# Deterministic Control over High-Z Doping of Polydicyclopentadiene-Based Aerogel Coatings

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ⓈSupporting Information

**ABSTRACT:** We report on simple and efficient routes to dope polydicyclopentadiene (PDCPD)-based aerogels and their coatings with high-Z tracer elements. Initially, direct halogenation of PDCPD wet gels and aerogels with elemental iodine or bromine was studied. Although several pathways were identified that allowed doping of PDCPD aerogels by direct addition of bromine or iodine to the unsaturated polymer backbone, they all provided limited control over the amount and uniformity of doping, especially at very low dopant concentrations. Deterministic control over the doping level in polymeric aerogels and aerogel coatings was then achieved by developing a copolymerization approach with iodine and tin containing comonomers. Our results highlight the versatility of the ring-opening metathesis polymerization (ROMP)-based copolymerization approach in terms of functionalization and doping of low density polymeric aerogels and their coatings.



**KEYWORDS:** doping, aerogels, ring-opening metathesis polymerization (ROMP), dicyclopentadiene, tin, iodine
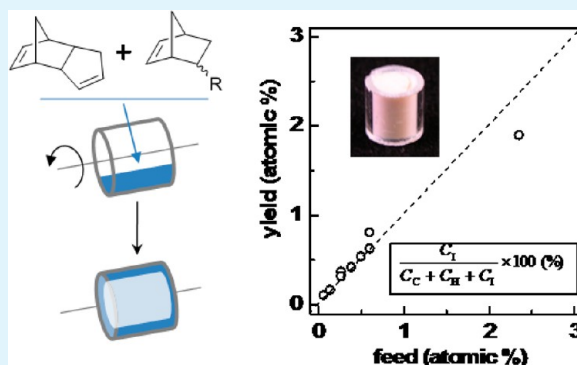
## 1. INTRODUCTION

Aerogels with ultralow density and open-pore structure have received considerable interest because of their great potential for thermal/acoustic insulation, optical and electrical applications, cosmic dust collection, additives or encapsulation medium, catalysis, and life science.[1−4] Continued progress in new synthetic methodologies combined with new generations of precursor systems will have an enormous impact on the ease and level of control over the chemistry of aerogels. Recently, we reported a new approach to fabricate low density (0.03−0.05 g cm$^{-3}$) polymeric aerogel coatings on the inside of nonplanar substrates such as cylinder and sphere,[5−9] while most of previous aerogel works have focused on the utilization of bulk aerogels. Detailed understanding and control over the chemistry and the gelation behavior open the door to many interesting new coating applications such as superhydrophobic surfaces, antireflection coatings, column chromatography, and porous polymer membranes.[10,11] The methodology is not limited to polymeric gels, but it also applies to functional inorganic coatings with TiO$_2$, SiO$_2$, and Fe$_2$O$_3$ aerogels.[9]

Although the coating and doping of low density porous polymer films are a topic of general interest, our study has been motivated by LLNL's need to fabricate foam-lined indirect-drive ignition targets for inertial confinement fusion (ICF) experiments at the National Ignition Facility (NIF).[6] These targets consist of small spherical shells, called ablators, whose inside wall is coated with a thin layer of low density hydrocarbon (CH)-based foam that may be used either (i) to support and define the shape of cryogenic liquid or solid deuterium-tritium (DT) fuel for the fusion reaction or (ii) as a scaffold to bring dopants for diagnostics and nuclear physics experiments in direct contact with the DT fuel. In our previous studies,[5−7] we reported the preparation of low-density, uniform thickness (from 10 to 100 μm) CH-based polymeric aerogel coatings on nonplanar substrates employing a ring-opening metathesis polymerization (ROMP) approach to copolymerize dicyclopentadiene (DCPD) with norbornene-based monomers (NB-R). Recently, the ROMP approach has received a considerable interest as a promising new route for the preparation of polymeric aerogels or polymer-cross-linked inorganic aerogels.[12,13] The objective of this study is to provide simple and reliable control over the doping of high-Z tracers into polydicyclopentadiene (PDCPD)-based aerogel systems. Several different physical/chemical approaches for doping of foams and aerogels with high-Z elements have been developed depending on the desired features.[14−17] For our specific application, doping is needed to bring high-Z tracers in close proximity to the fuel and to increase the weak X-ray absorption

Scheme 1. Synthetic Scheme of Comonomers Used in This Study: (a) Bisiodo Norbornene, NB-I$_2$, and (b) Tin Norbornene, NB-Sn, Monomers
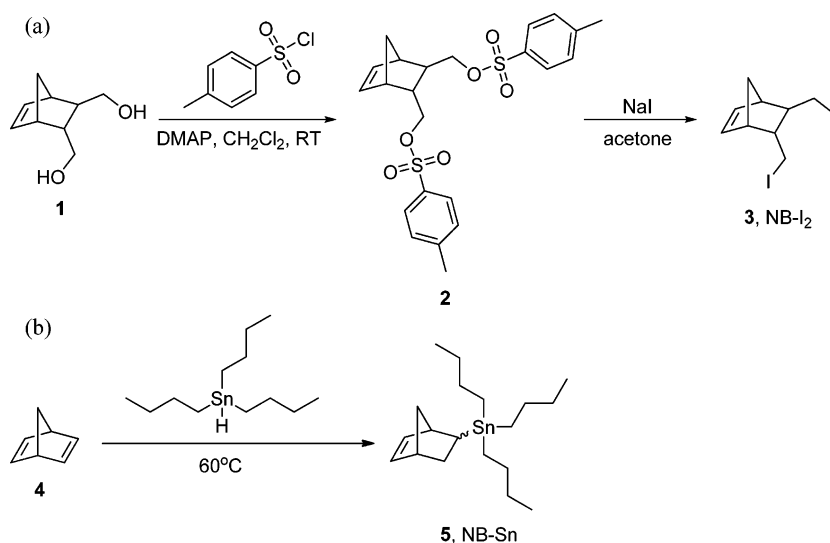


contrast of CH-based foams for nondestructive characterization using X-ray radiography. In one approach, we explored a direct polymer modification of the unsaturated polymer backbone of our ROMP-based polymeric systems by bromine/iodine addition. Although simple to perform, this approach provides limited control over doping uniformity and concentration. To overcome these limitations, we developed a copolymerization approach including the synthesis of functionalized copolymers required for this approach. Through this study, we report on the deterministic incorporation of high-Z tracer elements such as iodine and tin into low density polymeric aerogel coatings.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** Dicyclopentadiene (DCPD, Aldrich), norbornene (NB, 99%, Aldrich), a first generation Grubbs' catalyst, bis-(tricyclohexylphosphine)benzylidene ruthenium dichloride (+97%, Aldrich), 5-norbornene-2-exo,3-exo-dimethanol (1, 97%, Aldrich), 2,5-norbornadiene (4, +97%, TCI), tributyltin hydride (97%, Aldrich) and other chemicals were used as received unless noted otherwise. As supplied, the DCPD is a mixture of mostly endo and exo isomers. Toluene (anhydrous, 99.8%, Aldrich) was degassed by bubbling with high purity nitrogen prior to use.

