Modular and Processable Fluoropolymers Prepared via a Safe, Mild, Iodo–Ene Polymerization

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Supporting Information

ABSTRACT: Fluoropolymers have infiltrated society as coatings and insulators. However, low processability, few opportunities for polymer functionalization, and explosive monomers hampering academic investigation of these materials have precluded the extension of the unique properties of perfluorocarbons to the cutting edge of material science. Here, we present semifluorinated iodo–ene polymers as a scaffold to overcome fluoropolymer limitations. A sodium dithionate initiated polymerization of perfluorodioildiodes and dienes allows for high-molecular-weight polymers (>100 kDa) to be prepared in the presence of oxygen and water with up to 59 wt % fluorine content. These conditions are sufficiently mild to enable the polymerization of functional dienes, leading to biodegradable fluoropolymers. The iodo–ene polymerization results in the addition of polarizable iodine atoms, which improve polymer processability; yet, these atoms can be removed after processing for enhanced stability. Displacement of the iodine atoms with thiols or azides facilitates covalent surface modification and cross-linking. Finally, the low bond dissociation energy of the C–I bond allows allyl group addition as well as photo-cross-linking. Collectively, the simple synthesis and modular nature of the semifluorinated iodo–ene polymers will enable the convergence of perfluorocarbons and advanced materials.

Since the accidental discovery of poly(tetrafluoroethylene) (PTFE, 1, Figure 1A) in 1938, fluoropolymers have found widespread utility due to the high chemical and thermal stability of the C–F bond and nonpolarizability of perfluorocarbons.1 PTFE, commonly known as Teflon, is fully integrated into modern society and can be found in everyday materials such as nonstick pans, weather-proof clothing, dental floss, and insulators for electronics.2 Despite the success of PTFE, it has significant mechanical, chemical, and safety limitations,3–7 which have prevented the advancement of fluorinated polymers into sophisticated, multifunctional, dynamic materials.

The primary mechanical challenges of PTFE are its high crystallinity and poor solubility, which prohibit facile melt processing and solution casting techniques commonly employed for thermoplastics.8 To overcome the processability challenges of PTFE, numerous other fluoropolymers have been manufactured including fluorinated ethylene propylene (FEP, 2), poly(tetrafluoroethylene-co-perfluoroproplylvinylether) (FPA, 3), Teflon AF (4), poly(ethylene-co-tetrafluoroethylene) (ETFE, 5), and poly(vinylidene difluoride) (PVDF, 6).8–10 By drastically lowering the weight percent fluorine, PVDF can be easily melt-processed and dissolved in select organic solvents. This allows for manipulation into plastics and films but at the cost of significantly lower thermal and chemical resistance.8–13 FEP and PFA retain high weight percent of fluorine but lower crystallinity through the addition of bulkier substituents, allowing these polymers to be melt-processed into bulk materials with advantageous thermal and chemical resistance. However, FEP and PFA remain insoluble in organic or fluororous solvent and maintain high melt viscosity.14 Teflon AF’s amorphous nature leads to it being one of the most processable commercial fluoropolymers, even displaying some solubility in fluororous solvents15 while retaining similar thermal and chemical stability as PTFE.16 Although displaying advantageous properties, the widespread use of Teflon AF has been limited by its costly preparation.17

Although the inertness of the C–F bond is a hallmark of perfluorocarbons, it hinders the diversification of fluorinated materials. The covalent functionalization of fluoropolymers is desirable for cross-linking, surface modification, and the creation of advanced fluororous materials. Cross-linking is a common approach to reduce creep, the deformation of materials under stress, which is a common problem for PTFE.5,6 Current methods for cross-linking PTFE require extreme conditions, preventing their widespread use.18 High-energy methods such as ionizing radiation and plasma treatment have also been utilized to functionalize PTFE films, allowing for covalent attachment of small molecules and polymers to surfaces.19–21 Other fluoropolymers have been functionalized by fluoride elimination (PVDF, 6), reduction (FEP, 2),22 or photo-cross-linking fluorinated polyethers with...
activated acrylate end-groups.\textsuperscript{25} Taken together, these harsh conditions highlight the difficulty in advancing the applications of fluoropolymers.

