative to the innate (as prepared) state of ALC-xx. In that regard, it is worth nothing that the highest recovery rate was observed with DEG-4, which, based on the IR data of Table 1, did not show any free NH after one heating–stretching cycle.

Finally, the fill factor, $FF(N)$, has been proposed as a combined index of performance and was calculated from the ratio of the shaded S-shaped area to the total area of the “box” shown in Figure 11C. Obviously, calculation of that ratio is sensitive to the upper and lower temperature limits. As a conservative upper limit we took the maximum temperature for all experiments, $T_g + 10 ^\circ C$ (against the recommended $T_g + 20 ^\circ C$). The selection of the lower limit, namely, the onset of recovery (Stage 4), was based on $R_t(N)$ as follows: first, we noted the temperature of the maximum slope (eq 4) of the corresponding Figure 11B of every ALC-xx in every cycle; then we located the temperature at the foot of Stage 4 where the recovery rate was at just 3% of the maximum rate. That temperature was set as the onset of recovery in every Figure 11C corresponding to every ALC-xx in every cycle. By its construction, $FF(N)$ combines contributions from all three $R_r(N)$, $R_t(N)$, and $R_f(N)$ and was also monitored and recorded for all samples during all five cycles. Fill factors (Figure 12, Table S.6.4) started lower in the first cycle but generally no lower than 0.5 (except for TTEG-4, where $FF(1) = 0.4$). After samples were broken in in their first cycles, all fill factors were over 0.60, most over 0.65, and in some cases reached 0.70. Those fill factors are in the range for high-speed elastomers and are considered high.

Overall, the strategy of using poly(isocyanurate-urethane) aerogels as lightweight alternative to shape memory polymers has been fruitful, leading to materials showing a robust shape memory effect. According to Figure 9, ALC-xx can very well serve as deployable panels in applications where weight is at a premium, e.g., as mirrors or antennas in space. Figure 14 shows that ALC-xx can also be molded into complex shapes and programmed to perform more advanced functions mimicking, for example, the complicated muscle coordination of a human hand holding a pen. The slow recovery reported in Figure 14 should not be considered as a deterrent. In practice, fast recovery will be driven by heating with a thin wire resistor embedded within an object.

3. CONCLUSION

As a polymeric class, polyisocyanurates have received a low level of attention as base materials for polymeric aerogels. As shown here though, the isocyanurate ring can be an effective cross-linking node for imparting both rubber-like elasticity and
Interestingly, commercial thermal insulators like glass or rock wool, under further investigation. The properties of those composites are mainly by aerogels. The synthesis of polymeric aerogels, respectively. Given the specific trisiscyanurate node used in this work (a hexamethylene disocyanate derivative), longer diols (selected from the ethylene glycol family) and solvents with enhanced H-bonding ability (like acetone) lead to extensive shrinkage and dense polymers; thereby, they were not suitable for shape memory aerogel synthesis. Once the correct conditions were identified with the help of design-of-experiments statistical methods, poly(isocyanurate-urethane) aerogels showed a robust shape memory effect with high fixity and recovery ratios and fill factors. Since aerogels are low-density materials, large-scale applications of shape memory polymers, as in deployable panels and biomimetic devices, are becoming amount-of-material applications of shape memory polymers, as in deployable panels and biomimetic devices, are becoming amount-of-material efficient and within reach. Owing to the necessary compromise between conflicting requirements for rubber-like superelasticity and particle network formation, the aerogel framework of ACL-xx consisted of large particles (by aerogel standards). As represented in the Introduction, aerogels with nanostructures consisting of large particles may not be suitable for typical aerogel applications like in thermal insulation. Nevertheless, preliminary results show that the room-temperature thermal conductivity of several ACL-xx selected randomly was in the 0.052 ± 0.005 W m−1 K−1 range, namely, similar to several commercial thermal insulators like glass or rock wool. Interestingly, filling the pores of ACL-xx with silica aerogel (0.015 W m−1 K−1) caused a drop of the thermal conductivity to around 0.027 W m−1 K−1, namely, within a range accessible mainly by aerogels. The properties of those composites are under further investigation.

4. EXPERIMENTAL SECTION

4.1. Materials. All reagents and solvents were used as received unless noted otherwise. The isocyanurate node (N3300A) was obtained courtesy of Covestro LLC (Pittsburgh, PA) under the trade name Desmodur N3300A. Diols (ACL) (ethylene glycol (EG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol (TTEG)), the catalyst (dibutyltin dilaurate (DBTDL)), and solvents (anhydrous acetonitrile and anhydrous acetone) were purchased from Sigma-Aldrich. Siphon-grade CO2 was purchased from Ozark Gas Co.