**2.2. Synthesis of Norbornene-Based Comonomers with High-Z Elements.** Scheme 1 summarizes the synthesis of norbornene-based comonomers containing iodine or tin as a pendant group, similar to previous reports.[5,18−20] In brief, the iodine containing monomer, bisiodo-norbornene (3, NB-I$_2$), was prepared by tosylating the corresponding norbornene diol 1 in the presence of 4-(dimethylamino)pyridine (DMAP) followed by tosyl displacement of bis-tosylated compound 2 using sodium iodide.[5] Direct reaction of norbornene diol 1 with TsCl formed bistosylated compound 2 as well as monosubstituted tosyl norbornene and cyclic ether norbornene byproducts, and subsequent precipitation of the mixture in diethyl ether gave bis-tosylated norbornene as white powder (see Supporting Information, Scheme S1 and Figures S1 and S2).

The tin containing monomer, tributyltin-norbornene (5, NB-Sn) was prepared by hydrostannation of norbonadiene (4) with tributyltin hydride (Bu$_3$SnH) as an organotin hydride, similar to the previous studies about the free radical addition of trimethyltin hydride (Me$_3$SnH) to norbonadiene.[18,19] They showed that the hydrostannation reaction can be carried out by heating the reactants at an elevated temperature or by UV irradiation. Although Zyder et al. already demonstrated hydrostannation of norbornadiene with Bu$_3$SnH through the photochemical reaction catalyzed by molybdenum

complex,[20] we used the addition of Bu$_3$SnH to norbornadiene at 60 °C. The free radical addition of R$_3$SnH to norbornadiene 4 formed a mixture of four isomeric products including norbornenes with the organotin in the endo-5, exo-5, or syn-7 positions, and nortricyclene (see Supporting Information, Scheme S2 and Figures S3 and S4).[18,19] Complete isolation of these isomers has not been reported yet. Thus, the mixture of four isomers was used without further purification and hereinafter is referred to as NB-Sn. Full details on the synthesis of monomers and NMR and GC-MS characterization are described in the Supporting Information.

Typically for the synthesis of NB-I$_2$, 5-norbornene-2-exo,3-exodimethanol (1) (5.00 g, 32.4 mmol, 1.0 equiv) and DMAP (15.84 g, 129.6 mmol, 4.0 equiv) were dissolved in dichloromethane (DCM, 150 mL) and cooled to 0 °C. Tosyl chloride (TsCl, 18.53 g, 97.2 mmol, 3.0 equiv) was slowly added and stirred at 0 °C for 1 h. The mixture was warmed to room temperature and stirred for 2 days. At the end of the reaction, the salt was removed by filtration. Additional DCM (200 mL) and 1 M HCl (200 mL) were added to the residue and partitioned. The DCM layer was washed with saturated NaHCO$_3$ (200 mL), brine (200 mL), and water (200 mL), dried (MgSO$_4$), and evaporated in vacuo to yield a residue. The residue was taken up in diethyl ether, and the resulting precipitate was washed copiously with ether and dried in a vacuum oven overnight. The bistosylated adduct 2 was obtained as a white powder and used without further purification. $^1$H NMR (600 MHz in CDCl$_3$): $\delta$ 7.80 (d, $J$ = 8.3 Hz, 4H), 7.39 (d, $J$ = 7.9 Hz, 4H), 6.13 (s, 2H), 4.11−3.89 (m, 4H), 2.71 (s, 2H), 2.49 (br, 6H), 1.86 (br s, 2H), 1.31 (s, 2H). Then the bistosylated compound 2 (1.40 g, 3.0 mmol, 1.0 equiv) was dissolved in dry acetone (30 mL) and treated with NaI (1.82 g, 12.1 mmol, 4.0 equiv). The resulting suspension was refluxed at 70 °C for two days at the end of which the mixture was cooled to room temperature and concentrated under reduced pressure. The residue was dissolved in ether, washed with aqueous sodium thiosulfate, water, and brine, and dried over MgSO$_4$. The mixture was purified by flash column chromatography on silica gel (hexanes) to furnish the bisiodo-norbornene adduct 3 as a colorless liquid (0.82 g, 73%). $R_f$ = 0.50 (hexanes); $^1$H NMR (600 MHz in CDCl$_3$): $\delta$ 6.22 (br s, 2H), 3.59−3.56 (m, 2H), 3.07−3.04 (m, 4H), 2.07−2.06 (m, 2H), 1.45 (d, $J$ = 9.4 Hz, 1H), 1.38 (d, $J$ = 9.4 Hz, 1H).

