

Alginate Aerogels Crosslinked with Isophorone-Based Polyurea: The Missing Link between Rigid Aromatic and Flexible Aliphatic Nanostructured Networks

Argyrios Gomatos, Grigorios Raptopoulos, Dimitrios Papadakis, Georgia Prapa, Adél Len, Zoltán Dudás, József Kalmár,* Konstantina Mergia,* and Patrina Paraskevopoulou*



Cite This: <https://doi.org/10.1021/acsapm.6c02361>



Read Online

ACCESS |

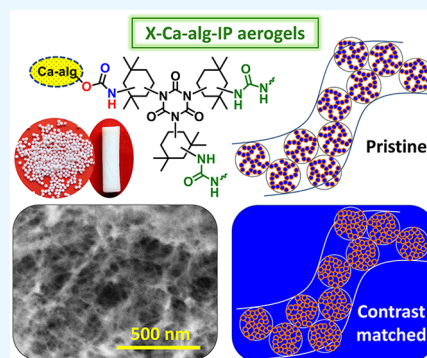
Metrics & More

Article Recommendations

Supporting Information

ABSTRACT: Polyurea-cross-linked alginate (X-Ca-alg-IP) aerogels, prepared from calcium alginate (Ca-alg) gels and the isocyanurate trimer of rigid aliphatic isophorone diisocyanate (IP), provide insight into the role of the cross-linker molecular structure in the nanoscale and macroscopic properties of X-biopolymer aerogels. Keeping all other synthetic conditions the same, the polyurea (PUA) loading in X-Ca-alg-IP (40–46% w/w) was lower than what was obtained using flexible aliphatic (56% w/w) or rigid aromatic (60% w/w) triisocyanate monomers, reflecting differences in monomer reactivity and packing efficiency of the resulting PUA. Cross-linking preserved the macro/mesoporous nanoscale architecture of the native Ca-alg backbone, maintaining high porosity (up to 95% v/v) and specific surface area (up to 393 m² g^{−1}). Small-angle neutron scattering (SANS) confirmed that the nanostructure and mass-fractal organization are largely preserved by the cross-linking process that produced a conformal interfacial layer of PUA around the primary Ca-alg skeletal particles, with an estimated thickness on the order of 2–3 nm. Compared to other X-biopolymer aerogels, X-Ca-alg-IP aerogels showed significantly enhanced stiffness, with Young's moduli in the range of 11–16 MPa. These results highlight the critical role of the molecular structure of the cross-linker in tailoring the structure–property relationships in X-biopolymer aerogels for advanced and sustainable environmental and biomedical applications.

KEYWORDS: alginate, aerogels, cross-linked aerogels, X-aerogels, biopolymer aerogels, isophorone diisocyanate, SANS, impulse excitation technique



1. INTRODUCTION

First invented by Kistler in the 1930s,^{1,2} aerogels are nanostructured solid colloidal or polymeric networks expanded throughout their entire volume by a gas.³ Although it was evident from the beginning that aerogels could be of virtually any chemical composition, early research focused on silica and other inorganic aerogels. Organic aerogels (based on natural or synthetic organic polymers), hybrid organic–inorganic aerogels, as well as carbon aerogels, were developed later.⁴ In recent years, driven by an increasing emphasis on sustainability in both material fabrication and end use, biopolymer-based aerogels are attracting growing attention for environmental, biomedical, and food applications.^{4,5}

Alginates are naturally occurring polysaccharides extracted from brown algae. They are linear block copolymers composed of two diastereomeric monomers, namely β -(1→4)-linked D-mannuronic acid (M) and α -(1→4)-linked L-guluronic acid (G) (Figure 1). In aqueous solutions, alginates readily form gels through interaction with divalent or multivalent cations; these gels can subsequently be converted into aerogels. The cations coordinate with the carboxylate groups of adjacent

alginate chains, thereby inducing immediate ionotropic gelation.^{6–8} Another approach that provides close control over the shape of the gels (in monolithic, fibrous, or bead form) is via the reaction of aqueous alginate solutions with acetic anhydride or acetic acid to form thixotropic gel-like solutions, which then can be converted to regular gels either by nonsolvent-induced phase separation or by ionotropic gelation.⁹ Similar to other biopolymer-based aerogels, alginate aerogels are biodegradable, biocompatible, and nontoxic. Consequently, beyond conventional aerogel applications such as thermal insulation, catalysis, and adsorption, alginate aerogels show considerable potential for applications in biomedicine (e.g., for drug delivery) and in the food industry.^{4,5,10–14}

Received: June 2, 2026

Revised: July 3, 2026

Accepted: July 6, 2026

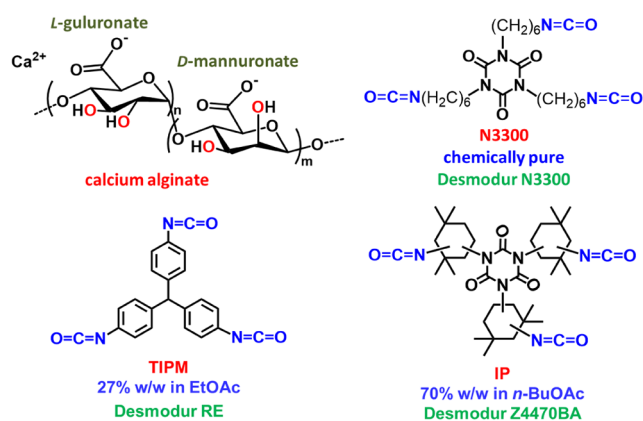


Figure 1. The structures of calcium alginate (Ca-alg) and the triisocyanates present in the commercial products Desmodur N3300 (N3300; trimer of hexamethylene diisocyanate), Desmodur RE (RE; tris(4-isocyanatophenyl)methane), and Desmodur Z4470BA (IP; isocyanurate-based trimer of isophorone diisocyanate—as a mixture of isomers).

Despite these positive attributes, a major limitation of most biopolymer-based aerogels is their inherently poor mechanical performance, which restricts their practical applicability. This issue has been successfully addressed through covalent cross-linking of the biopolymer backbone with a polymer. This approach, commonly referred to as the polymer-cross-linked aerogel (X-aerogel) technology, was initially developed for inorganic oxide aerogels.^{15–20} In the most common implementation of this technology, innate functional groups (–OH or –NH₂) and adsorbed water on the surface of preformed biopolymer gels react with multifunctional isocyanates. The ensuing reaction sequence results in the formation of a nanometer-thin polyurea (PUA) coating over the entire skeletal framework of the gel. The coating is anchored to the framework through urethane and/or urea linkages, and most importantly, it bridges the interparticle necks that constitute the weakest points of the biopolymer skeleton, thereby reinforcing the structure. The X-aerogel technology has been applied with remarkable success to several biopolymers carrying –OH or –NH₂ groups in their structure, including alginate,^{21–26} chitosan,²³ and cellulose,²⁷ cross-linked with PUA derived from flexible aliphatic (N3300),^{21,23,25} rigid aromatic (RE),^{24,25} or rigid aliphatic (IP)²⁶ triisocyanates (Figure 1).

Isophorone diisocyanate (IPDI) is one of the most commercially important aliphatic diisocyanates.²⁸ Because of its rigid cyclic aliphatic structure, IPDI produces PUA chains that are inherently stiffer than those derived from other, more flexible diisocyanates.²⁹ As a result, IPDI has been widely employed as a self-healing agent^{30–33} and as an additive to enhance the mechanical properties of biopolymer-based materials.³⁴ Similar to other aliphatic diisocyanates, the use of IPDI in a condensed, isocyanurate-based trimer form (abbreviated as IP; Figure 1) is often preferred, as it offers improved control over reactivity, along with reduced volatility and lower exposure potential.²⁸ This aspect is particularly important for IPDI, which is a known respiratory sensitizer.³⁵ Furthermore, like other triisocyanate monomers (Figure 1), IP yields cross-linked polymer networks with enhanced mechanical performance. Despite these attributes, however, IP has not been used for cross-linking of inorganic or synthetic polymer

aerogels and has been used only scarcely for biopolymer aerogels.²⁶

Based on the above, herein we present a systematic investigation of X-alginate aerogels cross-linked with PUA derived from IP (Figure 1). The physicochemical characteristics, mechanical performance, and nanoscale structural organization of the resulting materials are examined in detail, with particular emphasis on insights obtained from small-angle neutron scattering (SANS). The rigid aliphatic molecular structure of IP bridges the gap between flexible/aliphatic and rigid/aromatic triisocyanates, and thereby, whenever literature data are available, results from this work are compared with corresponding X-alginate aerogels derived from the isocyanurate-based flexible aliphatic trimer of hexamethylene diisocyanate (N3300; Figure 1) and the aromatic tris(4-isocyanatophenyl)methane (RE; Figure 1). The properties of X-alginate aerogels, particularly their nanoscale architecture as determined via SANS,²⁵ have proven to be key parameters for their implementation in diverse applications, including environmental remediation^{36–40} and biomedicine.^{41–43}

2. EXPERIMENTAL SECTION

2.1. Materials

Sodium alginate (Na-alg) was purchased from Duchefa Biochemie (Haarlem, The Netherlands). CaCl₂·2H₂O and dialysis tubing cellulose membrane (diameter: 25 mm) were purchased from Sigma. Trace-metal grade HNO₃ 67–69% and trace-metal grade H₂O₂ 30% were purchased from Fisher Chemical. Desmodur Z4470BA—trimer of isophorone diisocyanate, 70% solution in *n*-butyl acetate (*n*-BuOAc)—was generously provided by Covestro AG. Acetonitrile (MeCN) (HPLC grade) and acetone were purchased from Fluka and were used as received. Deionized water was used throughout all experiments. Deuterium oxide (D₂O, ≥ 99.9 atom % D) was purchased from Sigma-Aldrich and used as received.

2.2. Preparation of Native Ca-Alginate (Ca-Alg) Hydrogel and Aerogel Beads and Monoliths

Ca-alg hydrogels and aerogels in the form of beads were prepared following literature procedures.²¹ In brief, aqueous Na-alg solutions (1%, 2%, or 3% w/w, as indicated in Table S1) were prepared by dissolving Na-alg (1.0, 2.0, or 3.0 g) in H₂O (99.0, 98.0, or 97.0 g) at 25 °C. The solution was added dropwise, using a 25 mL buret, into a solution of CaCl₂ (0.2, 0.5, or 1.0 M, as indicated in Table S1) under mild magnetic stirring. Spherical hydrogel Ca-alg beads formed instantly and were allowed to age for 24 h in the CaCl₂ bath.

For monolithic Ca-alg hydrogels and aerogels, aqueous Na-alg solutions (2% or 3% w/w, as indicated in Table S2) were prepared as described above and placed into dialysis tubing cellulose membranes. The membranes were then immersed in a CaCl₂ solution (0.2 M) for gelation and aging (24 h).

After aging, gels were either used for cross-linking (Section 2.3) or were stepwise solvent-exchanged with acetone/H₂O mixtures (30, 60, 90% v/v) and dry acetone (4×). The gels were then dried using supercritical CO₂ to produce native Ca-alg aerogels.

2.3. Preparation of Polyurea-Cross-Linked Ca-Alginate (X-Ca-Alg-IP) Aerogel Beads and Monoliths

X-Ca-alg-IP aerogel beads and monoliths were prepared by slightly modified literature procedures.^{21,23,24} Ca-alg hydrogel beads and monoliths from Section 2.2 were solvent-exchanged with MeCN/H₂O mixtures (30, 60, 90% v/v) and then with dry MeCN (4×). The gels were then immersed in a solution of IP in *n*-BuOAc/MeCN (solution volume 4× that of the gels) for 24 h. The IP solution was prepared by mixing Desmodur Z4470BA with dry MeCN. Its concentration was 0.56 M for the beads (Table S1) and 0.06, 0.13, 0.22, 0.40, or 0.60 M for the monoliths (as indicated in Table S2).

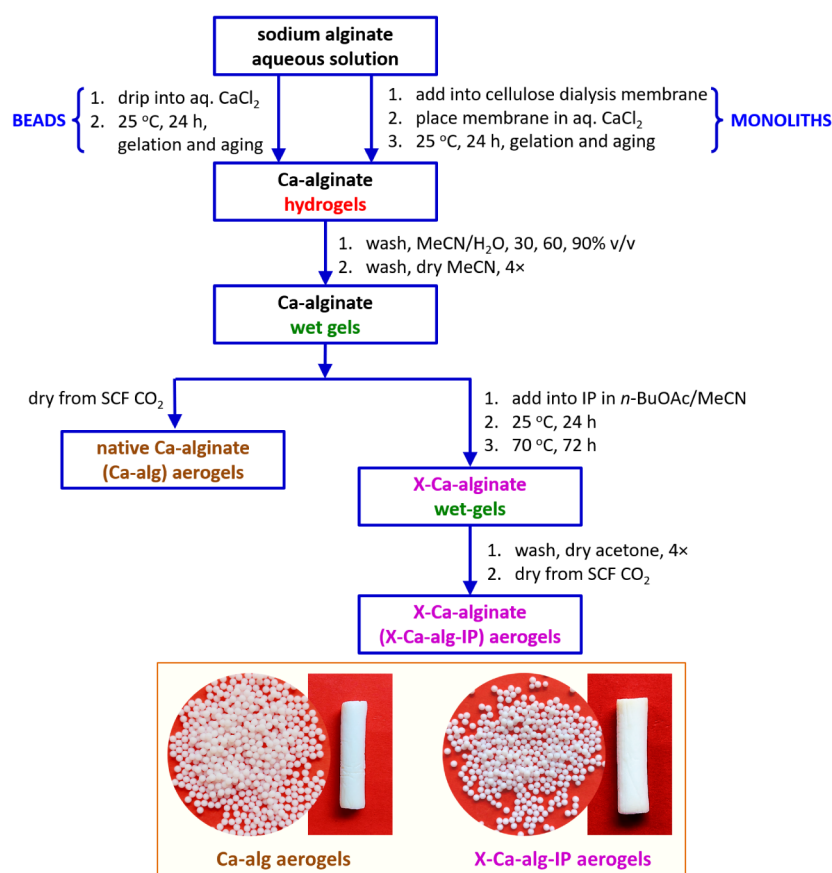


Figure 2. Preparation flow-chart (top) and optical photographs (bottom) of Ca-alg and X-Ca-alg-IP aerogel beads and monoliths as indicated.