A final challenge of fluoropolymer research is the safety of the fluorinated ethylene monomers. Tetrafluoroethylene (TFE) is explosive on contact with organic compounds,\textsuperscript{24} limiting its academic use\textsuperscript{25–27} and making copolymers such as ETFE (S) especially dangerous to produce. Additionally, many of the fluoropolymers are prepared via emulsion polymerization, which requires fluorosurfactants that are prone to bioaccumulation.\textsuperscript{7,28,29} Methods to prepare fluoropolymers that do not require explosive monomers or persistent surfactants will make these materials more accessible and expand both the academic and industrial applications.

Here we report the preparation of semifluorinated polymers under mild conditions with safe, commercially available monomers and no need for surfactant. We employ a step-growth iodo–ene polymerization, which results in two iodine atoms installed within the backbone of every repeat unit (7, Figure 1B). The large, polarizable iodine atoms enhance the processability, yet can be easily removed after processing to result in thermally stable fluoropolymers. Furthermore, the iodine atoms provide a functional handle for postpolymerization modification and cross-linking (8) via S$_2$2 displacement of iodine or homolytic cleavage of the C–I bond. The fluorine content can be tuned by varying the monomers ($z$ and R in 7). Additionally, other functionality can be installed into the backbone of the polymer by diene selection (R in 7). Through these strategies, we are able to prepare fluoropolymers that (1) are soluble in organic solvent, (2) are treatable with heat and base into thermally stable films, (3) are readily covalently modified or cross-linked with a variety of chemistries, and (4) are photocured into gels. Notably, the fluorine content within these polymers is on the backbone, making them distinct from existing approaches to impart standard polymers (e.g., acrylates, styrenes) with fluororous character.\textsuperscript{30–34} or through fluorination reactions as a postpolymerization modification.\textsuperscript{35,36}

The addition of perfluoroalkyl iodides into alkenes, the iodo–ene reaction (Figure S1), is an established method to install fluorinated chains onto a molecule.\textsuperscript{37–42} It was first explored as a polymerization method using diiodoperfluorohexane and 1,9-decadiene in 1993 by Wilson and Griffin, who employed heat and azobis(isobutyronitrile) (AIBN) to access short semifluorinated polymers.\textsuperscript{43} A few years later, Percec and co-workers employed Pd(PPh$_3$)$_4$ at room temperature to install perfluoroalkyl iodides into alkenes,44 we looked to revisit this polymerization using a Tris(bipyridine)-ruthenium(II) chloride (Ru(bpy)$_3$Cl$_2$) catalyst and blue light to obtain polymers with $M_n$ up to 30 kDa.\textsuperscript{45,46} Although the photoinitiated polymerization is an improvement, we looked to establish a simpler, greener method that did not require deoxygenation and produced high-molecular-weight semifluorinated polymers. Upon method development, we demonstrate the utility and versatility of these unique fluoropolymers.

\section*{RESULTS AND DISCUSSION}

Inspired by reports of sodium dithionate (Na$_2$S$_2$O$_4$) initiated addition of perfluoroalkyl iodides into alkenes,\textsuperscript{47} we looked to employ these conditions for the polymerization of diiodoperfluorohexane and dienes. We were particularly interested in the brief communication by Rong and Keece, who demonstrated that sonication of perfluorobutyl iodide and 1-hexene in acetonitrile and water gave high yields of iodo–ene product in 1 h.\textsuperscript{48} We envisioned that these rapid and mild reaction conditions would enable high-molecular-weight polymers and expand the scope of monomers compatible with the iodo–ene polymerization. Our optimization of the sodium dithionate initiated iodo–ene polymerization began with monomers 1,9-decadiene (9) and diiodoperfluorohexane (10a) to produce semifluorinated polymer 11a (Scheme 1). Dimethyl carbonate (DMC) was employed as a cosolvent because of its precedent for increasing reaction rates and decreasing chain transfer.\textsuperscript{49} Within 30 min of sonicating 9 and 10a under these conditions, precipitate was evident, suggesting polymer formation (Figure S2). Isolation of the precipitate and nuclear magnetic resonance (NMR) analysis indicated polymer 11a (Table 1, Scheme 1).