For the synthesis of NB-Sn, freshly distilled 2,5-norbornadiene (4, 0.118 mol, 12 mL) was heated to 60 °C in an argon atmosphere. Tributyltin hydride (0.117 mol, 31.5 mL) was added dropwise over 1 h and allowed to react for another 3 h. All volatile materials were then evaporated under reduced pressure at 120 °C. The crude product was redistilled to give a mixture of endo/exo isomers 5, bp 150−165 °C
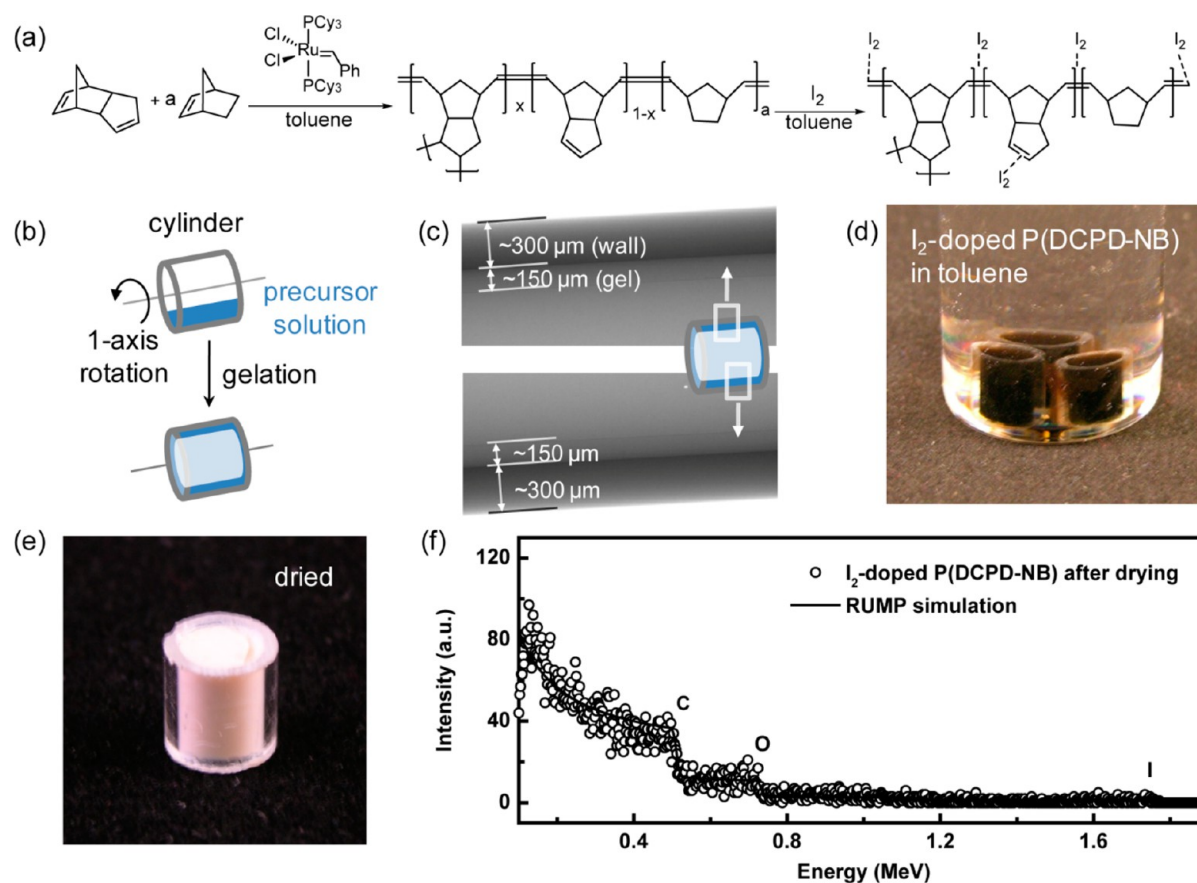
**Figure 1.** Doping of PDCPD-based aerogels and coatings. (a) A synthetic scheme of ring-opening metathesis polymerization of DCPD and NB followed by direct doping of iodine in toluene. (b) Schematic representation of the coating experiment of the precursor solution. (c) X-ray radiograph for a P(DCPD-*r*-NB) wet gel coated on a cylindrical substrate (NMR tube). (d,e) Photos of liquid-phase iodine doped P(DCPD-*r*-NB) before and after drying. (f) RBS analysis of a liquid-phase $I_2$ doped aerogel sample.

(0.2 mmHg) (16.0 g, 35%), as a colorless oil. $^1$H NMR (600 MHz, CDCl$_3$): δ 5.97 (m, 2H), 2.93 (m, 2H), 1.50 (m, 9H), 1.31 (m, 9H), 0.91 (m, 12H), 0.84 (m, 4H), 0.76 (m, 4H). $^{13}$C NMR (150 MHz, CDCl$_3$): δ 136.85, 136.27, 135.54, 135.19, 132.27, 77.16, 50.52, 49.56, 48.24, 46.24, 46.21, 45.14, 43.12, 41.98, 34.98, 33.54, 33.41, 31.39, 30.82, 29.52, 29.50, 29.45, 28.74, 28.29, 27.71, 26.19, 21.29, 20.41, 13.87, 13.86, 10.47, 10.17, 10.00, 9.96, 9.36, 9.12, 8.95.

**2.3. Preparation of Poly(dicyclopentadiene)-Based Copolymer Aerogels.** Poly(dicyclopentadiene-*random*-substituted norbornene) P(DCPD-*r*-NB-R) copolymer aerogels were prepared by ring-opening metathesis polymerization (ROMP) of DCPD and NB-R in toluene employing a first generation Grubbs' catalyst followed by supercritical $CO_2$ drying of wet gels. Different P(DCPD-*r*-NB-R) (100/*x*) (v/v) copolymer wet-gels were obtained by controlling the feed ratios of DCPD and NB-R solutions by volume (see Supporting Information, Tables S1 and S2). For example, to fabricate 50 mg/cm$^3$ P(DCPD-*r*-NB-R) (100/10) (v/v) aerogels, separate solutions of DCPD (50 mg/cm$^3$, 0.38 M) and NB-R (0.53 M, e.g., 50 mg/cm$^3$ for NB) monomers in toluene were prepared and then mixed as needed (0.91 mL of the DCPD and 0.09 mL of the NB-R solution for a 100/10 (v/v) aerogel). After adding an aliquot of the catalyst (0.1 mg) dissolved in toluene, the mixture was gelled in a sealed vial under ambient conditions. Next, wet gels were placed into an agitated acetone bath for 2–3 days and then transferred to a Polaron critical point dryer. Acetone-filled gels were exchanged with a continuous flow of liquid $CO_2$ at 850 psi at 10 °C. Once acetone was completely removed, the temperature and pressure in the dryer were increased to the supercritical regime (50 °C and ~1500 psi) and kept for 2–4 h. The pressure was then allowed to slowly decrease to atmospheric pressure while keeping the temperature constant. Dry aerogels were subsequently recovered by slowly cooling down to room temperature.

**2.4. Direct Modification of PDCPD-Based Wet Gels and Aerogels.** Direct doping was achieved by halogenation of the unsaturated backbone of PDCPD wet gels and aerogels using iodine or bromine.[21−23] Two different approaches were explored: (i) For liquid-phase doping, wet-gels were immersed in a solution of a halogen in toluene followed by drying; (ii) For gas-phase doping, the aerogels were stored in a closed container containing iodine or bromine vapor.