Subsequently, the system was placed in an oven at 70 °C for 72 h to promote cross-linking. The resulting polyurea-cross-linked Ca-alginate (X-Ca-alg-IP) gels were then solvent-exchanged with acetone (4x) and dried under supercritical CO_2 conditions to yield the corresponding X-Ca-alg aerogels.

Sample nomenclature follows the following convention. In general, native calcium alginate aerogels are referred to as Ca-alg, or more specifically, when synthetic conditions must be mentioned, as Ca-alg-B (or M)-x.y, where “B” and “M” stand for beads and monoliths, respectively, “x” stands for the concentration of the Na-alg solution, and “y” is an incremental sample identifier. Similarly, Ca-alg aerogels cross-linked with IP-derived PUA are referred to as X-Ca-alg-IP or X-Ca-alg-IP-B (or M)-x.y, whereas “B”, “M”, “x” and “y” have the same meaning as in native aerogels. Aerogels cross-linked with N3300 and RE are referred to as X-Ca-alg-N3300 and X-Ca-alg-RE, respectively.

2.4. Methods

Supercritical drying was carried out in an autoclave (E3100, Quorum Technologies, East Sussex, UK). Gels were placed in the autoclave at 12 °C and were covered with acetone. Liquid CO_2 was allowed into the autoclave; acetone was drained out as it was being displaced by liquid CO_2 (5x; 1 per 30 min). Afterward, the temperature of the autoclave was raised to 45 °C; the pressure of the closed system followed the temperature spontaneously, reaching 100 bar; these conditions were maintained for 1 h. Finally, the pressure was gradually released, allowing supercritical CO_2 to escape as a gas, leaving behind the corresponding aerogels.

^{13}C and ^{15}N Cross-Polarization Magic Angle Spinning (CPMAS) NMR spectra were obtained with a 600 MHz Varian spectrometer (Varian, Palo Alto, CA, USA) operating at 150.80 MHz for ^{13}C and 60.79 MHz for ^{15}N . The sample spinning rate used was 5 kHz, and the temperature was set at 25 °C.

ATR-FTIR spectra were obtained with a Shimadzu FTIR IRAffinity-1 spectrometer equipped with an ATR Shimadzu

QATR10 single-reflection attachment. Spectra were recorded in the wavenumber range 400–4000 cm^{-1} .

Thermogravimetric analysis (TGA) was performed using a Mettler-Toledo TGA/DSC1 instrument (Schwerzenbach, Switzerland). Samples were placed in platinum crucibles. An empty platinum crucible was used as a reference. Samples were heated from ambient temperatures to 800 °C in a 50 mL min^{-1} flow of N_2 at a heating rate of 10 °C min^{-1} .

N_2 -sorption measurements were made on a Micromeritics TriStar II 3020 surface area and porosity analyzer (Micromeritics, Norcross, GA, USA). Prior to analysis, all samples were degassed at 80 °C for 24 h using a Micromeritics VacPrep 061 (Micromeritics, Norcross, GA, USA). Skeletal densities (ρ_s) were determined by He pycnometry using a Micromeritics AccuPyc II 1340 pycnometer (Micromeritics, Norcross, GA, USA). Bulk densities (ρ_b) of the samples were calculated from their weight and natural dimensions.

To determine the calcium content of Ca-alg and X-Ca-alg-IP aerogel beads, beads (20 mg) were subjected to wet digestion in an Ethos Lean Compact Microwave Digestion (Milestone) instrument with trace-metal-grade HNO_3 and H_2O_2 . The digestate was diluted and analyzed with inductively coupled plasma mass spectrometry (ICP-MS) employing an Agilent 7700 series ICP-MS instrument.

The morphology of the aerogel samples was imaged by using low-voltage scanning electron microscopy (LV-SEM) on a Thermo Scientific Scios 2 instrument. The specimens were mounted on the sample holder by using vacuum-resistant carbon tape. Because of the low accelerating voltage and reduced electron beam current, charging effects were minimized. This enabled high-magnification imaging of freshly fractured aerogel surfaces in their native state without the need for any conductive coating.⁴⁴

The detailed description of the small-angle neutron scattering (SANS) experimental setup, the measurement process, and the data evaluation is given in our previous publication.²⁵ Briefly, the measurements were carried out on the Yellow Submarine instrument

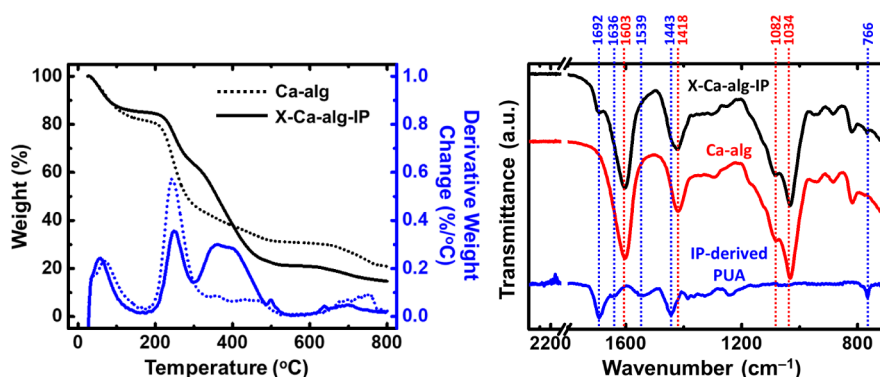


Figure 3. Left: Thermogravimetric analysis (TGA, under Ar) and corresponding differential thermogravimetric analysis (DTG) curves of representative X-Ca-alg-IP (solid line) and Ca-alg (dotted line) aerogels. Right: ATR-FTIR spectra of X-Ca-alg-IP, Ca-alg, and IP-derived PUA aerogels as indicated. Dashed lines indicate characteristic absorption bands of Ca-alg (red) and IP-derived PUA (blue), discussed in the text.

at the Budapest Neutron Center, following procedures described previously.^{45,46} A momentum transfer (Q) range of 0.007–0.400 Å^{−1} was covered. The measured scattering intensities were corrected for sample transmission, empty cell and solvent scattering, detector sensitivity, and background. Structural parameters were estimated by the model-based analysis of the corrected scattering intensity (I) vs Q profiles. For this, combined power-law and Guinier approximations were applied to the entire SANS profiles via the unified single-level Beaucage model, covering the entire experimental Q range simultaneously.^{47,48} Curve fitting was performed using nonlinear least-squares routines in the SASView software (Version 5.0.6). Initially, dry, as-prepared X-Ca-alg-IP aerogel beads were densely packed into 5.0 mm thick quartz cuvettes and measured without any prior treatment. The same samples were then filled with a D₂O/H₂O mixture. The D₂O/H₂O (51:49 v/v) mixture was selected to approximate contrast matching of the native Ca-alg framework, as detailed in our earlier work.^{25,45} Under these conditions, the scattering contribution of the pristine alginate matrix is significantly reduced, allowing enhanced sensitivity to the PUA phase associated with the cross-linking layer.

For mechanical testing, disc-shaped specimens (0.7–2.1 mm thick, 11–12.5 mm in diameter) of X-Ca-alg-IP monoliths were cut using a diamond disc blade under dry conditions. The Young's modulus (E), the shear modulus (G) and the Poisson's ratio (μ) of X-Ca-alg-IP specimens were determined by employing the Impulse Excitation Technique (IET)⁴⁹ using the Buzz-o-Sonic system (BuzzMac International LLC, USA). For the IET measurements, the disc-shaped specimens were supported on a foam substrate and automatically excited by a motor-driven metal rod (2 cm in length and 2 mm in diameter). A microphone positioned near the sample transmitted the resulting sound vibrations to the signal-processing unit. The first and second natural resonance frequencies ($f_{1,2}$), corresponding to flexural and torsional (antiflexural) vibration modes (Figure S1), were identified and subsequently used to calculate the corresponding Young's modulus values ($E_{1,2}$) using eq 1, where d , m , t , and ρ represent the diameter, mass, thickness, and density of the specimen, respectively, and μ is determined according to ASTM E1876–15⁵⁰ as a function of $2t/d$ and $f_{1,2}$. $K_{1,2}$ are the first and second natural geometric factors listed in ASTM E1876–15 as a function of μ and $2t/d$. The Young's modulus values obtained from the first and second modes ($E_{1,2}$) were compared for consistency, and the final Young's modulus (E) was taken as their average. G was determined using eq 2. The physical properties of the measured samples, together with the corresponding resonance frequencies (f_1 : antiflexural mode; f_2 : axisymmetric flexural mode), are summarized in Table S4.

$$E_{1,2} = \frac{12\pi d^2 f_{1,2}^2 m(1 - \mu^2)}{K_{1,2}^2 t^3} = \frac{3\pi^2 d^4 f_{1,2}^2 \rho(1 - \mu^2)}{K_{1,2}^2 t^2} \quad (1)$$

$$G = \frac{E}{2(1 + \mu)} \quad (2)$$

3. RESULTS AND DISCUSSION

3.1. Preparation of X-Ca-Alg-IP Aerogels

The preparation of both X-Ca-alg-IP aerogel beads and monoliths is summarized in Figure 2. Ca-alg hydrogel beads were obtained by the dropwise addition of an aqueous Na-alg solution into an aqueous Ca(II) solution. The Na-alg concentration was set at three levels: 1%, 2%, and 3% w/w; the Ca(II) concentration was varied between 0.2 and 1.0 M (Table S1). For the preparation of Ca-alg monoliths in a cylindrical shape, aqueous Na-alg solutions (2% or 3% w/w; Table S2) were poured into dialysis tube-shaped membranes (25 mm in diameter), which were then immersed in a CaCl₂ solution (0.2 M) for gelation. After gelation and aging for 24 h, Ca-alg gels (beads or monoliths) were solvent-exchanged with MeCN and then immersed in a solution of the triisocyanate (IP) in *n*-BuOAc/MeCN (0.56 M for beads, Table S1; 0.06, 0.13, 0.22, 0.40, or 0.60 M, Table S2) for 24 h to allow diffusion throughout the gel network. Subsequently, the samples were heated at 70 °C for 72 h to accelerate and complete the cross-linking process. Following drying with supercritical fluid CO₂, the corresponding X-Ca-alg-IP aerogel beads and monoliths were obtained.

For beads, different Ca(II) concentrations in the gelation bath were investigated to assess their effect on the composition and material properties of the resulting X-Ca-alg-IP aerogels. As discussed in Section 3.2, the Ca(II) concentration has little or no effect on the aerogel properties. Therefore, for the preparation of monoliths, a single Ca(II) concentration (0.2 M) was used. On the other hand, the concentration of the IP solution was varied (Table S2) in order to tune the PUA content and, thereby, the mechanical properties of the resulting X-Ca-alg-IP aerogels (Section 3.4).