\begin{figure}[ht]
\centering
\includegraphics[width=\textwidth]{Figure1.png}
\caption{(A) Common industrial fluoropolymers prepared with decreasing fluorous content. Generally, stability and melting points correlate with increased weight percent fluorine, whereas there is an inverse relationship with processability. (B) Iodo–ene fluoropolymers reported herein that are processable, tunable, simple to prepare, and can be readily modified through postpolymerization modification to improve stability or functionality.}
\end{figure}

\begin{table}[ht]
\centering
\caption{Preparation of Semifluorinated Polymers (11a–d) with Varying Fluorous Blocks}
\label{table1}
\begin{tabular}{|c|c|c|c|c|}
\hline
\textbf{9} & \textbf{10a} & \textbf{10b} & \textbf{10c} & \textbf{10d} \\
\hline
11a & $z=6$ & 4.8 & 1.0 & 0.0 \\
11b & $z=6$ & 4.8 & 1.0 & 0.0 \\
11c & $z=4$ & 4.8 & 1.0 & 0.0 \\
11d & $z=4.6,8$ & 991
\hline
\end{tabular}
\end{table}
Entry 1), which was compared to a standard prepared via AIBN initiation. $^1$H NMR, $^{19}$F NMR (Figure S3), thermal gravimetric analysis (TGA), and differential scanning calorimetry (DSC) analysis (Figure S4) all indicate that both sodium dithionate and AIBN initiation produce 11a. Although the repeat units of these polymers are identical, the molecular weights are significantly different. After only 30 min at room temperature, the dithionate initiation yielded a 25 kDa polymer. In comparison, slow ramping of heat from 80 to 160 °C over a period of 4 h with sequential addition of AIBN every 10 min, a previously optimized method, gave 10 kDa polymers (Table 1, Entries 1 vs 2).$^{30}$ These molecular-weight data were obtained with size exclusion chromatography (SEC) in tetrahydrofuran (THF), as was previously reported. The molecular weights are calculated through calibration with poly(styrene) standards. In all other cases, SEC analysis performed in DMSO at 65 °C at a flow rate of 0.35 mL·min$^{-1}$. $^{31}$M$\text{\textsubscript{n}}$ and $^{32}$D calculated through calibration with poly(methyl methacrylate) standards. $^3$Bimodal distribution in SEC is likely due to early termination.

### Table 1. Optimization of Polymerization Conditions

| entry # | polymer | z | solvent     | energy input | time (hours) | $M\text{\textsubscript{n}}$ (kDa) | $n$ | $^{D}$ |
|---------|---------|---|-------------|--------------|--------------|-----------------------------------|----|-------|
| 1       | 11a     | 6 | MeCN/DMC/H$_2$O | sonication  | 0.5          | 25.0$^{b}$                         | 35 | 2.07  |
| 2       | 11a     | 6 | neat plus AIBN$^{a}$ | heat       | 4            | 10.0$^{a}$                         | 14 | 1.65  |
| 3       | 11a     | 6 | MeCN/DMC/H$_2$O | sonication  | 0.5          | 67.9                              | 98 | 1.88  |
| 4       | 11a     | 6 | neat plus AIBN$^{a}$ | heat       | 4            | 57.3                              | 83 | 1.38  |
| 5       | 11a     | 6 | MeCN/DMC/H$_2$O | sonication  | 8            | 101                               | 147| 1.88  |
| 6       | 11a     | 6 | MeCN/DMC/H$_2$O | sonication  | 14           | 128                               | 184| 1.28  |
| 7       | 11a     | 6 | MeCN/DMC/H$_2$O | heating     | 14           | 198                               | 286| 1.43  |
| 8       | 11a     | 6 | MeCN/DMC/H$_2$O | 365 nm UV   | 14           | 112$^{c}$                         | 161| 1.31  |
| 9       | 11a     | 6 | DMSO         | room temp.  | 48           | 36.0                              | 65 | 1.80  |
| 10      | 11a     | 6 | MeCN/H$_2$O  | sonication  | 14           | 187$^{b}$                         | 270| 1.27  |
| 11      | 11a     | 6 | H$_2$O       | sonication  | 14           | 25.9                              | 37 | 1.53  |
| 12      | 11b     | 8 | MeCN/DMC/H$_2$O | sonication  | 14           | 192                               | 277| 1.30  |
| 13      | 11c     | 4 | MeCN/DMC/H$_2$O | sonication  | 14           | 86.5$^{c}$                        | 125| 1.52  |
| 14      | 11d     | 4, 6, 8 | MeCN/DMC/H$_2$O | sonication  | 14           | 83.7$^{c}$                        | 121| 1.67  |