Typically, for liquid-phase $I_2$ doping, wet-gels of PDCPD (or P(DCPD-*r*-NB)) were immersed for 2−3 days in an excess (~20× to a wet gel volume) of a dilute solution of iodine (1 mg/mL) in toluene, washed with toluene, and then placed into an agitated acetone bath for another 2−3 days. Finally, the doped wet-gels were transferred to a Polaron critical point dryer and dried as described earlier. For gas-phase $I_2$ doping, dried pieces of PDCPD aerogels were stored for 2−3 days in a capped glass jar containing iodine crystals. The $I_2$-doped aerogels were then stored under vacuum for 7 days prior to further analysis. For liquid-phase $Br_2$ doping, a doping solution was prepared by dissolving 2,6-lutidine (0.30 mL, 0.28 g, 2.58 mmol) and $Br_2$ (0.1 mL, 0.31 g, 1.95 mmol) in toluene (10 mL), as described in the report.[21] Then, a PDCPD wet gel sample cast in a glass mold (~0.2 mL) was immersed in the bromine solution (~10 mL), allowed to react for 2−3 days, washed with toluene, and placed into an agitated acetone bath for another 2−3 days. The doped wet-gels were transferred to a Polaron critical point dryer for drying. For a gas-phase $Br_2$ doping, several droplets of liquid $Br_2$ were first added in a capped glass jar. To avoid direct contact between the liquid bromine and the dried PDCPD aerogels, the samples were placed in a secondary vial, which then was placed into the glass jar and allowed to react for 2−3 days. The $Br_2$-doped aerogels were stored under vacuum for 7 days prior to further analysis.

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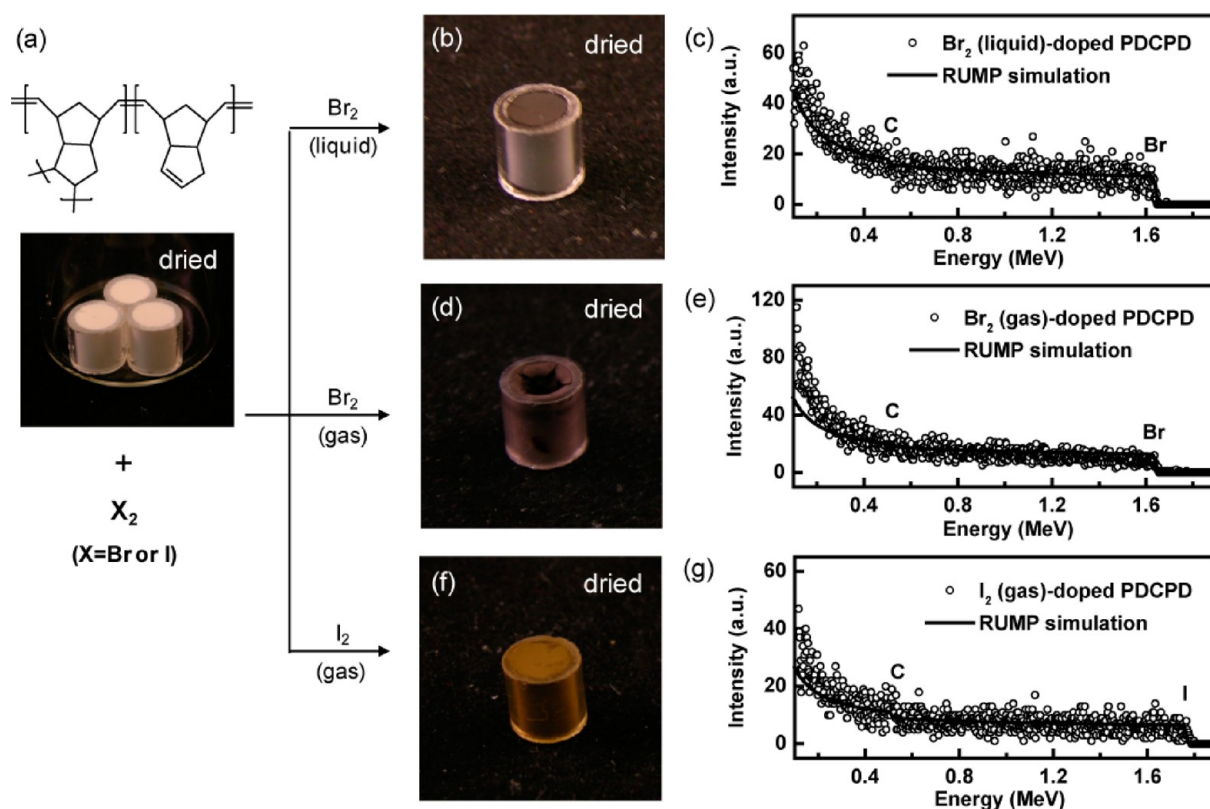dx.doi.org/10.1021/am4021878 | *ACS Appl. Mater. Interfaces* 2013, 5, 8111−8119

**Figure 2.** Direct halogenation of PDCPD wet gels and aerogels. (a) A scheme of a direct reaction of PDCPD using bromine or iodine. (b−g) Photos and RBS spectra for PDCPD aerogels after liquid-phase $Br_2$ doping followed by drying (b,c), gas-phase $Br_2$ doping (d,e), and gas-phase $I_2$ doping (f,g).

## 2.5. General Characterization.

The composition of doped aerogels was measured by Rutherford backscattering spectrometry (RBS). The 4 MV ion accelerator (NEC, model 4UH) at Lawrence Livermore National Laboratory was used to perform RBS measurements with 2.0 MeV $^4He^+$ ions incident normal to the sample surface and backscattered into a detector at 164° relative to the incident beam direction. During the ion-beam analysis, samples were neutralized by coirradiation with a 500 eV electron beam. Analysis of RBS spectra was done using the stopping powers and scattering cross sections of the RUMP code[24] with an assumption of a specimen composition of $C_{10}H_{12}X_n$, where X is the dopant. It was observed that the measured concentrations of iodine or bromine decreased over time under He ion irradiation. The initial composition was thus determined by extrapolating the dose dependencies to zero dose.[5] Tin doped aerogels did not exhibit ion-beam-induced loss of the dopant. The morphology of samples was investigated with a Jeol JSM-7401F scanning electron microscope (SEM) at an acceleration voltage of 2−3 kV in a lower secondary electron image (LEI) mode with no sputter coating. Rheological properties of the precursor solutions during gelation were characterized with a Rheometrics Fluids Spectrometer RFS 8400 in a dynamic-time-sweep mode with a Couette geometry (a 17 mm radius cup and a 16 mm radius bob).[7] Measurements were carried out at room temperature with a strain amplitude of 5% of the 1 mm gap between the cup and the bob and a frequency of 1 rad per second. To minimize solvent evaporation, the cup was covered with a custom built lid.