Representative optical photographs of X-Ca-alg-IP aerogel beads and monoliths are shown in Figure 2. The bead diameters ranged from 2.1 to 2.5 mm for all samples, and the monolith diameters were in the range of 10.0–12.5 mm. Consistent with prior literature,^{21,23} both X-Ca-alg-IP aerogel beads and monoliths were slightly larger compared to their native Ca-alg counterparts. Lower drying shrinkage relative to the native networks has been a consistent observation across the polymer-cross-linked aerogel domain, from inorganic (e.g., silica)^{16,51–54} to organic (polymeric)^{55–58} and across various

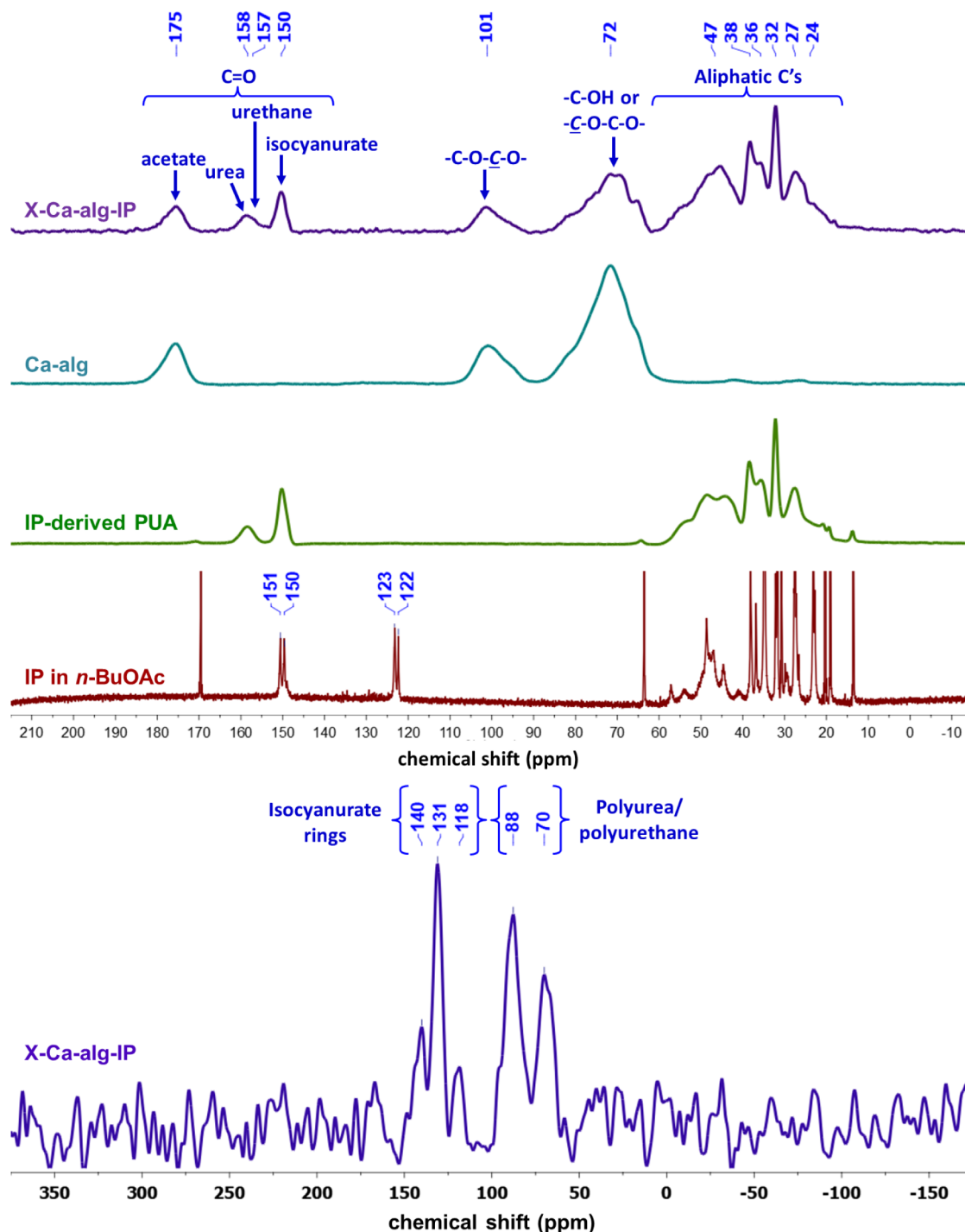


Figure 4. Top: ^{13}C CPMAS NMR spectra of X-Ca-alg-IP, Ca-alg and IP-derived PUA aerogels, and ^{13}C liquid NMR spectrum of monomer IP (Desmodur Z4470BA) as indicated. Bottom: ^{15}N CPMAS NMR spectrum of X-Ca-alg-IP aerogels.

types of cross-linking polymers. This has been attributed to the location of the cross-linking polymer and the rigidization brought upon the native network, halting drying shrinkage. Representative bead diameter distributions are shown in Figure S2.

The cross-linking mechanism for preformed biopolymer gels is summarized in Figure S3. As already established,^{21,23,24} the reaction of the $-\text{OH}$ groups of the alginate with one of the $-\text{NCO}$ groups of the triisocyanate (IP) formed urethane linkages along the alginate backbone. The remaining $-\text{NCO}$ groups were hydrolyzed by gelation water, remaining strongly

adsorbed on the surface of the alginate gel network, yielding amines that subsequently reacted with free IP molecules within the pores to form urea groups. This process continues through repeated hydrolysis of the dangling $-\text{NCO}$ groups and reaction with fresh IP molecules in the pores until the alginate network becomes coated and cross-linked with PUA. The cross-linking process has been confirmed with ATR-FTIR and ^{13}C CPMAS spectroscopy (Section 3.2).

3.2. Chemical Characterization of X-Ca-Alg-IP Aerogels

The uptake of material by Ca-alg during the cross-linking process was confirmed with comparative thermogravimetric analysis (TGA) of Ca-alg and X-Ca-alg (Figure 3 left). The chemical identity of the cross-linking polymer was probed with ATR-FTIR spectroscopy (Figure 3, right), ^{13}C (Figure 4, top), and ^{15}N CPMAS (Figure 4, bottom) NMR. Finally, the amount of the cross-linking polymer was quantified from the skeletal densities of Ca-alg, X-Ca-alg-IP, and IP-derived PUA aerogels.²¹ These values were cross-checked with the TGA data and were confirmed from the calcium content of both Ca-alg and X-Ca-alg-IP aerogels using ICP-MS.

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTG) of native Ca-alg aerogels (Figure 3 left) show three decomposition steps, in agreement with previous findings.^{21,23,59,60} The first step, below 100 °C, is attributed to the loss of water. The major step, from 200 to 300 °C, is attributed to the degradation of the Ca-alg polymer chain. Further decomposition steps up to 800 °C can be attributed to tar cracking, char formation, and the degradation of inorganic residues.⁶¹ For X-Ca-alg-IP aerogels, a second major DTG peak from 300 to 500 °C is observed and attributed to the decomposition of the urethane linkages, urea, and isocyanurate groups.^{58,60,62,63} Residual mass at 800 °C (~15%) is lower than that of native Ca-alg (~21%), consistent with the noncarbonizable nature of aliphatic PUAs.⁶⁴

ATR-FTIR spectra of X-Ca-alg-IP aerogels are shown in Figure 3 (right), together with those of native Ca-alg aerogels and IP-derived PUA for comparison. In both native and cross-linked samples, the characteristic bands of the alginate backbone can be clearly observed.^{21,59} Bands at 1603 cm^{-1} and 1418 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the Ca(II)-coordinated carboxylate groups, while bands at 1082 cm^{-1} and 1034 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of the C–O–C groups of the sugar rings. Additional bands associated with IP-derived PUA are also present in the X-Ca-alg-IP spectrum. Specifically, the bands at 1692, 1443, and 766 cm^{-1} , attributed to the stretching vibration of carbonyl groups of the isocyanurate ring, C–H bending, and out-of-plane CH bending in the cyclohexyl ring or deformation of the isocyanurate ring, respectively, are observed in both spectra of X-Ca-alg-IP and IP-derived PUA, while bands at 1636 and 1539 cm^{-1} , attributed to the stretching vibration of urea carbonyl groups and N–H scissoring, respectively, appearing overlapping with Ca-alg bands. The absence of bands at 2260–2270 cm^{-1} indicates no unreacted isocyanate groups.

The solid-state ^{13}C CPMAS NMR spectrum of X-Ca-alg-IP aerogels is shown in Figure 4 (top), along with the spectra of native Ca-alg aerogels and IP-derived PUA. Consistent with the literature,^{21,23} the characteristic peaks of the alginate backbone, corresponding to the carboxylate carbonyls, the acetal carbons (–C–O–C–O–), and the ring carbons attached to oxygen (–OH or –O–) appeared at 175, 101, and 72 ppm, respectively. The peak at 158 ppm in the spectrum of X-Ca-alg-IP was attributed to urea carbonyls,⁶⁴ and the shoulder at 157 ppm to the carbonyls of the urethane linkages.^{60,62,65–67} It is noteworthy that the 158 ppm/shoulder pattern is identical to what has been observed with biopolymers (i.e., alginate, chitosan)^{21,23} and silica⁵² aerogels cross-linked with another aliphatic triisocyanate (N3300; Figure 1) via an analogous mechanism to that of Figure S3. Carbonyls of the isocyanurate ring of IP-derived PUA

appeared at 150 ppm,^{60,64} while resonances in the range of 24–47 ppm were assigned to the aliphatic carbons of IP.

The liquid-phase ^{13}C NMR spectrum of the IP monomer (Desmodur Z4470BA; Figure 1) is also included in Figure 4 (top) for comparison. As evidenced by the presence of two major isocyanurate carbonyl peaks at 151 and 150 ppm and two peaks at 123 and 122 ppm, assigned to secondary and primary isocyanate groups,^{68,69} respectively, the starting material consisted of at least two of the four possible isomers shown in Figure S4. It should also be noted that due to substitution on the cyclohexane rings, additional *cis* and *trans* configurations are possible for each constitutional isomer shown in Figure S4.^{68,69} The isocyanurate isomeric structures present in the monomer are expected to be transferred intact into the Ca-alg and X-Ca-alg-IP aerogels, partly explaining the broadness of the isocyanurate carbonyl in the solid-state spectra of the X-Ca-alg-IP aerogels. On the other hand, the absence of the isocyanate resonances from the solid-state spectra confirms the complete reaction of the isocyanate groups, in agreement with the ATR-FTIR data.

The solid-state ^{15}N CPMAS NMR spectrum of X-Ca-alg-IP is shown in Figure 4 (bottom) and is also consistent with the formation of PUA during cross-linking: the spectrum shows two clusters of peaks at 140/131/118 ppm and 88/79 ppm, assigned to the nitrogens on the isomeric isocyanurate rings of IP and to the nitrogens of the urea/urethane groups, respectively.^{21,70} The multiplicities of the resonances are attributed to the presence of various triisocyanate isomers.

The polymer ratio (Ca-alg/PUA) in the X-Ca-alg-IP aerogel beads was determined based on skeletal density measurements. Specifically, the PUA and Ca-alg content in X-Ca-alg-IP aerogels were calculated from the skeletal densities of Ca-alg, X-Ca-alg-IP, and IP-derived PUA aerogels (Table S1), as has been reported before.²¹ In turn, the amount of Ca was calculated from the amount of Ca-alg in X-Ca-alg aerogels and was also independently determined using ICP-MS. The results from the two methods for the Ca content in X-Ca-alg-IP aerogels were in good agreement and in line with the theoretical amount of calcium expected if all –COO^- groups of the alginate backbone were neutralized (~10% w/w). Indeed, as confirmed by the data in Table S1, the amount of Ca was found to be around 10% w/w for all native Ca-alg samples. In turn, the amount of Ca was independent of the Ca(II) concentration of the gelation bath, meaning that the 0.2 M bath of Ca(II) already provided a high excess of Ca(II) compared to the available coordination sites. As shown further in Table S1, the PUA content of X-Ca-alg-IP aerogels was found within overlapping ranges of 37–45%, 40–46%, and 42–48% w/w for aerogels prepared from 1%, 2%, and 3% w/w Na-alg solutions, respectively. These values agree within 10%–15% with the TGA data (Figure 3 left). In conclusion, the amount of PUA in X-Ca-alg-IP was practically independent of the concentration of Na-alg in the sol and the concentration of Ca(II) in the gelation bath. By comparison, the PUA content in X-Ca-alg-N3300 and X-Ca-alg-RE aerogel beads (also from 2% w/w Na-alg solutions) cross-linked with the same concentration (0.5–0.6 M) of either flexible aliphatic Desmodur N3300 triisocyanate or rigid aromatic Desmodur RE triisocyanate was higher (56% w/w and 60% w/w, respectively),²⁵ probably reflecting monomer reactivity and stereochemical factors affecting packing.

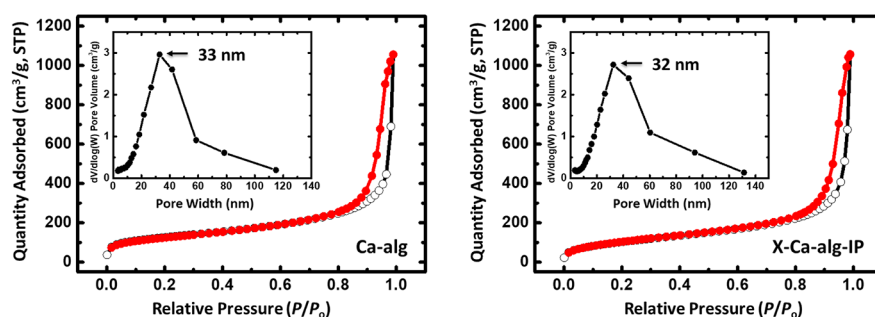


Figure 5. Representative N_2 -sorption isotherms for Ca-alg and X-Ca-alg-IP aerogels, along with the corresponding pore size distributions by the Barrett–Joyner–Halenda method (insets) as indicated.