$^{a}$AIBN employed instead of Na$_2$S$_2$O$_4$/NaHCO$_3$. $^{b}$SEC analysis performed in THF at 40 °C at a flow rate of 0.7 mL/min. $M\text{\textsubscript{n}}$ and $^{D}$ calculated through calibration with poly(styrene) standards. In all other cases, SEC analysis performed in DMSO at 65 °C at a flow rate of 0.35 mL·min$^{-1}$. $M\text{\textsubscript{n}}$ and $^{D}$ calculated through calibration with poly(methyl methacrylate) standards. $^{c}$Bimodal distribution in SEC is likely due to early termination.

![Table 1. Optimization of Polymerization Conditions](image)

**Figure 2.** (A) Preparation of end-capped iodo–ene fluoropolymers using alkene 12. (B) Stacked $^1$H NMR spectra of end-capped polymers 13 compared to 11a (red, top). $^1$H NMR signals from the end-cap are highlighted in gray. (C) Table of weight percent end-cap employed in the polymerization and the resulting molecular weight determined through NMR and SEC. (D) SEC traces for polymer 11a (red, solid) compared to 13 with varied weight percent 12 (green, orange, blue, dashed). SEC traces were obtained from 3 mg/mL solutions of fluoropolymers in DMSO and analyzed on an Agilent Mixed-B column with DMSO eluent at 65 °C.
SEC in 65 °C dimethyl sulfoxide (DMSO) using an Agilent Mixed-B column, emulating conditions that were previously reported for PVDF analysis. SEC analysis of 11a in DMSO corroborated that the sodium dithionate conditions yielded higher-molecular-weight polymer (Table 1, Entries 3 and 4), yet did not match the THF SEC data (discussed in further detail below). Using SEC in DMSO, further investigation of polymer 11a prepared via sonication in the presence of sodium dithionate was performed. Analysis at multiple time points demonstrated that although the polymer quickly precipitates, the reaction requires 14 h to reach the maximum size of 128 kDa. At both 30 min and 8 h (Table 1, Entries 3 and 5), the polymer dispersity remains the same, although the SEC trace indicates further conversion. At the 14 h time point, dispersity drops significantly while the molecular weight grows. This is likely due to the lower solubility of high-molecular-weight polymer resulting in precipitation and a kinetic molecular-weight distribution. Analysis of the polymer precipitate before and after washing showed nearly identical molecular weights (Figure S5). The end-capping approach also allows for the molecular weight of the semifluorinated polymers to be controlled, a feat that has not been achieved with chain growth methods industrially employed for fluoropolymer synthesis. Current methods to obtain 10−100 kDa PTFE include fragmenting larger PTFE with ionizing radiation or through polymerization of TFE in supercritical CO2 or fluoroform. We found that the polymerization proceeded readily with C4, C6, and C8 diiodoperfluoroalkanes 10a−c to yield polymers 11a−c (Figure S6). Thin films of polymers 11a−c were prepared by drop-casting from THF, dimethylformamide (DMF), or DMSO solutions, and contact angles of water were measured to gain insight on the fluororous character of the respective polymers, as compared to PVDF films (Figure S7). Despite having a lower weight percent of fluorine than PVDF, polymers 11a−c all have larger contact angles, suggesting that consecutive CF2 groups enhance fluorous
was prepared and quickly diluted with 15% tetramethylguanidine (TMG) and then drop-cast onto a glass slide and annealed at 100 °C.