## 3. RESULTS AND DISCUSSION

Figures 1a and 1b show a schematic of our approach to prepare polydicyclopentadiene (PDCPD)-based copolymer aerogels and their coatings by ring-opening metathesis polymerization (ROMP) employing a first generation Grubbs' catalyst. The copolymerization of dicyclopentadiene (DCPD) and a linear comonomer of norbornene (NB) provided the control over the viscosity of the precursor solution required for the fabrication of thin gel coatings inside rotating shells and cylinders. Here, our strategy is to reduce shear, and thus shear induced damage, by increasing the viscosity of the gel precursor solution at the gel point, as detailed in our previous reports.[5,7] Figure 1c shows a typical X-ray radiograph (with an Xradia VersaXRM-500 microscope) of a wet-gel coating (P(DCPD-*r*-NB) (100/20) at 50 mg/mL) prepared inside a rotating thin-walled (~300 μm) NMR tube. The 2D projection reveals the formation of a uniform gel layer with ~150 μm thickness. However, it became very difficult to directly image a thin layer of CH-based aerogels (~0.05 g/cm³) on the inside of a shell/tube once the wet gels were dried.

The presence of unsaturated carbon double bonds in the backbone is a characteristic feature of ROMP polymers that can be used for further functionalization.[21−23,25−28] Electrophilic addition of a halogen to unsaturated polymers is a well-known method for polymer modification. Although there are already a number of reports on halogenation reactions of soluble polymers and copolymers,[21−23] studies on insoluble polymeric gels and aerogel systems such as cross-linked PDCPD networks are rarely reported. In this study, two independent routes toward high-Z element doped aerogels were compared: (i) direct reaction of the wet-gel with a halogen (iodine and bromine) containing solution followed by drying of the doped wet-gels (liquid-phase doping), and (ii) gas-phase doping by exposing the dried aerogel to halogen vapor in a closed container. An example for the first halogenation approach is liquid-phase iodine doping of P(DCPD-*r*-NB) (or PDCPD) wet gels (Figure 1d). The wet gel turns black during the
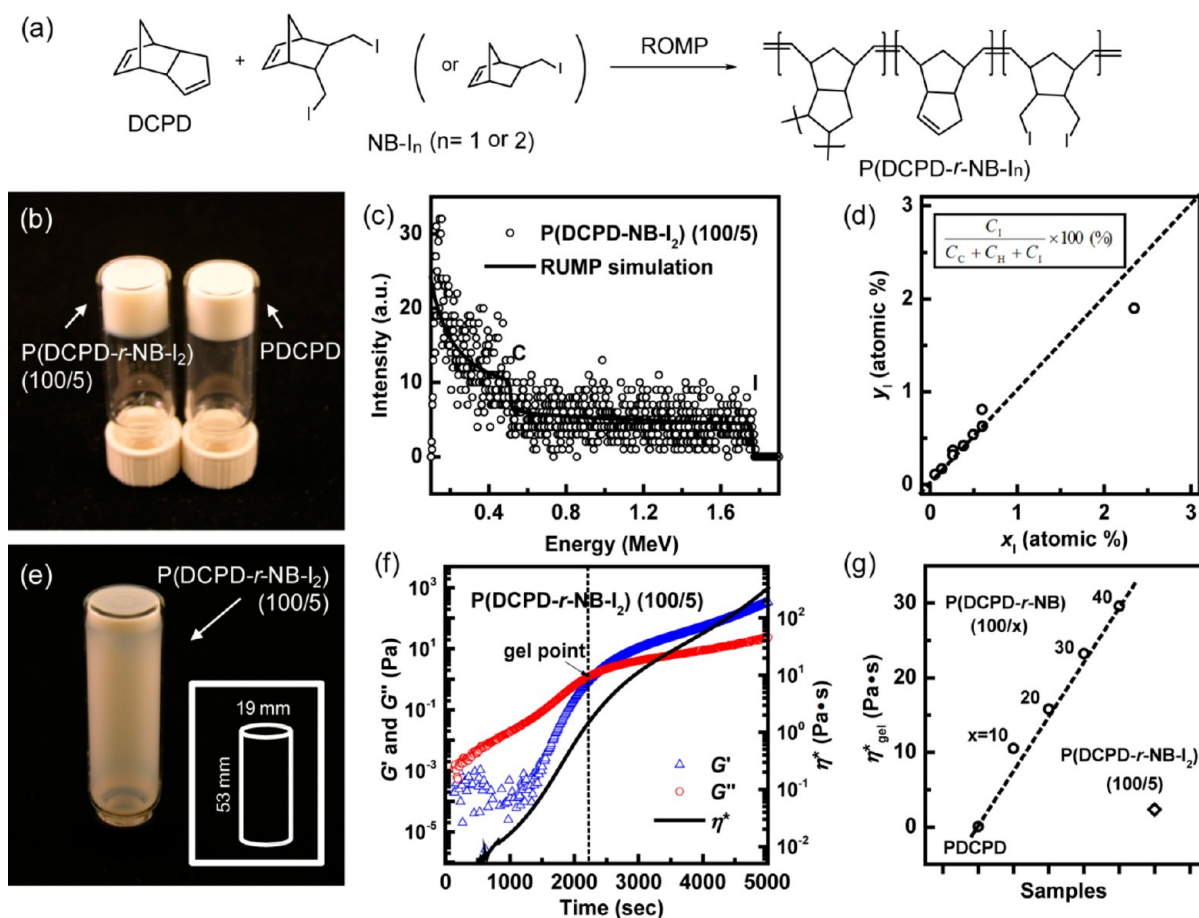
**Figure 3.** Copolymerization approach to iodine doped PDCPD. (a) Iodine doped P(DCPD-$r$-NB-I$_n$) was prepared from a ROMP reaction of DCPD and NB-I$_n$ in toluene. (b) Photos of iodine doped aerogels. (c,d) A typical example of RBS measurements and summarized results in P(DCPD-$r$-NB-I$_n$) aerogels with different iodine concentrations. (e) A photo of aerogel coating prepared from a solution mixture of DCPD/NB-I$_2$ (100/5 at 50 mg/cm$^3$) in toluene. (f,g) Rheology measurement during the gelation of P(DCPD-$r$-NB-I$_2$) (100/5) as compared with those of PDCPD and P(DCPD-$r$-NB) (100/$x$).