3.3. Material Properties of X-Ca-Alg-IP Aerogels

3.3.1. General. All aerogels in this study were low-density materials, with X-Ca-alg-IP aerogels consistently displaying only slightly higher bulk densities ($0.07\text{--}0.23\text{ g cm}^{-3}$) than their native Ca-alg counterparts ($0.05\text{--}0.16\text{ g cm}^{-3}$), despite the PUA uptake—a fact attributed to their lower drying shrinkage. Results are summarized in Table S1. As expected, bulk densities followed an increasing trend with higher Na-alg concentrations in the sol. For comparison, X-Ca-alg-IP aerogels coming from a 2% Na-alg solutions and cross-linked with IP (this study) were more dense (0.12 g cm^{-3}) than the corresponding native Ca-alg aerogels (0.09 g cm^{-3}), but less dense than the corresponding X-Ca-alginate aerogels cross-linked with either flexible-aliphatic N3300 (X-Ca-alg-N3300; 0.19 g cm^{-3}) or rigid-aromatic RE (X-Ca-alg-RE; 0.18 g cm^{-3}), reflecting partly the lower PUA content of X-Ca-alg-IP aerogels (42% vs 56% and 60% w/w, respectively) and partly their higher porosity (92% vs 87% and 88% v/v, respectively).²⁵

Skeletal densities decreased upon cross-linking, adopting intermediate values ($1.43\text{--}1.58\text{ g cm}^{-3}$) between those of the native Ca-alg aerogels ($1.91\text{--}2.14\text{ g cm}^{-3}$) and of the IP-derived PUA (1.117 g cm^{-3}).⁶⁴ Among the X-Ca-alg-IP samples, skeletal densities slightly decreased with increasing Na-alg concentration in the sol. Keeping all other parameters equal, the skeletal densities of the X-Ca-alg-IP aerogels coming from a 2% Na-alg sol (1.47 g cm^{-3}) were similar to the skeletal densities of X-Ca-alg-N3300 aerogels (1.43 g cm^{-3}) or X-Ca-alg-RE aerogels (1.44 g cm^{-3}).²⁵

3.3.2. The Porous Structure. The porous structure of Ca-alg and X-Ca-alg-IP aerogels was characterized using N_2 -sorption porosimetry, and, where possible, experimental values were compared with those calculated from bulk and skeletal density data. Typical N_2 -sorption isotherms are shown in Figure 5, and data are summarized in Table S1. Percent porosities calculated from bulk and skeletal density data of the native Ca-alg aerogels fall in the range of 92–97% v/v. Cross-linking led to a slight decrease in porosity: X-Ca-alg-IP aerogels from 1% and 2% w/w Na-alg sols had porosities in the range of 91–95% v/v, and those from 3% w/w solutions had porosities in the 84–86% v/v range. As mentioned above, the porosities of X-Ca-alg-N3300 and X-Ca-alg-RE aerogels from 2% w/w Na-alg sols were 87% and 88% v/v, respectively.²⁵

The N_2 -sorption isotherms of both Ca-alg and X-Ca-alg-IP aerogels (Figure 5) displayed hysteresis loops but did not reach saturation, consistent with predominantly macroporous materials with some mesoporosity. Indeed, in all cases, the specific total pore volumes, V_{Total} calculated from bulk (ρ_b) and skeletal density (ρ_s) data via $V_{\text{Total}} = (1/\rho_b) - (1/\rho_s)$, were much larger than the specific pore volumes in the 1.7–300 nm range probed by the N_2 -sorption method ($V_{1.7-300\text{ nm}}$)—see Table S1.

The BET specific surface areas of native Ca-alg aerogels were relatively high, from $422\text{--}487\text{ m}^2\text{ g}^{-1}$ (Table S1), while 14–18% of those values were assigned to micropores via t -plot analysis according to the Harkins and Jura model,^{71,72} consistent with previous results.^{21,23,24,59} BET surface areas of the X-Ca-alg-IP aerogels of this study remained notably high (in the $354\text{--}393\text{ m}^2\text{ g}^{-1}$ range)

compared to X-Ca-alg-N3300. Specifically, the BET surface area of the X-Ca-alg-IP aerogels made with a 2% Na-alg solution was $385\text{ m}^2\text{ g}^{-1}$, while the BET surface area of the corresponding X-Ca-alg-N3300 was $265\text{ m}^2\text{ g}^{-1}$.²⁵ In general, the decrease in the BET surface area upon cross-linking can be associated with the formation of a conformal PUA coating that fills smaller skeletal crevices, smooths fine surface features, and reduces the accessible surface area without disrupting the overall hierarchical nanoscale framework. Indeed, all micropore-assigned surface area in native Ca-alg aerogels was lost after cross-linking with either IP (Table S1) or N3300, as reported previously,^{21,23} consistent in both cases with the confinement of a rather compact cross-linking polymer in the space between the elementary building blocks of the alginate skeletal network. By the same token, it is also noted that the surface area of similarly obtained (from a 2% Na-alg sol) X-Ca-alg-RE aerogels was higher ($425\text{ m}^2\text{ g}^{-1}$) with a significant ($\sim 12\%$) portion assigned to micropores, which is attributed to the rigid, inflexible aromatic structure of RE. It is noted that all polymeric aerogels derived from RE, including PUAs,^{24,64,73} polyurethanes,^{62,65,67} polyamides,⁷⁴ and polyimides,⁷⁵ include micropores.

The accumulated IP-derived PUA did not significantly affect the BJH pore size distributions of pores in the mesopore range (1.7–300 nm, shown as insets in Figure 5), which were broad and similar in all native and polyurea-cross-linked aerogels, with maxima in the 27–34 nm range. Average pore diameters in the 1.7–300 nm range remained largely unaffected by cross-linking and were close to the maxima of the corresponding pore-size distributions. In contrast, average pore diameters calculated via the $4 \times V_{\text{Total}}/\sigma_{\text{BET}}$ method were several times larger than the pore sizes in the 1.7–300 nm range, reflecting the macroporous nature of the samples, as is clearly visible from the SEM images (Figure 6).

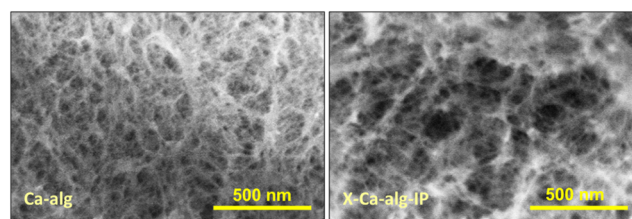


Figure 6. Representative SEM images of native Ca-alg and X-Ca-alg-IP aerogels as indicated.

It has been reported in the literature that polyurea cross-linking renders X-alginate aerogels hydrophobic, in contrast to native alginate aerogels, which are inherently hydrophilic.²¹ Indeed, the water contact angle of a $5\text{ }\mu\text{L}$ droplet on X-Ca-alg-IP aerogels was in the range of $120\text{--}125^\circ$, exhibiting the rose-petal effect.⁷⁶ These values are consistent with those reported in the literature for X-Ca-alg-N3300 (up to $119 \pm 2^\circ$).²¹ A more detailed investigation of surface wettability and related properties of these materials is currently underway.

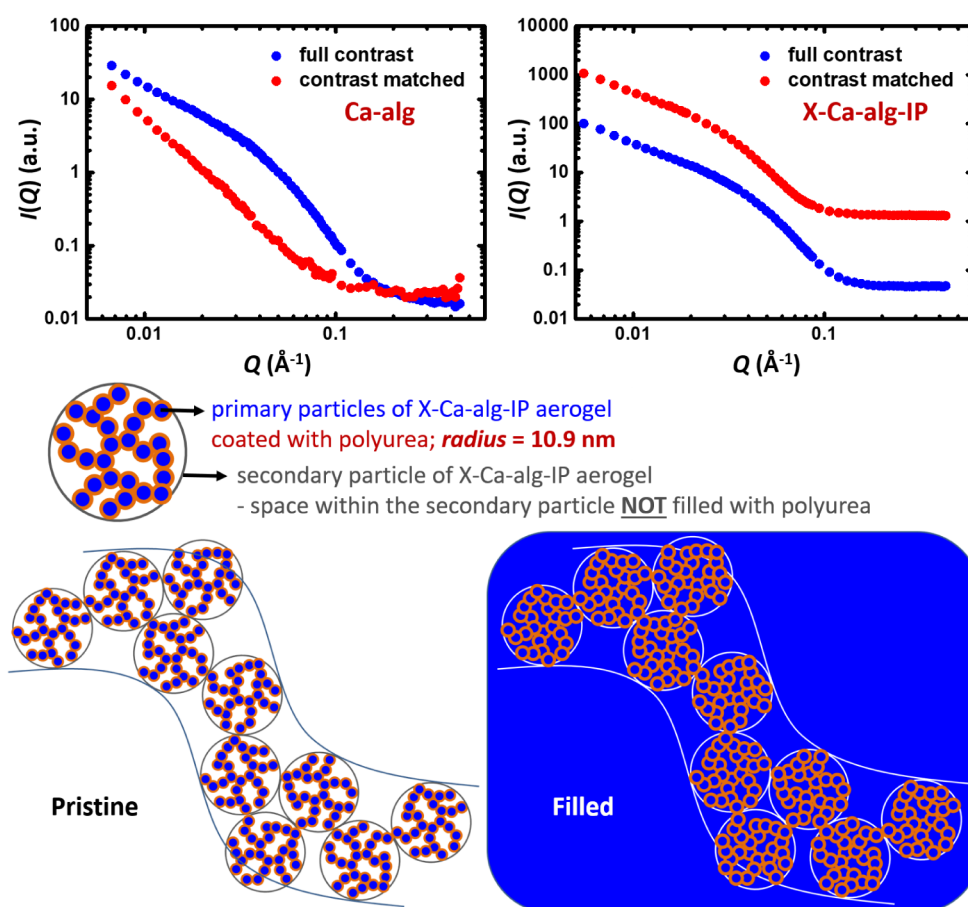


Figure 7. Top: SANS profiles of Ca-alg (A; data for Ca-alg from ref. 25) and X-Ca-alg-IP (B) aerogels. Full-contrast data of pristine (dry) aerogels were obtained first; the same samples were contrast-matched for the Ca-alg network by filling with a D_2O/H_2O mixture (51/49 v/v) and were measured again. Structural parameters derived from these SANS data are given in Table S3. Bottom: Nanoscale structures of X-Ca-alg-IP aerogels, according to SANS (see text). The panel labeled “Filled” denotes a sample filled with a contrast-matching agent (D_2O/H_2O mixture, 51:49 v/v).

3.3.3. The Solid Skeletal Network. The skeletal network was visualized with scanning electron microscopy (SEM), and its elementary building blocks were probed with small-angle neutron scattering (SANS).

SEM images (Figure 6) show that the characteristic fibrous morphology of native Ca-alg aerogels is retained after cross-linking, consistent with PUA accumulation templated by the surface functionality of the skeletal network, as described in Figure S3.^{21,23,24}

On the other hand, SANS probes structural correlations over length scales of approximately 1–100 nm and is, therefore, directly sensitive to the nanoscale building blocks of the alginate aerogel skeleton, their aggregation into secondary structures, and the nature of their interfacial regions.⁷⁷ Beyond providing particle dimensions and fractal characteristics, SANS is particularly powerful for multiphase soft materials, as contrast variation via isotopic substitution enables selective observation of specific structural components within complex hierarchical systems. In the system studied here, X-Ca-alg-IP aerogels, SANS indicates the preservation of the overall nanoscale architecture, complementing N_2 -sorption porosimetry, which reveals modifications in the finest porosity.

Figure 7 (top) compares the SANS profiles of Ca-alg²⁵ and X-Ca-alg-IP aerogels measured under full contrast (dry state) and after contrast matching of the alginate network by filling the pore space with a D_2O/H_2O (51:49 v/v) mixture.⁴⁵ Under full contrast conditions, both materials exhibit extended power-law scattering, characteristic of nanoscale primary particles aggregated into mass-fractal secondary structures, which, in turn, assemble to form fibrous skeletal architectures as seen in SEM and previously reported for other organic aerogels, notably certain polyimides⁷⁸ and PUAs.^{70,76}

Parameters obtained from the analysis of the scattering profiles using the Beaucage Unified Model are summarized in Table S3.

The high- Q region of native dry Ca-alg aerogels displays a power-law slope of -4.55 , exceeding the Porod value of -4.00 expected for sharp interfaces, indicating that the interfacial regions of the primary particles are not abrupt but instead consist of continuous density gradients across the particle boundaries.⁷⁹ The Guinier knee (the curved region in the scattering profile) that follows the high- Q power-law region provides the radius of gyration (R_g) of the primary particles. Assuming spherical geometry, the primary particle radius (R) was calculated from R_g according to $R = \sqrt{5/3} R_g$, yielding $R = 8.3 \pm 0.1$ nm. Following the Guinier knee, the subsequent low- Q power-law exponent (2.05) gives the mass fractal dimension of the assembly of primary particles into secondary particles. All power-law exponents, as well as the R and R_g values, are provided in Table S3.

Upon D_2O/H_2O (51:49 v/v) mixture, approximate contrast matching of the Ca-alg phase renders the alginate cores effectively invisible to neutrons, and the scattering profile is dominated by a single high- Q power law with a slope equal to -3.72 . As matching suppresses scattering from uniform regions having approximately the same scattering length density as the solvent, the new scattering profile can be interpreted as a transition from geometric interface-dominated scattering in the native Ca-alg aerogels to fluctuation-dominated scattering arising from correlated density variations within the density-gradient halo surrounding the practically invisible contrast-matched Ca-alg particles. The slight shift of the contrast-matched profile toward lower Q (by approximately 0.02 – 0.03 $\text{\AA}^{-1}$) indicates only a modest increase in the associated correlation length upon solvent infiltration. Because Ca-alg does not swell in water,⁴⁵

and the contrast-matched cores no longer contribute to the measured intensity, this shift is consistent with hydration-induced broadening of the diffuse interfacial density gradient rather than physical swelling of the solid primary particles themselves.