4.2. Synthesis of Shape Memory Poly(ISOcyanurate-urethane) Aerogels. In a typical process, N3300A as received (Desmodur N3300A, 0.504 g, 1.00 mmol) and the respective diol (EG, DEG, TEG, and TTEG, 1.50 mmol) were dissolved in an anhydrous acetonitrile/acetone mixture according to a central composite rotatory design (CCRD) model (Appendix I in Supporting Information). The solution was stirred in a three-neck round-bottom flask at 23 °C under N2 for 10 min, and DBTDL (5 µL) was added. The resulting sol was stirred for another 5 min and poured into molds. Smaller rectangular specimens for dynamic mechanical analysis were cut from cylindrical samples prepared using plastic syringes as molds (All Plastic Norm-Ject Syringes, 20 mL, Fisher Scientific Catalogue No. 14-817-32, 2.53 cm i.d.). Larger rectangular samples (e.g., Figures 1 and 9) were prepared using plastic containers (Style Selections 16”×12.75” Plastic Multi-Use Insert Drawer Organizer, Model No. 39001, Lowe’s Item No. 105922). Molds for bionic hands (Figure 14) were prepared via a 3-stage process: first, the negative of a volunteer’s hand was reproduced into Alja-Safe (Crystalline Silica-Free Alginate for Molding Body Parts),85 plaster (DAP 4-lb Carton Plaster of Paris Model 10318, Lowe’s Item No. 41323) was cast into the alginate mold in order to produce the exact (positive) replica of the hand; finally, the plaster mold was used to make the final mold using AeroMarine Products AM 128 Silicone Mold Making Rubber RTV.86 Molds with sol were sealed with Parafilm and kept at room temperature for gelation. The gelation time varied from 7 min to about 3 h 40 min depending on the chemical identity of the alcohol, the monomer concentration, and the fraction of CH2CN in the solvent system. Gels were aged for 24 h in their molds at room temperature. Subsequently, gels were removed from the molds, washed with acetone (4× 8 h, using 4× the volume of the gel each time), and dried with CO2 taken out as a supercritical fluid (SCF). Samples were referred to as ACL-xx, where ALC stands for the abbreviation of the diol (Scheme 1) and xx denotes the position in the domain of the independent variables (Scheme 2B).

4.3. Methods. 4.3.1. Drying. Drying of wet-gels was carried out in an autoclave (SPIDRY Jumbo Supercritical Point Dryer, SPI Supplies, Inc. West Chester, PA, or a Spa-edSFE system, Applied Separations, Allentown, PA). Samples were loaded into the autoclave at room temperature and covered with acetone. The pressure vessel was closed, and liquid CO2 was allowed in at room temperature. Acetone was drained out from the pressure vessel while more liquid CO2 was allowed in. Samples were kept under liquid CO2 for 30 min. Then liquid CO2 was drained out while more liquid CO2 was allowed in. The cycle was repeated several times until all acetone had been extracted out of the pores of the samples. Subsequently, the temperature of the autoclave was raised to 40 °C, and that condition was maintained for 1 h. Finally, supercritical fluid (SCF) CO2 was vented off as a gas.

4.3.2. Chemical Characterization. Solid-state CP/MAS 13C NMR spectra were obtained with samples cut into small pieces on a Bruker Avance III 400 MHz spectrometer with a carbon frequency of 100 MHz using a 7 mm Bruker MAS probe at a magic angle spinning rate of 5 kHz with broad-band proton suppression and the CP TOSS pulse sequence. The Total Suppression of Spinning Sidebands (TOSS) pulse sequence was applied by using a series of four properly timed 180° pulses on the proton channel at different points of a cycle before acquisition of the FID, after an initial excitation with a 90° pulse on the proton channel. The 90° excitation pulse on the proton and the 180° excitation pulse on carbon were set to 4.2 and 10 μs, respectively. A contact time of 2 ms was used for cross-polarization. Solid-state 13C NMR spectra were referenced externally to glycyan (carbonyl carbon at 176.03 ppm). Chemical shifts are reported versus TMS (0 ppm).
Solid-state CP MAS 13N NMR spectra were also obtained on the same Bruker Avance III 400 MHz Spectrometer with a nitrogen frequency of 40.557 MHz using a 7 mm Bruker MAS probe with broad-band proton suppression and magic angle spinning rate of 5 kHz. For cross-polarization, a 90° proton excitation pulse was set to 4.2 μs with 2 ms contact time. Chemical shifts are reported versus liquid ammonia (0 ppm) and were externally referenced to glycine (amine nitrogen at 33.40 ppm). In all solid-state NMR experiments the relaxation delay was set at 5 s.