reaction with a dilute solution of iodine in toluene. The photo of the dried aerogel shown in Figure 1e demonstrates that liquid phase doping with iodine did not lead to shrinkage during subsequent processing steps. However, the disappearance of the black color during solvent exchange and supercritical drying suggests that iodine was not permanently added to the polymer backbone. Indeed, RBS analysis (Figure 1f) of the dried, discolored aerogel revealed a composition of C$_{10}$H$_{12}$O$_{1.5}$I$_{0.005}$. Thus, only ~0.02 at. % of the iodine remained in the sample. This indicates that the iodine reaction is reversible and thus limits the usefulness of the liquid phase doping approach. Further discussion on the oxidation behavior of PDCPD systems was reported in other references.[8,25]

To overcome the inefficiency of liquid-phase iodine doping, several other routes for direct halogenation of PDCPD wet gels and/or aerogels have been explored (Figure 2). First, a dilute solution of bromine in conjunction with 2,6-lutidine (a bulky base) was used to dope PDCPD wet gels in a manner similar to that described in a previous report of polymer bromination.[21] The solution of the reagents initially has a reddish-brown color, and the discoloration of the Br$_2$/toluene solution during reaction with PDCPD wet gels is considered as an indicator for the reaction. The reaction was completed within 1 h, and the wet gels became dark black. Compared to liquid-phase iodine doping, bromine doping seems to be more stable during

subsequent solvent exchange and drying as indicated by the brownish color of the dried aerogel. The photo of the dried sample shown in Figure 2b shows no indication for volume shrinkage, and its composition was determined to be C$_{10}$H$_{12}$Br$_{1.5}$, about 7.6 at. % of bromine (Figure 2c). For gas-phase doping, Br$_2$ vapor at standard temperature and pressure was used (~0.3 atm or 228 mmHg at 25 °C). To avoid direct contact between bromine and the dried PDCPD aerogel, several droplets of the reddish liquid were added to the bottom of a glass jar and several pieces of aerogels were placed in a secondary vial that then was placed into the bromine containing glass jar. Vaporized bromine undergoes a fast reaction with PDCPD aerogels and the composition of gas-phase bromine doped PDCPD was determined to be C$_{10}$H$_{12}$Br$_{2.8}$ or ~11.3 at. % bromine (Figures 2d and 2e). However, the sample monolith collapsed during the doping, thus rendering this approach useless. Finally, PDCPD aerogels were doped by exposing them to iodine vapor at room temperature (the iodine sublimation vapor pressure is 0.3 mmHg at 25 °C). This procedure is among the oldest methods for the visualization of organic compounds in thin layer chromatography (TLC).[29] As expected, iodine shows a high affinity with PDCPD aerogels, and the aerogels became dark upon iodine exposure with no noticeable collapse (Figure 2f). The advantage of gas-phase iodine doping is that it does not require further solvent
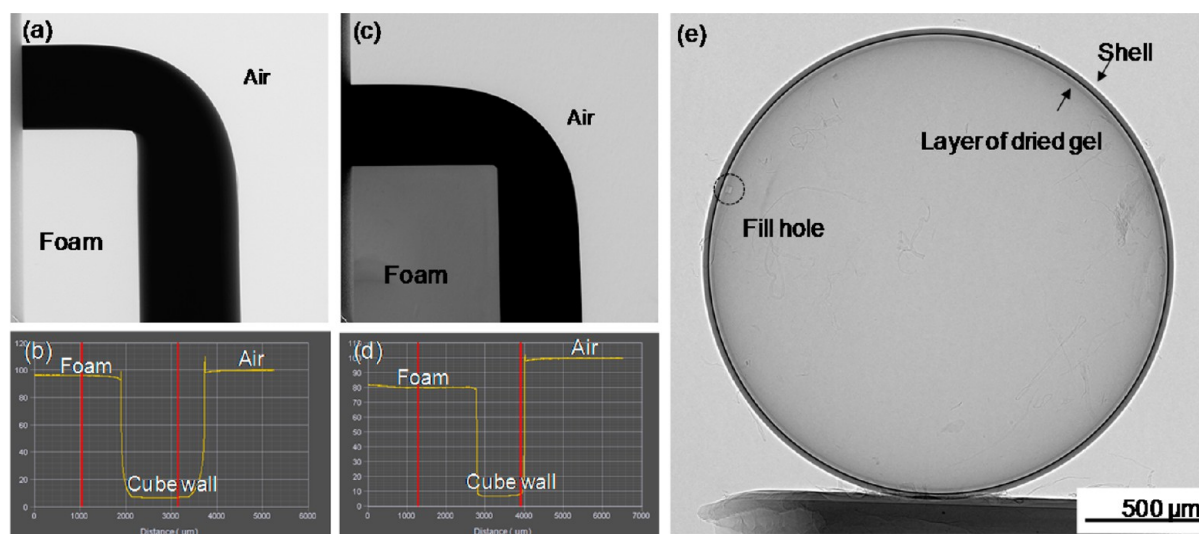
**Figure 4.** X-ray radiograph and line scan for (a,b) nondoped PDCPD (at 25 mg/cm$^3$) and (c,d) iodine doped P(DCPD-r-NB-r-NB-I) (100/15/7.5 at 25 mg/cm$^3$) aerogels in a cube (1 cm × 1 cm × 1 cm), and (e) P(DCPD-r-NB-I$_2$) (100/5 at 50 mg/cm$^3$) aerogel coating on the inside wall of a spherical diamond shell (radius of 1 mm).

exchange and drying steps that led to the loss of iodine observed in liquid-phase doping. Figure 2g shows the results of RBS analysis of a gas-phase iodine-doped sample stored under vacuum for 7 days. The material has a composition of $C_{10}H_{12}I_{0.43}$ (corresponding to ~1.9 at. % iodine that is much higher than the iodine concentration obtained by liquid phase iodine doping, $C_{10}H_{12}O_{1.5}I_{0.005}$). Control experiments revealed that only a small fraction of the initially incorporated iodine got removed during the extended vacuum treatment. (The composition before vacuum treatments was determined to be $C_{10}H_{12}I_{0.68}$, which corresponds to an iodine concentration of ~3.0 at.%; data is not shown). Thus both liquid-phase bromine doping and gas-phase iodine doping represent pathways forward for doping PDCPD aerogels with high-Z elements. The control over dopant concentration and distribution, however, is limited in both methods since, for example, the dopant distribution depends on the diffusion kinetics within the porous material. Indeed, liquid-phase doping of PDCPD wet gels with more diluted Br$_2$ solutions resulted in nonuniformly doped gels with a darker skin layer and a lighter (less-doped) region in the center of the bulk sample.