Both before and after contrast matching, the SANS profiles of X-Ca-alg-IP aerogels closely resemble each other and those of dry native Ca-alg, showing distinct high- and low- Q power-law regions separated by a Guinier knee. Upon contrast matching, the X-Ca-alg-IP profile shifts slightly to lower Q (by $\sim 0.01 \text{ \AA}^{-1}$) indicating a modest increase in the characteristic correlation length upon solvent infiltration. The similarity between the pristine and contrast-matched scattering profiles is consistent with solvent access to interparticle voids.⁸⁰ Thus, PUA deposition appears to occur conformally along the surfaces of existing Ca-alg primary particles rather than filling the secondary structural elements.

The high- Q slope of the full-contrast (dry) profile of X-Ca-alg-IP aerogels is -5.86 ± 0.2 , which is more negative than both the Porod slope and the high- Q slope of the dry native Ca-alg aerogels (-4.55 ± 0.3). This slope is attributed to the IP-derived PUA coating surrounding the primary particles, indicating an extended diffuse interfacial region with continuously varying scattering length density rather than a sharp core-shell boundary. The low- Q slope (~ -2.19) remains unchanged between the full-contrast and the contrast-matched ($\text{D}_2\text{O}/\text{H}_2\text{O}$ -filled) X-Ca-alg-IP samples, corresponding to a mass-fractal dimension of ~ 2.2 . The invariance of the mass-fractal exponent suggests that PUA formation modifies the interfacial structure while largely preserving the aggregation topology, consistent with cross-linking proceeding under strong templating, while the hierarchical architecture is inherited from the original Ca-alg core.

Guinier analysis of dry X-Ca-alg-IP aerogels provides an estimate of the apparent primary radius of $10.9 \pm 0.2 \text{ nm}$, compared with $8.3 \pm 0.1 \text{ nm}$ for native Ca-alg. Upon contrast matching of the Ca-alg core, substantially larger apparent radii are obtained ($14.6 \pm 0.3 \text{ nm}$), reflecting neutron scattering from hydrated polymer-solvent density correlations surrounding the contrast-matched cores rather than from particle boundaries. In other words, the increase in apparent size reflects swelling of a solvent-accessible interfacial region—the IP shell. Hydration expands the spatial extent over which density correlations persist, shifting the Guinier regime toward lower Q without altering aggregate topology. The persistence of well-defined scattering, together with these hydration effects, provides strong evidence that solvent not only permeates secondary aggregates but also reaches the Ca-alg core particles, which validates and supports the interpretation of the contrast-matched measurements.

Figure 7 (bottom) illustrates the hierarchical topology of X-Ca-alg-IP aerogels as inferred from SANS analysis. Although the schematic representation may visually resemble a core-shell structure, the SANS data do not support the presence of an abrupt interface, and therefore, a classical core-shell model is not appropriate for quantitative description. In other words, the polymer coating cannot be described as a sharp core-shell boundary but rather as a conformal, density-modified interfacial layer surrounding the Ca-alg particles. This interpretation is consistent with well-established concepts in polymer physics, whereby polymer properties in the vicinity of an interface differ from bulk behavior, giving rise to an interphase region characterized by gradual changes in density and molecular mobility. Such interphases typically extend over a few nanometers from the surface,^{81,82} consistent with the thickness scale of the density gradient within the conformal PUA coating identified by SANS in this work.

Upon filling with the $\text{D}_2\text{O}/\text{H}_2\text{O}$ (51:49 v/v) mixture, the scattering contribution of the native Ca-alg framework is strongly reduced, indicating approximate contrast matching of the Ca-alg phase. Under these conditions, the remaining scattering from X-Ca-alg-IP is primarily associated with the IP-derived PUA phase and the corresponding interfacial regions. Because contrast-matched conditions probe the solvated structure, estimation of coating dimensions is more reliably based on dry, full-contrast measurements. Differences between the apparent radii of native and cross-linked samples therefore provide an estimate of the effective thickness of the density-

modified PUA layer (approximately 2–3 nm). It is noted that in structures arising from the aggregation of primary particles into fractal networks, the characteristic pore dimensions are typically of the same order of magnitude as the particle and aggregate length scales that define the network topology.^{83,84} Accordingly, the SANS-derived primary particle radius of Ca-alg ($\sim 8.3 \text{ nm}$) is consistent with mesoporous structures in the $\sim 8 \text{ nm}$ range, in agreement with N_2 sorption data for Ca-alg aerogels derived from 2% w/w sols (pore diameters 15–16 nm, Table S1). The formation of a conformal 2–3 nm PUA interphase is expected to modify the effective interparticle separation and is consistent with the observed shift toward larger apparent pore diameters (17–18 nm, Table S1) in the cross-linked system.

By comparison, X-Ca-alg-IP aerogels exhibit a similar hierarchical organization to X-Ca-alg-N3300 aerogels cross-linked with flexible-aliphatic N3300 (refer to Figure 1),²⁵ as evidenced by similar low- Q fractal exponents (-2.19 vs -2.02) and comparable contrast-matched correlation sizes ($R_g = 113 \pm 2 \text{ \AA}$ for IP and $122 \pm 4 \text{ \AA}$ for N3300, corresponding to apparent radii of 14.6 ± 0.3 and $16.0 \pm 0.5 \text{ nm}$, respectively; Table S3). The primary distinction lies in the packing efficiency of the deposited PUA. Flexible N3300 chains can fold and pack efficiently around the alginate framework, producing higher-density PUAs⁸⁵ ($1.20\text{--}1.31 \text{ g cm}^{-3}$ vs 1.117 g cm^{-3} from IP, respectively) and smaller apparent dry particle radii ($8.8 \pm 0.1 \text{ nm}$ vs $10.9 \pm 0.2 \text{ nm}$ from IP; Table S3). By the same token, the rigid structure and isomeric constitution of the IP monomer hinder dense packing, yielding a less compact conformal coating that expands the scattering density envelope despite lower overall polymer content (44% w/w vs 56% w/w for N3300). The larger swelling radius observed for N3300 under contrast matching ($16.0 \pm 0.5 \text{ nm}$; Table S3) is also consistent with greater conformational flexibility and enhanced solvent uptake. The characteristic primary particle sizes obtained from SANS ($\sim 8\text{--}11 \text{ nm}$) are consistent with the mesopore size range determined by N_2 -sorption, supporting a structural picture in which pores arise from the packing of these primary building blocks.

In contrast to aliphatic systems, previous studies have shown that cross-linking with the more reactive aromatic triisocyanate (RE; Figure 1) yields a distinctly different nanoscale structure. Highlighting the effects of reaction kinetics and polymer rigidity, rapid polymerization promotes nucleation within interparticle voids, resulting in partial filling of secondary particles with microporous RE-derived PUA.²⁵

3.4. Elastic Properties of X-Ca-Alg-IP Aerogels

The elastic properties of X-Ca-alg-IP aerogels were evaluated using the impulse excitation technique (IET),⁴⁹ using cylindrical samples of variable bulk densities (Table S2) prepared by varying the Na-alg concentration in the sol and the IP concentration in the cross-linking bath, as discussed in Section 3.1. Cylindrical samples were subsequently cut into thin disc-shaped specimens (0.7–2.1 mm thick and 11–12.5 mm in diameter). The specifications of the samples used for testing are summarized in Table S4 of the Supporting Information. Representative amplitude vs time waveforms and their corresponding frequency spectra are shown for selected specimens (X-Ca-alg-IP-M2.3-1 and X-Ca-alg-IP-M2.1-1) in Figure S5 at two resonant frequencies. (Note: The last number (–1, –2, or –3) in the sample names is simply an index identifying the specific specimen, as described in Table S4.)

Figure 8 shows the elastic modulus, shear modulus, and Poisson's ratio data derived from the IET measurements for the various preparation conditions reflected by the sample names (refer to the Experimental Section). While all X-Ca-alg-IP aerogels exhibited Poisson's ratios within the expected range for elastic polymeric materials (0.2–0.5),⁸⁶ both the elastic and shear moduli increased as the Na-alg concentration in the sol

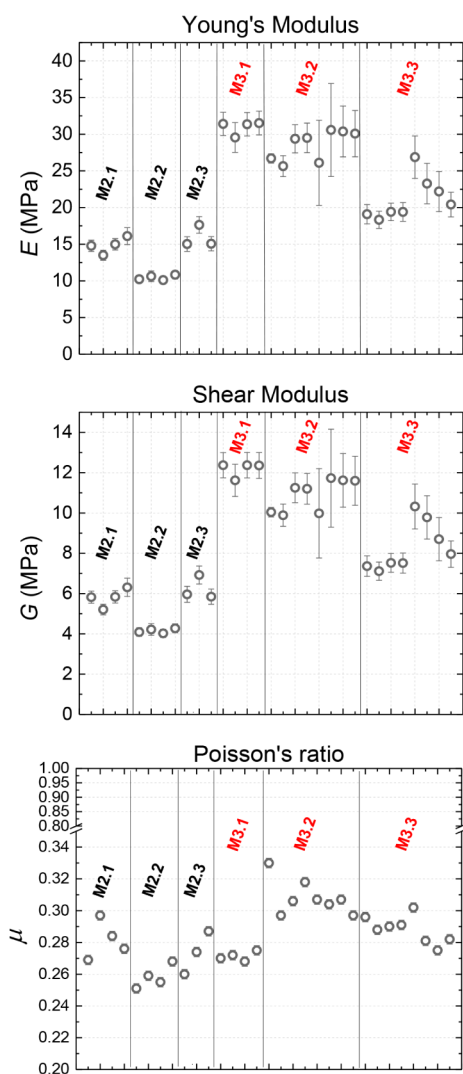


Figure 8. Elastic modulus (E ; top), shear modulus (G ; middle), and Poisson's ratio (μ ; bottom) of X-Ca-alg-IP aerogels as indicated. Vertical lines delineate measurements of several specimens of the same sample.

increased. The average values of the elastic properties derived for each material are summarized, together with relevant material properties, in Table S5.

The dependence of Young's modulus and sound velocity on bulk density and porosity is shown in Figure 9. It is noted that the sound velocity (v) is related to Young's modulus (E) and bulk density (ρ_b) via the equation $v = (E/\rho_b)^{1/2}$. According to Figure 9, the concentration of the Na-alg precursor solution is the single most important factor influencing the Young's modulus of the aerogels. For example, samples X-Ca-alg-IP-M3.2 and X-Ca-alg-IP-M2.1 carry similar relative amounts of PUA ($\sim 30\%$ w/w), but the Young's modulus of X-Ca-alg-IP-M3.2 is approximately twice that of X-Ca-alg-IP-M2.1 (28.5 vs 14.8 MPa). This is directly related to the strong dependence of stiffness (Young's modulus) on bulk density (0.133 ± 0.004 g cm $^{-3}$ vs 0.106 ± 0.002 g cm $^{-3}$), which in turn is governed by the amount of Ca-alg on the backbone, and is controlled by the concentration of the Na-alg solution, consistent with our previous studies.²¹ Notably, no clear correlation was observed between Young's modulus and average pore diameters (Figure S6).

Focusing attention within families of X-Ca-alg-IP aerogels sharing the same Ca-alg backbone, variations in the PUA content of X-Ca-alg-IP-M2 aerogels had a limited influence on Young's modulus; samples exhibited moduli in the range of 10–16 MPa, with only a slight upward trend as the bulk density increased. In contrast, increasing the PUA content of X-Ca-alg-IP-M3 aerogels was accompanied by a decrease in the Young's modulus (from 31 to 21 MPa: Table S5 and Figure 9). The observed behavior suggests a deviation from the idealized structure in Figure 7 (bottom), as accelerated cross-linking at higher IP concentrations on the denser Ca-alg network produces a more heterogeneous PUA distribution, which, in turn, alters the effective stiffness of the backbone-coating system. The sound velocity (Table S5 and Figure 9) combines bulk density and Young's modulus information, resulting in opposite trends in X-Ca-alg-IP-M2 and X-Ca-alg-IP-M3 aerogels as a function of density. On the other hand, as expected for porous solids, both the Young's modulus and the speed of sound exhibit opposite trends with bulk density and porosity; that is, any increase (or decrease) with density is accompanied by a corresponding decrease (or increase) with porosity (Figure 9).

Figure 10 shows the sensitivity of the Young's modulus to bulk density. A power-law scaling relationship, $E \propto \rho_b^a$, is observed. The exponent a was found to be equal to 3.1 ± 0.4 , which is close to the values reported previously for X-Ca-alg-N3300 aerogels ($a = 2.1\text{--}2.7$).²¹ These exponents are between those for native Ca-alg aerogels (around 4.0)²¹ and N3300-derived PUA ($a = 1.63$)⁶⁴ aerogels, indicating that the stiffness of X-Ca-alg aerogels is affected by both the alginate network and the PUA. By comparison to other aerogels from the literature, the sensitivity of the stiffness of all X-Ca-alg aerogels to bulk density is comparable to that of native silica ($a = 2.59\text{--}3.53$)¹⁸ or X-silica cross-linked with Desmodur N3200 ($a = 3.10$)⁵¹ but higher than X-vanadia aerogels cross-linked with Desmodur N3200 ($a = 1.87$).¹⁸

For a direct comparison of the effect of cross-linking with rigid-aliphatic IP-based PUA versus flexible-aliphatic N3300-based PUA, we compare the Young's modulus of X-Ca-alg-IP-M2 and X-Ca-alg-N3300 aerogels, both derived from 2% Na-alg solutions, at similar densities. The bulk density of the X-Ca-alg-IP-M2 aerogels (this study) was in the range of 0.105–0.116 g cm $^{-3}$ (Table S5), while the bulk density of the corresponding native Ca-alg aerogel was 0.054 g cm $^{-3}$,²¹ and that of X-Ca-alg-N3300 was in the range of 0.08–0.12 g cm $^{-3}$.²¹ The Young's modulus increased from 3.3 MPa for the native Ca-alg backbone to 3.5–11 MPa for X-Ca-alg-N3300 and further to 11–16 MPa for X-Ca-alg-IP-M2. Notably, the IP-derived PUA content in X-Ca-alg-IP-M2 was lower than the N3300-derived PUA content in X-Ca-alg-N3300 (Section 3.2), yet it produced a higher modulus. Given the rigidity of the IP-derived conformal PUA coating, as inferred from the SANS analysis of the backbone, the higher modulus of X-Ca-alg-IP-M2 aerogels relative to X-Ca-alg-N3300 with less cross-linker was attributed to the greater molecular rigidity of the IP structure.