Attenuated total reflectance (ATR) FTIR spectroscopy was carried out with a Nicolet-FTIR spectrometer model 750, equipped with a ATR accessory model 0012-3XXT. Samples were cut to the size of the ATR crystal (ZnSe, rectangular, 20 mm × 50 mm), and ATR-FTIR spectra were obtained by pressing them against the crystal with the ATR unit’s pressure device (gripper). Maximum throughput of the infrared beam to the detector was achieved via optical alignment that was performed with no sample on the crystal. Data were collected at an incident beam angle of 45° over 32 scans with a resolution of 2 cm⁻¹. In the ATR mode, the penetration depth (pd) and thereby the effective path length (number of reflections × pd) of the infrared beam are directly proportional to the wavelength. Thereby, an ATR correction was applied to the raw data by multiplying the spectra with a wavelength-dependent factor (roughly λ/5) that adjusts the relative peak intensities. In order to evaluate H-bonding, the ν(N–H) bands were deconvoluted into three Gaussian-shaped peaks. Peak curve fitting was performed using the Origin 8.5 software program.

4.3.3. Physical Characterization. Bulk densities (ρb) were calculated from the weight and the physical dimensions of the samples. Skeletal densities (ρs) were determined with helium pycnometry using a Micromeritics AccuPyc II 1340 instrument.

4.3.4. Structural Characterization. Structural characterization was carried out using scanning electron microscopy (SEM) with Au-coated samples on a Hitachi model S-4700 field-emission microscope.

4.3.5. Thermomechanical Characterization. Thermomechanical characterization was carried out in the tension mode with a TA Instruments Q800 Dynamic Mechanical Analyzer (DMA) equipped with a tension clamp (TA Instruments part no. 984016.901). All specimens for testing had a rectangular geometry (length 20 mm; width 15 mm; thickness 3 mm) in the spirit of ASTM D790-1087 and ASTM D4065;88 they were cut off with a knife under N2 in a glovebox, from larger cylindrical samples dipped in liquid N2. In order to ensure uniform thickness, the surface of all rectangular pieces was smoothened, while still frozen, with a 3 M sand paper (320 grit, part no. 98401). In general, all samples were placed in the load cell at room temperature. The exact length of all samples was measured by the instrument under a small tensile force (0.01 N) that prevents bending. The temperature was stepped to the initial testing temperature, and then equilibrated at the particular temperature for 5 min. Subsequently, samples were stretched with a small tensile force (0.01 N), and the length of the sample was measured by the instrument and stored. Next, specimens were stretched at a constant force rate of 1 N min⁻¹ up to a little below their break point (typically around 60% strain), and then they were cooled, while under the final stress, at 5 °C min⁻¹ to their fixation temperature (Tf ≪ Tg) where Tg is the glass transition temperature (Tg ≥ Tg) while strain was still recorded. As a control, a sample was also heated at 3 °C min⁻¹ as well as at 5 °C min⁻¹). Samples were held at Tg of 15 min, and the cycle was repeated. Five such cycles were run successively for each sample, and data were analyzed for the fixation and recovery properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b01020.

Appendix I (Design, formulation, and gelation times of ALC-xx); Appendix II (General material properties of ALC-xx); Appendix III (Fitting bulk densities of ALC-xx to system variables); Appendix IV (SEM of all ALC-xx); Appendix V (ATR-FTIR of DEG-2, DEG-4, TEG-8, and TTEG-2); Appendix VI (Glass transition data); Appendix VII (Tensile testing and stress relaxation of DEG-4); Appendix VIII (Figures of merit for the SME of all ALC-xx) (PDF)

Movie of a demonstration of superelasticity (MPG)
Movie of a demonstration of a deployable panel (MPG)
Movie of a bionic hand (MPG)

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Notes

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(61) It is noted that the extinction coefficient of free NH is about 3 times lower than that of H-bonded N−H.