To address these limitations, we developed a copolymerization approach using comonomers functionalized with the desired high-Z element. To test the incorporation of iodine using this approach, we first prepared (bis)iodo-norbornene monomers, NB-I$_2$ (Scheme 1a).[5] Figure 3a shows the synthetic scheme of fabricating P(DCPD-r-NB-I$_2$) (100/x) (v/v) copolymer gels by ROMP of a mixture of DCPD (50 mg/cm$^3$) and NB-I$_2$ (0.53 M) in toluene. The proposed chemical structure of the copolymer is based on the assumption that the strained norbornene-derived double bond in the DCPD monomer is much more reactive than the cyclopentene-derived double bond and that olefin addition contributes to the formation of cross-linked PDCPD.[26,30] Figure 3b shows a typical example of P(DCPD-r-NB-I$_2$) (100/5 at 50 mg/cm$^3$) aerogels in conjunction with PDCPD (at 50 mg/cm$^3$). No collapse or volume shrinkage of the P(DCPD-r-NB-I$_2$) (100/5 at 50 mg/cm$^3$) gels during solvent exchange and drying was observed. The composition was determined to be $C_{10}H_{12}I_{0.15}$, corresponding to an iodine concentration of ~0.81 at. %

(Figure 3c). Considering that a backscattered ion creates a gradual energy loss dependent on the distance traversed in the sample, the intensity of ions versus energy at a specific energy range could be regarded as the depth profile of specific element. A constant height of the curve in the energy range of iodine could be an indirect evidence for the uniform distribution of iodine atoms over the sample. Various P(DCPD-r-NB-I$_n$) (100/x) aerogels with different mixing ratios, x, of DCPD to NB-I$_2$ (or NB-I) ranging from 0.5 to 25 (corresponding to $x_i$ from 0.05 to 2.35 at. %) were prepared, and the iodine concentration was measured by RBS. As revealed in Figure 3d, the measured iodine concentration, $y_i$, in aerogels shows excellent agreement with the value, $x_i$, predicted from the feed ratio of the monomer solutions. High monomer-to-polymer conversions in the copolymerized PDCPD networks and the deterministic control of high-Z elements in aerogels demonstrate the evidence on successful incorporation of monomers in the polymer gels (see Supporting Information, Tables S1 and S2). Interestingly, very uniform aerogel coatings were obtained from P(DCPD-r-NB-I$_2$) (100/5 at 50 mg/cm$^3$) precursor solutions using a rotating cylinder configuration (Figure 3e). To better predict the coating behavior, we studied the rheological behavior of a DCPD/NB-I$_2$ (100/5) mixture during gelation and compared the results to our previous DCPD/NB work (Figures 3f and 3g).[5,7] Isothermal dynamic time tests at a given frequency and strain (1 rad s$^{-1}$, 5%) show that both shear moduli and complex viscosity increase over time. A sudden increase in moduli and viscosity in a short period of time is a typical change in gelation. In this study, we determined the crossover point of the storage (G') and the loss (G'') moduli as a practical gel point when the elastic properties of the gels become dominant, although the actual gel point (independent of frequency) can alternatively be given the common crossing point of all the tan δ versus time curves at different oscillation frequencies.[13] A significant increase in viscosity, $\eta^*_{gel}$, near the gel point, from 0.08 Pa·s for pure DCPD to 2.35 Pa·s was observed, which makes the DCPD/NB-I$_2$ system more robust for coating applications and helps to improve the uniformity of the coatings.
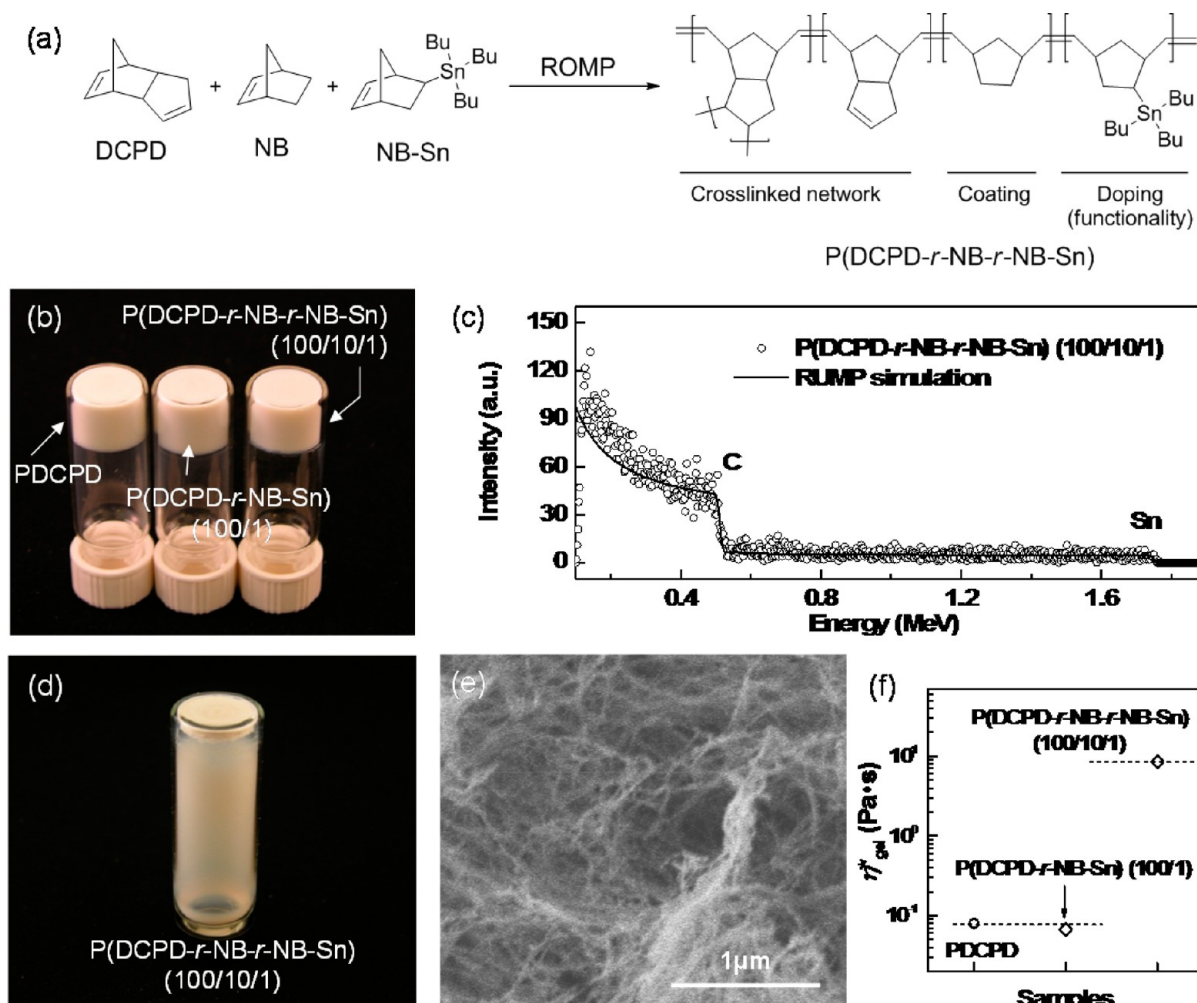
**Figure 5.** Copolymerization approach to tin doped PDCPD. (a) Tin doped P(DCPD-r-NB-r-NB-Sn) was prepared from a ROMP reaction of DCPD, NB, and NB-Sn solutions in toluene. (b) Photos of tin doped aerogels. (c) A typical example of a RBS measurement. (d) A photo of aerogel coatings prepared from a solution mixture of DCPD/NB/NB-Sn (100/10/1 at 50 mg/cm$^3$) in toluene. (e) SEM image of P(DCPD-r-NB-r-NB-Sn) (100/10/1). (f) Summarized result of rheology measurement during the gelation of P(DCPD-r-NB-r-NB-Sn) (100/10/1) as compared with those of PDCPD and P(DCPD-r-NB-Sn) (100/1).