4. CONCLUSIONS

Polyurea-cross-linked alginate (X-Ca-alg-IP) aerogels, derived from calcium alginate (Ca-alg) preformed gels and the isocyanurate trimer of rigid aliphatic isophorone diisocyanate (IP), have provided further insight into the role of the cross-

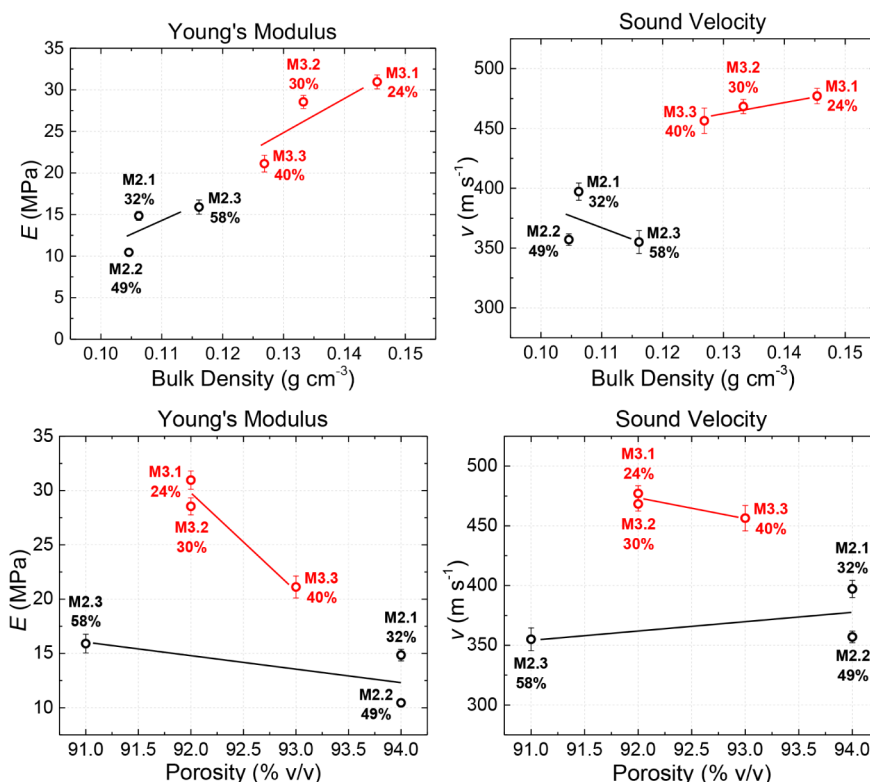


Figure 9. Young's modulus (E ; left) and sound velocity (v ; right) as a function of bulk density (ρ_b ; top) and porosity (Π ; bottom). The PUA content of each material (% w/w) is included in the graphs along each data point. Solid lines have been added to guide the eye.

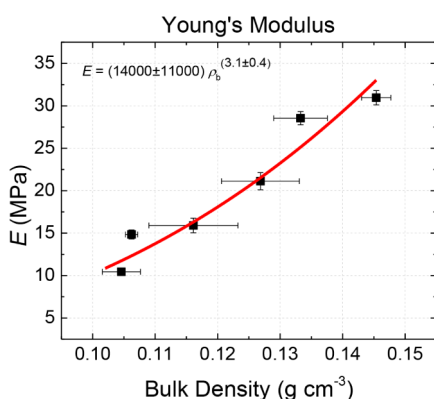


Figure 10. Young's modulus (E) as a function of bulk density (ρ_b) for X-Ca-alg-IP aerogels. The solid line represents a fit to the scaling law $E \propto \rho_b^a$.

linker's molecular structure on the properties of X-biopolymer aerogels.

Compared to other X-Ca-alginate aerogels prepared under nearly identical conditions, X-Ca-alg-IP aerogels had a lower PUA content: 40–46% w/w vs 56% w/w for X-Ca-alg-N3300 and 60% w/w for X-Ca-alg-RE, which were cross-linked with a flexible aliphatic and a rigid aromatic polyurea, respectively. This difference has been attributed to variations in monomer reactivity and stereochemical constraints affecting network formation and packing efficiency of the resulting PUA.

N_2 -sorption porosimetry and SEM demonstrated that, on one hand, cross-linking clogged micropores but, on the other, had a minimal effect on the macro/mesoporous structure, preserving both high porosity (up to 95% v/v) and specific surface area (up to $393 \text{ m}^2 \text{ g}^{-1}$), although both were slightly

reduced compared to native Ca-alg aerogels, as typically observed for X-aerogels. More detailed structural analysis of the solid network with SANS revealed that the PUA phase forms a diffuse interfacial region around the primary particles, with an estimated thickness on the order of 2–3 nm. By comparison, the X-Ca-alg-IP aerogels of this study and the X-Ca-alg-N3300 aerogels from previous work exhibit nearly identical hierarchical organization, as reflected by similar low- Q mass fractal exponents (2.19 vs 2.02) and comparable correlation sizes ($R_g = 113 \pm 2 \text{ \AA}$ vs $122 \pm 4 \text{ \AA}$), confirming that PUA formation primarily modifies the interfacial structure rather than the aggregation topology. Therefore, all differences in the properties of the respective X-aerogels can be attributed to the rigid versus flexible nature of the IP and N3300 monomers, respectively.

In this context, the higher molecular rigidity of IP relative to N3300 translates into enhanced stiffness, yielding higher Young's modulus values for X-Ca-alg-IP than for both native Ca-alg aerogels and those cross-linked with the more flexible aliphatic N3300, despite the lower PUA content. For example, the Young's modulus values of X-Ca-alg-IP aerogels were in the range of 11–16 MPa, whereas those of native Ca-alg and X-Ca-alg-N3300 aerogels were 3 MPa and 3.5–11 MPa, respectively.

Overall, IP-derived PUA acts as an intermediate system between flexible aliphatic and rigid aromatic cross-linkers, combining nanoscale structural retention with enhanced mechanical performance. Consistent with other studies on purely organic polymer aerogels, these results underscore the critical role of the molecular structure of the cross-linker in tuning structure–property relationships in X-biopolymer aerogels and support the development of mechanically robust,

highly porous materials for advanced environmental and biomedical applications.

Finally, in combination with the N_2 -sorption studies, the SANS results reported here have implications extending well beyond the immediate scope of this work. The disappearance of the microporosity present in native Ca-alg after cross-linking indicates that PUA forms a continuous, tight, conformal coating around the primary particles of the alginate backbone. However, as demonstrated by the SANS contrast-matching experiments, this PUA coating can be swollen by water, which can thereby access the alginate core, rendering the contrast-matching experiments possible in the first place. This finding is important because it provides a mechanistic explanation for the previously reported uptake of UO_2^{2+} and Hg^{2+} ions by X-Ca-alg aerogels and warrants further systematic investigation of the selective ion uptake by X-alginate networks.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.6c02361>.

Figure S1. The first two modes of vibration of a disc: (a) flexural and (b) antilexural. Dashed lines indicate nodal lines, and arrows denote the direction of motion; Figure S2. Representative bead diameter distributions of Ca-alg and X-Ca-alg-IP aerogel beads, as indicated. (Bead diameters were measured with ImageJ; histograms were calculated using OriginPro 9.0.) Mean diameters, full width at half maxima (fwhm) and sample sizes (N) are shown within the frames; Figure S3. Schematic representation of the cross-linking process of preformed Ca-alg networks with IP; Figure S4. The structures of the four possible constitutional isomers of the isocyanurate-based trimer of isophorone diisocyanate (IP), potentially present in the commercial product Desmodur Z4470BA; Figure S5. Left: Amplitude vs time waveform of the (a) 1st resonant mode (antilexure) of specimen X-Ca-alg-IP-M2.3–1, (c) 2nd resonant mode (axisymmetric flexure) of specimen X-Ca-alg-IP-M2.3–3, (e) 1st resonant mode (antilexure) of specimen X-Ca-alg-IP-M2.1–1, (g) 2nd resonant mode (axisymmetric flexure) of specimen X-Ca-alg-IP-M2.1–1. Right: (b), (d), (f), (h) Power vs frequency spectra obtained by Fourier transformation of the corresponding waveforms shown on the left; Figure S6. Young's modulus as a function of the average pore diameter calculated by N_2 sorption (left) and from the skeletal densities (right) of X-Ca-alg-IP aerogels, as indicated. The PUA content of each material (% w/w) is also indicated on the graphs. Solid lines have been added to guide the eye; Table S1. Chemical composition and selected material properties of Ca-alg and X-Ca-alg-IP aerogel beads; Table S2. Chemical composition and selected material properties of X-Ca-alg-IP aerogel monoliths prepared for mechanical testing; Table S3. Structural parameters estimated by fitting the SANS profiles of full-contrast and of D_2O/H_2O -filled native (Ca-alg) and cross-linked (X-Ca-alg-N3300 and X-Ca-alg-IP) aerogels; Table S4. Specifications of X-Ca-alg-IP aerogel specimens and resonant frequencies (f_1 antilexure, f_2 axisymmetric flexure) used for mechanical testing by the IET method; and Table S5. Average values of the elastic properties of X-Ca-alg-IP

aerogels. Bulk and skeletal densities, as well as porosities, are also included for reference (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

József Kalmár – University of Debrecen, Department of Inorganic and Analytical Chemistry, HUN-REN-DE Mechanisms of Complex Homogeneous and Heterogeneous Chemical Reactions Research Group, Debrecen H-4032, Hungary; orcid.org/0000-0002-2422-6106; Email: kalmar.jozsef@science.unideb.hu

Konstantina Mergia – Institute of Nuclear and Radiological Science and Technology, Energy and Safety, National Centre for Scientific Research "Demokritos", Athens 15341, Greece; Email: kmergia@ipta.demokritos.gr

Patrino Paraskevopoulou – Inorganic Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Athens 15771, Greece; orcid.org/0000-0002-5166-8946; Email: paraskevopoulou@chem.uoa.gr

Authors

Argyrios Gomas – Inorganic Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Athens 15771, Greece

Grigorios Raptopoulos – Inorganic Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Athens 15771, Greece

Dimitrios Papadakis – Institute of Nuclear and Radiological Science and Technology, Energy and Safety, National Centre for Scientific Research "Demokritos", Athens 15341, Greece

Georgia Prapa – Inorganic Chemistry Laboratory, Department of Chemistry, National and Kapodistrian University of Athens, Athens 15771, Greece

Adél Len – Budapest Neutron Centre, Institute for Energy Security and Environmental Safety, HUN-REN Centre for Energy Research, Budapest H-1121, Hungary; University of Pécs, Faculty of Engineering and Information Technology, Pécs H-7624, Hungary

Zoltán Dudás – Budapest Neutron Centre, Institute for Energy Security and Environmental Safety, HUN-REN Centre for Energy Research, Budapest H-1121, Hungary

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsapm.6c02361>

Funding

APC Funding Statement: The open access publishing of this article is financially supported by HEAL-Link.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Work carried out in the framework of the COST Action "Advanced Engineering and Research of AeroGels for Environment and Life Sciences" (AERoGELS, ref CA18125) was funded by the European Commission. The General Secretariat for Research and Innovation, Greece, and the Special Account for Research Grants of the National and Kapodistrian University of Athens are acknowledged for partial support. The CERIC-ERIC (proposal number 20207082) is acknowledged for access to experimental facilities (solid-state

NMR) at the National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia. We thank the Chemistry Laboratory of the Hellenic Army Biological Research Center, Athens, Greece, for assistance with ICP-MS. The authors are grateful to Dr. Zoltán Balogh (Budapest Neutron Centre and University of Debrecen) for assistance in processing SANS data, and to Covestro AG for kindly providing samples of Desmodur Z4470 BA.

REFERENCES

- (1) Kistler, S. S. Coherent Expanded Aerogels and Jellies. *Nature* **1931**, 127 (3211), 741.
- (2) Kistler, S. S. The Relation between Heat Conductivity and Structure in Silica Aerogel. *J. Phys. Chem.* **1935**, 39 (1), 79–86.
- (3) Leventis, N.; Sadekar, A.; Chandrasekaran, N.; Sotiriou-Leventis, C. Click Synthesis of Monolithic Silicon Carbide Aerogels from Polyacrylonitrile-Coated 3D Silica Networks. *Chem. Mater.* **2010**, 22 (9), 2790–2803.
- (4) *Springer Handbook of Aerogels*; Aegerter, M. A.; Leventis, N.; Koebel, M.; Steiner, S. A., III Eds.; Springer: 2023.
- (5) García-González, C. A.; Blanco-Vales, M.; Barros, J.; Boccia, A. C.; Budtova, T.; Durães, L.; Erkey, C.; Gallo, M.; Herman, P.; Kalmár, J.; Iglesias-Mejuto, A.; Malfait, W. J.; Zhao, S.; Manzocco, L.; Plazzotta, S.; Milovanovic, S.; Neagu, M.; Nita, L. E.; Paraskevopoulou, P.; Roig, A.; Simón-Vázquez, R.; Smirnova, I.; Tomović, Ž.; López-Iglesias, C. Review and Perspectives on the Sustainability of Organic Aerogels. *ACS Sustainable Chem. Eng.* **2025**, 13 (18), 6469–6492.
- (6) Gurikov, P.; Raman, S. P.; Weinrich, D.; Fricke, M.; Smirnova, I. A Novel Approach to Alginate Aerogels: Carbon Dioxide Induced Gelation. *RSC Adv.* **2015**, 5 (11), 7812–7818.
- (7) Li, L.; Fang, Y.; Vreeker, R.; Appelqvist, I.; Mendes, E. Reexamining the Egg-Box Model in Calcium–Alginate Gels with X-Ray Diffraction. *Biomacromolecules* **2007**, 8 (2), 464–468.
- (8) Trens, P.; Valentin, R.; Quignard, F. Cation Enhanced Hydrophilic Character of Textured Alginate Gel Beads. *Colloids Surf., A* **2007**, 296 (1), 230–237.
- (9) Leventis, N.; Soni, R.; Bartels, J.; Begag, R.; Asl, H. Y. Form-Factor Control of Alginate Aerogels Via Thixotropic Sols: From Monoliths to Fibers to Films. *ACS Appl. Mater. Interfaces* **2025**, 17 (6), 9891–9912.
- (10) Zhao, S.; Malfait, W. J.; Guerrero-Alburquerque, N.; Koebel, M. M.; Nyström, G. Biopolymer Aerogels and Foams: Chemistry, Properties, and Applications. *Angew. Chem., Int. Ed.* **2018**, 57 (26), 7580–7608.
- (11) Khalil, H. P. S. A.; Yahya, E. B.; Jummaat, F.; Adnan, A. S.; Olaiya, N. G.; Rizal, S.; Abdullah, C. K.; Pasquini, D.; Thomas, S. Biopolymers Based Aerogels: A Review on Revolutionary Solutions for Smart Therapeutics Delivery. *Prog. Mater. Sci.* **2023**, 131, 101014.
- (12) Abdullah, Zou, Y.; Farooq, S.; Walayat, N.; Zhang, H.; Faieta, M.; Pittia, P.; Huang, Q. Bio-Aerogels: Fabrication, Properties and Food Applications. *Crit. Rev. Food Sci. Nutr.* **2023**, 63, 6687–6709.
- (13) García-González, C. A.; Budtova, T.; Durães, L.; Erkey, C.; Del Gaudio, P.; Gurikov, P.; Koebel, M.; Liebner, F.; Neagu, M.; Smirnova, I. An Opinion Paper on Aerogels for Biomedical and Environmental Applications. *Molecules* **2019**, 24 (9), 1815.
- (14) Andreou, A.; Avdylyaj, L.; Valdramidis, V.; Vourliotaki, K. V.; Dasenaki, M.; Zoi, A. M.; Zoi, A.; Kaplanis, A.; Kollia, E.; Kopsacheili, A., et al. Ready-to-Eat Shelf-Stable Food Compositions Based on Aerogel and Xerogel Technology. WO 2,026,027,585 A1, 2026.
- (15) Leventis, N.; Chandrasekaran, N.; Sadekar, A. G.; Sotiriou-Leventis, C.; Lu, H. One-Pot Synthesis of Interpenetrating Inorganic/Organic Networks of CuO/Resorcinol-Formaldehyde Aerogels: Nanostructured Energetic Materials. *J. Am. Chem. Soc.* **2009**, 131 (13), 4576–4577.
- (16) Leventis, N.; Vassilaras, P.; Fabrizio, E. F.; Dass, A. Polymer Nanoencapsulated Rare Earth Aerogels: Chemically Complex but Stoichiometrically Similar Core–Shell Superstructures with Skeletal Properties of Pure Compounds. *J. Mater. Chem.* **2007**, 17 (15), 1502–1508.
- (17) Rewatkar, P. M.; Soni, R. U.; Sotiriou-Leventis, C.; Leventis, N. A Cobalt Sunrise: Thermite Based on LiClO₄-Filled Co(0) Aerogels Prepared from Polymer-Cross-Linked Cobaltia Xerogel Powders. *ACS Appl. Mater. Interfaces* **2019**, 11 (25), 22668–22676.
- (18) Luo, H.; Churu, G.; Fabrizio, E. F.; Schnobrich, J.; Hobbs, A.; Dass, A.; Mulik, S.; Zhang, Y.; Grady, B. P.; Capeceaturo, A.; Sotiriou-Leventis, C.; Lu, H.; Leventis, N. Synthesis and Characterization of the Physical, Chemical and Mechanical Properties of Isocyanate-Crosslinked Vanadia Aerogels. *J. Sol-Gel Sci. Technol.* **2008**, 48 (1), 113–134.
- (19) Leventis, N.; Sotiriou-Leventis, C.; Mulik, S.; Dass, A.; Schnobrich, J.; Hobbs, A.; Fabrizio, E. F.; Luo, H.; Churu, G.; Zhang, Y.; Lu, H. Polymer Nanoencapsulated Mesoporous Vanadia with Unusual Ductility at Cryogenic Temperatures. *J. Mater. Chem.* **2008**, 18 (21), 2475–2482.
- (20) Rewatkar, P. M.; Taghvaei, T.; Saeed, A. M.; Donthula, S.; Mandal, C.; Chandrasekaran, N.; Leventis, T.; Shruthi, T. K.; Sotiriou-Leventis, C.; Leventis, N. S. Monolithic SiC and Si₃N₄ Aerogels from Compressed Polymer-Cross-Linked Silica Xerogel Powders. *Chem. Mater.* **2018**, 30 (5), 1635–1647.
- (21) Paraskevopoulou, P.; Smirnova, I.; Athamneh, T.; Papastergiou, M.; Chriti, D.; Mali, G.; Čendak, T.; Chatzichristidi, M.; Raptopoulos, G.; Gurikov, P. Mechanically Strong Polyurea/Polyurethane-Cross-Linked Alginate Aerogels. *ACS Appl. Polym. Mater.* **2020**, 2 (5), 1974–1988.
- (22) Fricke, M.; Paraskevopoulou, P.; Gurikov, P.; Chriti, D.; Papastergiou, M.; Raptopoulos, G.; Athamneh, T.; Smirnova, I.; Movahed, S.; Weinrich, D., et al. Polyurea/Polyurethane-Crosslinked Alginate Aerogels. EP 3,848,409 A1, 2021.
- (23) Paraskevopoulou, P.; Smirnova, I.; Athamneh, T.; Papastergiou, M.; Chriti, D.; Mali, G.; Čendak, T.; Raptopoulos, G.; Gurikov, P. Polyurea-Crosslinked Biopolymer Aerogel Beads. *RSC Adv.* **2020**, 10 (67), 40843–40852.
- (24) Raptopoulos, G.; Papastergiou, M.; Chriti, D.; Effraimopoulou, E.; Čendak, T.; Samartzis, N.; Mali, G.; Ioannides, T.; Gurikov, P.; Smirnova, I.; Paraskevopoulou, P. Metal-Doped Carbons from Polyurea-Crosslinked Alginate Aerogel Beads. *Mater. Adv.* **2021**, 2 (8), 2684–2699.
- (25) Paraskevopoulou, P.; Raptopoulos, G.; Len, A.; Dudás, Z.; Fábrián, I.; Kalmár, J. Fundamental Skeletal Nanostructure of Nanoporous Polymer-Cross-Linked Alginate Aerogels and Its Relevance To Environmental Remediation. *ACS Appl. Nano Mater.* **2021**, 4 (10), 10575–10583.
- (26) *Science and Industry: Challenges and Opportunities*, Hubicki, Z. ed.; Wydawnictwo Uniwersytetu Marii Curie-Skłodowskiej: Lublin, 2025.
- (27) Iglesias-Mejuto, A.; Raptopoulos, G.; Malandain, N.; Neves Amaral, M.; Ardao, I.; Finšgar, M.; Laromaine, A.; Roig, A.; Pinto Reis, C.; García-González, C. A.; Paraskevopoulou, P. 3D-Printed Cellulose Aerogels Minimally Cross-Linked with Polyurea: A Robust Strategy for Tissue Engineering. *ACS Appl. Mater. Interfaces* **2025**, 17 (23), 34444–34457.
- (28) Spence, M. W.; Plehiers, P. M. A Brief Overview of Properties and Reactions of Diisocyanates. *Toxicol Ind. Health* **2022**, 38 (9), 495–499.
- (29) Xu, C.; Hong, Y. Rational Design of Biodegradable Thermoplastic Polyurethanes for Tissue Repair. *Bioact. Mater.* **2022**, 15, 250–271.
- (30) Yang, J.; Keller, M. W.; Moore, J. S.; White, S. R.; Sottos, N. R. Microencapsulation of Isocyanates for Self-Healing Polymers. *Macromolecules* **2008**, 41 (24), 9650–9655.
- (31) Avdeliodi, E.; Soto Beobide, A.; Voyiatzis, G. A.; Bokias, G.; Kallitsis, J. K. Novolac-Based Microcapsules Containing Isocyanate Reagents for Self-Healing Applications. *Prog. Org. Coat.* **2022**, 173, 107204.