One application of iodine doping important to us is to increase the weak X-ray absorption contrast of low-density CH-based foams for nondestructive X-ray radiography characterization of foam coatings prepared inside an ablator shell. Figure 4 shows typical examples of X-ray radiographs and line scan images for nondoped PDCPD and iodine doped copolymer aerogel after drying. In nondoped PDCPD (Figures 4a and 4b), the X-ray absorption contrast (~4%) was so weak that it was very difficult to recognize the difference between the dried foam and air. In sharp contrast, the foam of P(DCPD-r-NB-r-NB-I) (100/15/7.5) with 0.42 at. % iodine became dark in the X-ray radiograph with a significant X-ray absorption up to ~20%, as compared to air (Figure 4c and 4d). To validate the use of the copolymerization approach for aerogel coatings, we prepared the coating of P(DCPD-r-NB-I$_2$) (100/5 at 50 mg/cm$^3$) on the inside of a spherical shell (2 mm diameter, 20 μm shell thickness, and 30 μm fill hole). A representative radiograph of an iodine-doped P(DCPD-r-NB-I$_2$) (100/5) shell inside a diamond ablator is shown in Figure 4e. A significant X-ray absorption contrast due to the doping of the iodine tracer element allows quick and reliable measurement of a thickness profile in aerogel coating applications. Further details on the

experimental procedures about filling of the precursor solution, gel layer formation, and supercritical drying process were described in our previous report.[6]

Finally, a tin-norbornene monomer, NB-Sn, with tin as a pendant group was prepared as shown in Scheme 1b.[18−20] Addition of small amounts of Sn tracers to ignition targets is intended for monitoring experimental conditions such as temperature during the fusion process. In this specific application, the target atomic ratio of Sn to C is ~0.001 (~0.1 at. %). A mixture of DCPD, NB, and NB-Sn solution with a ratio of 100:10:1 was used for the preparation of aerogels and coatings. The NB-Sn monomer was successfully copolymerized with DCPD and/or NB employing a first generation Grubbs's catalyst (Figure 5a), and Sn doped aerogels were obtained with no additional collapse or shrinkage during drying (Figure 5b). The composition of the dried P(DCPD-r-NB-r-NB-Sn) (100/10/1 at 50 mg/cm$^3$) was determined to be C$_{10}$H$_{12}$Sn$_{0.015}$, corresponding to about 0.068 at. % of tin incorporated in the polymer backbone (Figure 5c). The copolymerization of DCPD with NB-Sn with its bulky pendant group increased the gel time to ~3870 s for P(DCPD-r-NB-r-NB-Sn) (100/10/1 at 50 mg/cm$^3$) and ~1998 s for P(DCPD-

*r*-NB-Sn) (100/1) versus ∼491 s for PDCPD, similar to previous observation for P(DCPD-*r*-NB-R) gels. The addition of 10% NB was necessary to increase the viscosity of the precursor solution near the gel point that made the gel system more robust for coating conditions that involve shear. Consequently, we obtained uniform aerogel coatings in cylindrical geometry from the copolymerized P(DCPD-*r*-NB-*r*-NB-Sn) (100/10/1), while neither P(DCPD-*r*-NB-Sn) (100/1) nor PDCPD resulted in uniform coatings (Figure 5d). A typical SEM image of P(DCPD-*r*-NB-*r*-NB-Sn) (100/10/1) shows a porous network morphology of highly entangled, randomly oriented fibers (Figure 5e). Figure 5f clearly demonstrates the effect of NB on the viscosity near the gel point. This study demonstrates that the copolymerization approach combined with the synthesis of functional comonomers provides deterministic control over the doping of PDCPD-based aerogels with high-Z elements. It is worthwhile to mention that this comonomer approach is well suited for a lower concentration of dopants. However, adding comonomers at higher concentrations eventually decreases the overall degree of cross-linking in polymer networks and might be one factor to cause undesirable volume shrinkage during drying.

## 4. CONCLUSION

In summary, we have explored several routes to incorporate high-Z tracer elements in polydicyclopentadiene (PDCPD)-based aerogels and coatings used for the fabrication of ignition targets for inertial confinement fusion (ICF) experiments. First, we examined direct halogenation of the unsaturated carbon double bonds in the polymer backbone of PDCPD wet gels and aerogels. The success of this approach depends strongly on the balance between reactivity and stability. Second, we developed a copolymerization approach using functionalized comonomers with the desired high-Z element. Our results show that the copolymerization approach provides deterministic and precise control over the doping level in PDPD-based aerogels and their coatings, especially for very low dopant concentrations. The new approach for gaining proper control over the chemistry and functionalization of aerogels described herein could expand the use of polymeric aerogels and coatings in a wide range of applications in the fields of material, environmental, and industrial science.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Details on the experimental procedure on monomer synthesis, aerogel formulation, and their composition. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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