- (32) Li, Q.; Cao, L.; Wang, W.; Qin, X.; Chen, S. Photo-Responsive Rapid Self-Healing Polyurethane Elastomer with Anticorrosion and Antibacterial Functions. *Composites, Part A* **2022**, *163*, 107213.
- (33) Li, H.; Wang, X. Preparation of Microcapsules with IPDI Monomer and Isocyanate Prepolymer as Self-Healing Agent and Their Application in Self-Healing Materials. *Polymer* **2022**, *262*, 125478.
- (34) Xu, X.; Li, J.; Pan, X.; Lin, X.; Li, Z. Preparation of High Tensile Strength Modified Cellulose-Based Strippable Coating and Its Application on Radioactive Decontamination at Low-Temperature. *Mater. Today Commun.* **2023**, *34*, 105088.
- (35) Gibb, M.; Sayes, C. An in Vitro Alveolar Model Allows for the Rapid Assessment of Chemical Respiratory Sensitization with Modifiable Biomarker Endpoints. *Chem. Biol. Interact.* **2022**, *368*, 110232.
- (36) Paraskevopoulou, P.; Raptopoulos, G.; Leontaridou, F.; Papastergiou, M.; Sakellari, A.; Karavoltos, S. Evaluation of Polyurea-Crosslinked Alginate Aerogels for Seawater Decontamination. *Gels* **2021**, *7* (1), 27.
- (37) Georgiou, E.; Raptopoulos, G.; Papastergiou, M.; Paraskevopoulou, P.; Pashalidis, I. Extremely Efficient Uranium Removal from Aqueous Environments with Polyurea-Cross-Linked Alginate Aerogel Beads. *ACS Appl. Polym. Mater.* **2022**, *4* (2), 920–928.
- (38) Georgiou, E.; Pashalidis, I.; Raptopoulos, G.; Paraskevopoulou, P. Efficient Removal of Polyvalent Metal Ions (Eu(III) and Th(IV)) from Aqueous Solutions by Polyurea-Crosslinked Alginate Aerogels. *Gels* **2022**, *8* (8), 478.
- (39) Ioannidis, I.; Pashalidis, I.; Raptopoulos, G.; Paraskevopoulou, P. Radioactivity/Radionuclide (U-232 and Am-241) Removal from Waters by Polyurea-Crosslinked Alginate Aerogels in the Sub-Picomolar Concentration Range. *Gels* **2023**, *9* (3), 211.
- (40) Sigala, E.; Zoi, A.; Raptopoulos, G.; Sakellis, E.; Sakellari, A.; Karavoltos, S.; Paraskevopoulou, P. Removal of Mercury from Aqueous Environments Using Polyurea-Crosslinked Calcium Alginate Aerogels. *Gels* **2025**, *11* (6), 437.
- (41) Ghimire, S.; Sala, M. R.; Chandrasekaran, S.; Raptopoulos, G.; Worsley, M.; Paraskevopoulou, P.; Leventis, N.; Sabri, F. Noninvasive Detection, Tracking, and Characterization of Aerogel Implants Using Diagnostic Ultrasound. *Polymers* **2022**, *14* (4), 722.
- (42) Rodriguez Sala, M.; Ghimire, S.; Raptopoulos, G.; Paraskevopoulou, P.; Sabri, F. Investigation and Characterization of Time-Dependent Degradation of X-Ca-Alginate Aerogels for Bio-medical Applications. *J. Mater. Sci.* **2023**, *58* (30), 12331–12350.
- (43) Sala, M. R.; Raptopoulos, G.; Paraskevopoulou, P.; Skalli, O.; Sabri, F. Customization and Tuning of the Degradation Rate of X-Ca-Alginate Aerogels in the Presence of PC 12 Cells. *Soft Matter* **2026**, *22* (11), 2259–2269.
- (44) Juhász, L.; Moldován, K.; Gurikov, P.; Liebner, F.; Fábíán, I.; Kalmár, J.; Cserhádi, C. False Morphology of Aerogels Coated by Gold Coating for SEM Imaging. *Polymers* **2021**, *13* (4), 588.
- (45) Forgács, A.; Papp, V.; Paul, G.; Marchese, L.; Len, A.; Dudás, Z.; Fábíán, I.; Gurikov, P.; Kalmár, J. Mechanism of Hydration and Hydration Induced Structural Changes of Calcium Alginate Aerogel. *ACS Appl. Mater. Interfaces* **2021**, *13* (2), 2997–3010.
- (46) Lázár, I.; Forgács, A.; Horváth, A.; Király, G.; Nagy, G.; Len, A.; Dudás, Z.; Papp, V.; Balogh, Z.; Moldován, K.; Juhász, L.; Cserhádi, C.; Szántó, Z.; Fábíán, I.; Kalmár, J. Mechanism of Hydration of Biocompatible Silica-Casein Aerogels Probed by NMR and SANS Reveal Backbone Rigidity. *Appl. Surf. Sci.* **2020**, *531*, 147232.
- (47) Beaucage, G. Approximations Leading to a Unified Exponential/Power-Law Approach to Small-Angle Scattering. *J. Appl. Crystallogr.* **1995**, *28* (6), 717–728.
- (48) Hammouda, B. Analysis of the Beaucage Model. *J. Appl. Crystallogr.* **2010**, *43* (6), 1474–1478.
- (49) Reilly, P. M. Probability and Statistics for Engineers and Scientists by Ronald E. Walpole, Raymond H. Myers. Second Edition. Macmillan Publishing Co., Inc., New York, 1978. xii + 580 pp. U.S. \$16.95. ISBN 0-02-424110-5. *Can. J. Stat.* **1978**, *6*, 283–284.
- (50) ASTM. *Standard Test Method for Dynamic Young's Modulus, Shear Modulus, and Poisson's Ratio by Impulse Excitation of Vibration*; ASTM, <https://store.astm.org/e1876-15.html>. (Accessed 2026–05–05).
- (51) Katti, A.; Shimpi, N.; Roy, S.; Lu, H.; Fabrizio, E. F.; Dass, A.; Capadona, L. A.; Leventis, N. C. Physical, and Mechanical Characterization of Isocyanate Cross-Linked Amine-Modified Silica Aerogels. *Chem. Mater.* **2006**, *18* (2), 285–296.
- (52) Zhang, G.; Dass, A.; Rawashdeh, A.-M.-M.; Thomas, J.; Counsil, J. A.; Sotiriou-Leventis, C.; Fabrizio, E. F.; Ilhan, F.; Vassilaras, P.; Scheiman, D. A.; McCorkle, L.; Palczer, A.; Johnston, J. C.; Meador, M. A.; Leventis, N. Isocyanate-Crosslinked Silica Aerogel Monoliths: Preparation and Characterization. *J. Non-Cryst. Solids* **2004**, *350*, 152–164.
- (53) Ilhan, F.; Fabrizio, E. F.; McCorkle, L.; Scheiman, D. A.; Dass, A.; Palczer, A.; Meador, M. B.; Johnston, J. C.; Leventis, N. Hydrophobic Monolithic Aerogels by Nanocasting Polystyrene on Amine-Modified Silica. *J. Mater. Chem.* **2006**, *16* (29), 3046–3054.
- (54) Mandal, C.; Donthula, S.; Far, H. M.; Saeed, A. M.; Sotiriou-Leventis, C.; Leventis, N. Transparent, Mechanically Strong, Thermally Insulating Cross-Linked Silica Aerogels for Energy-Efficient Windows. *J. Sol-Gel Sci. Technol.* **2019**, *92* (1), 84–100.
- (55) Mohite, D. P.; Mahadik-Khanolkar, S.; Luo, H.; Lu, H.; Sotiriou-Leventis, C.; Leventis, N. Polydicyclopentadiene Aerogels Grafted with PMMA: I. Molecular and Interparticle Crosslinking. *Soft Matter* **2013**, *9* (5), 1516–1530.
- (56) Mohite, D. P.; Mahadik-Khanolkar, S.; Luo, H.; Lu, H.; Sotiriou-Leventis, C.; Leventis, N. Polydicyclopentadiene Aerogels Grafted with PMMA: II. Nanoscopic Characterization and Origin of Macroscopic Deformation. *Soft Matter* **2013**, *9* (5), 1531–1539.
- (57) Bang, A.; Mohite, D.; Saeed, A. M.; Leventis, N.; Sotiriou-Leventis, C. Polydicyclopentadiene Aerogels from First- versus Second-Generation Grubbs' Catalysts: A Molecular versus a Nanoscopic Perspective. *J. Sol-Gel Sci. Technol.* **2015**, *75* (2), 460–474.
- (58) Mulik, S.; Sotiriou-Leventis, C.; Leventis, N. Macroporous Electrically Conducting Carbon Networks by Pyrolysis of Isocyanate-Cross-Linked Resorcinol-Formaldehyde Aerogels. *Chem. Mater.* **2008**, *20* (22), 6985–6997.
- (59) Paraskevopoulou, P.; Gurikov, P.; Raptopoulos, G.; Chriti, D.; Papastergiou, M.; Kypridou, Z.; Skounakis, V.; Argyraki, A. Strategies toward Catalytic Biopolymers: Incorporation of Tungsten in Alginate Aerogels. *Polyhedron* **2018**, *154*, 209–216.
- (60) Papastergiou, M.; Chriti, D.; Damalas, D. E.; Raptopoulos, G.; Paraskevopoulou, P. Poly (Urethane-Acrylate) Aerogels from the Isocyanurate Trimer of Isophorone Diisocyanate. *J. Supercrit. Fluids* **2019**, *148*, 42–54.
- (61) Rowbotham, J. S.; Dyer, P. W.; Greenwell, H. C.; Selby, D.; Theodorou, M. K. Copper(II)-Mediated Thermolysis of Alginates: A Model Kinetic Study on the Influence of Metal Ions in the Thermochemical Processing of Macroalgae. *Interface Focus* **2013**, *3* (1), 20120046.
- (62) Papastergiou, M.; Kanellou, A.; Chriti, D.; Raptopoulos, G.; Paraskevopoulou, P. Poly (Urethane-Acrylate) Aerogels via Radical Polymerization of Dendritic Urethane-Acrylate Monomers. *Materials* **2018**, *11* (11), 2249.
- (63) Chriti, D.; Raptopoulos, G.; Papastergiou, M.; Paraskevopoulou, P. Millimeter-Size Spherical Polyurea Aerogel Beads with Narrow Size Distribution. *Gels* **2018**, *4* (3), 66.
- (64) Leventis, N.; Sotiriou-Leventis, C.; Chandrasekaran, N.; Mulik, S.; Larimore, Z. J.; Lu, H.; Churu, G.; Mang, J. T. Multifunctional Polyurea Aerogels from Isocyanates and Water. A Structure–Property Case Study. *Chem. Mater.* **2010**, *22* (24), 6692–6710.
- (65) Kanellou, A.; Anyfantis, G. C.; Chriti, D.; Raptopoulos, G.; Pitsikalis, M.; Paraskevopoulou, P. Poly (Urethane-Norbornene) Aerogels via Ring Opening Metathesis Polymerization of Dendritic Urethane-Norbornene Monomers: Structure-Property Relationships as a Function of an Aliphatic Versus an Aromatic Core and the Number of Peripheral Norbornene Moieties. *Molecules* **2018**, *23* (5), 1007.

- (66) Chidambareswarapattar, C.; McCarver, P. M.; Luo, H.; Lu, H.; Sotiriou-Leventis, C.; Leventis, N. Fractal Multiscale Nanoporous Polyurethanes: Flexible to Extremely Rigid Aerogels from Multifunctional Small Molecules. *Chem. Mater.* **2013**, *25* (15), 3205–3224.
- (67) Bang, A.; Buback, C.; Sotiriou-Leventis, C.; Leventis, N. Flexible Aerogels from Hyperbranched Polyurethanes: Probing the Role of Molecular Rigidity with Poly(Urethane Acrylates) Versus Poly(Urethane Norbornenes). *Chem. Mater.* **2014**, *26* (24), 6979–6993.
- (68) Hatada, K.; Ute, K.; Oka, K.-I.; Pappas, S. P. Unambiguous ¹³C-NMR Assignments for Isocyanate Carbons of Isophorone Diisocyanate and Reactivity of Isocyanate Groups in Z- and E-Stereoisomers. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28* (11), 3019–3027.
- (69) Bialas, N.; Höcker, H.; Marschner, M.; Ritter, W. ¹³C NMR Studies on the Relative Reactivity of Isocyanate Groups of Isophorone Diisocyanate Isomers. *Makromol. Chem.* **1990**, *191* (8), 1843–1852.
- (70) Taghvaei, T.; Donthula, S.; Rewatkar, P. M.; Majedi Far, H.; Sotiriou-Leventis, C.; Leventis, N. K-Index: A Descriptor, Predictor, and Correlator of Complex Nanomorphology to Other Material Properties. *ACS Nano* **2019**, *13* (3), 3677–3690.
- (71) Harkins, W. D.; Jura, G. Surfaces of Solids. XII. An Absolute Method for the Determination of the Area of a Finely Divided Crystalline Solid. *J. Am. Chem. Soc.* **1944**, *66* (8), 1362–1366.
- (72) Webb, P. A.; Orr, C. *Analytical Methods in Fine Particle Technology*; Micromeritics Instrument Corp, 1997.
- (73) Leventis, N.; Sotiriou-Leventis, C.; Saeed, A. M.; Donthula, S.; Majedi Far, H.; Rewatkar, P. M.; Kaiser, H.; Robertson, J. D.; Lu, H.; Churu, G. Nanoporous Polyurea from a Triisocyanate and Boric Acid: A Paradigm of a General Reaction Pathway for Isocyanates and Mineral Acids. *Chem. Mater.* **2016**, *28* (1), 67–78.
- (74) Leventis, N.; Chidambareswarapattar, C.; Mohite, D. P.; Larimore, Z. J.; Lu, H.; Sotiriou-Leventis, C. Multifunctional Porous Aramids (Aerogels) by Efficient Reaction of Carboxylic Acids and Isocyanates. *J. Mater. Chem.* **2011**, *21* (32), 11981–11986.
- (75) Chidambareswarapattar, C.; Xu, L.; Sotiriou-Leventis, C.; Leventis, N. Robust Monolithic Multiscale Nanoporous Polyimides and Conversion to Isomorphic Carbons. *RSC Adv.* **2013**, *3* (48), 26459–26469.
- (76) Leventis, N.; Chidambareswarapattar, C.; Bang, A.; Sotiriou-Leventis, C. Cocoon-in-Web-Like Superhydrophobic Aerogels from Hydrophilic Polyurea and Use in Environmental Remediation. *ACS Appl. Mater. Interfaces* **2014**, *6* (9), 6872–6882.
- (77) *Fractal Approach to Heterogeneous Chemistry: Surfaces, Colloids, Polymers*, Repr, A. N., ed.; Wiley: Chichester, 1992.
- (78) Chidambareswarapattar, C.; Larimore, Z.; Sotiriou-Leventis, C.; Mang, J. T.; Leventis, N. One-Step Room-Temperature Synthesis of Fibrous Polyimide Aerogels from Anhydrides and Isocyanates and Conversion to Isomorphic Carbons. *J. Mater. Chem.* **2010**, *20* (43), 9666.
- (79) Mohite, D. P.; Larimore, Z. J.; Lu, H.; Mang, J. T.; Sotiriou-Leventis, C.; Leventis, N. Monolithic Hierarchical Fractal Assemblies of Silica Nanoparticles Cross-Linked with Polynorbornene via ROMP: A Structure–Property Correlation from Molecular to Bulk through Nano. *Chem. Mater.* **2012**, *24* (17), 3434–3448.
- (80) Selmer, I.; Behnecke, A.-S.; Quiño, J.; Braeuer, A. S.; Gurikov, P.; Smirnova, I. Model Development for Sc-Drying Kinetics of Aerogels: Part 1. Monoliths and Single Particles. *J. Supercrit. Fluids* **2018**, *140*, 415–430.
- (81) Yamamoto, S.; Tsujii, Y.; Fukuda, T. Glass Transition Temperatures of High-Density Poly(Methyl Methacrylate) Brushes. *Macromolecules* **2002**, *35* (16), 6077–6079.
- (82) Mulik, S.; Sotiriou-Leventis, C.; Churu, G.; Lu, H.; Leventis, N. Cross-Linking 3D Assemblies of Nanoparticles into Mechanically Strong Aerogels by Surface-Initiated Free-Radical Polymerization. *Chem. Mater.* **2008**, *20* (15), 5035–5046.
- (83) Brinker, C. J.; Scherer, G. W. *Sol-Gel Science: the Physics and Chemistry of Sol-Gel Processing*; Gulf Professional Publishing, 1990.
- (84) Teixeira, J. Small-Angle Scattering by Fractal Systems. *J. Appl. Crystallogr.* **1988**, *21* (6), 781–785.
- (85) Leventis, N. Polyurea Aerogels: Synthesis, Material Properties, and Applications. *Polymers* **2022**, *14* (5), 969.
- (86) Greaves, G. N.; Greer, A. L.; Lakes, R. S.; Rouxel, T. Poisson's Ratio and Modern Materials. *Nat. Mater.* **2011**, *10* (11), 823–837.