Further characterization of the iodine-free materials is heavily dependent on the length of the polymer chain, contact angle measurements of polymer 11a—c, which employs monomers 10a—c in a ratio representative of crude perfluoroalkyldiodide. Thus, polymer 11d represents a low-cost iodo–ene polymer, providing opportunities for large-scale synthesis. To date, we have scaled the polymerization up to 4 g (Figure S8). Further characterization of polymers 11a—d by TGA show similar 10% mass loss temperatures of 290 °C because of the loss of iodine. DSC indicates that the glass transition temperature ($T_g$) of these materials is heavily dependent on the length of the fluoroblock (Table S1).

Having established that the semifluorinated iodo–ene polymers are sufficiently fluorous, we looked to leverage the iodine installed within the backbone and the diene composition to increase the wt % fluorine, biocompatibility, processability, as well as install functional handles for grafting and cross-linking. Chemical modifications to the diene monomer provide an avenue to further increase the fluorine content or incorporate additional functional groups. To create additional fluorous polymers using the iodo–ene polymerization, we prepared fluorinated diene 14 (Figure S9) and polymerized 14 with diiodoperfluoroctane 10b to result in polymer 18b (Figure 3A), increasing the wt % fluorine by 1.5X and achieving a structure just three CF$_2$ units from Teflon (Figure S10). We also explored the addition of more hydrophilic functionality and found that ether- and ester-containing dienes (15–17) both afforded semifluorinated polymers of significant molecular weight (Figure 3B). The sonication method proved particularly important for 20b, as diene 16 undergoes Cope rearrangement at elevated temperatures. Ester-containing semifluorinated polymer 19a is of particular interest, as it can undergo degradation into 22, which contains only C$_8$F$_{12}$ units that do not bioaccumulate.

We demonstrated the degradation of 19a under basic conditions in solution and on surfaces. After 6 h in basic conditions, ester-containing polymer 19a had significantly smaller $M_w$ (Figure S10), and the contact angle of surfaces coated with 19a had decreased, suggesting the presence of polar carboxylic acids (Figure 3C,D). In contrast, semifluorinated polymer 11a only showed minor changes in molecular weight and contact angle, consistent with elimination of iodine but not scission of the polymer backbone (Figures 3D and S11).

Iodine elimination represents another avenue for increasing the wt % fluorine as well as the thermal stability of the semifluorinated polymers. We found that quantitative elimination of iodine could be obtained by treatment with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Figure 4A). As previously reported, we could also remove the iodine atoms by treatment with AIBN and tributyltin hydride (HSnBu$_3$). We compared the properties of the eliminated polymer 23 and reduced polymer 24 to those of the initial iodo–ene product 11a. Interestingly, the contact angles did not undergo significant change in the eliminated product but were significantly increased in the reduced product (Figure S12). Both polymers 23 and 24 displayed superior thermal stability when compared to iodine-containing polymer 11a. TGA indicates that 11a undergoes loss of iodine at 300 °C.
contrast, the semifluorinated polymers without iodine display excellent thermal stability with degradation temperatures approaching 430 °C (Figure 4B and Table S1), rivaling that of PTFE. The chemical stability of polymers 23 and 24 is also excellent, showing no loss of fluorine upon treatment with acid, base, amine, or thiol (Figure S13).

Although the fluororous content and stability of the semifluorinated polymers 23 and 24 are desirable, a drop in processability is observed when iodine is removed. Because the iodine is facile to remove via heat or base, we proposed coating surfaces with 13 and then removing the iodine after processing (Figure S14). Toward this end, we prepared thin films of 13 and subjected them to 300 °C for 30 min (Figure 4C), which resulted in quantitative removal of iodine as determined by TGA (Figure S14). We also prepared films of 13 with 15 vol % tetramethyl guanidine (TMG) in toluene. The films were annealed at 100 °C for 10 min, resulting in elimination of the iodine (Figure 4D) as observed by 1H NMR (Figure 4E) and TGA (Figure S14). We also found that elimination was successful on the bulk polymer (Figure S15). In all cases, TGA data indicate improved thermal stability of surfaces and materials treated with heat or base.

The iodine atoms incorporated into the backbone of the iodo–ene polymers are not only a handle for increasing the processability; they also offer avenues to add chemical functionality for postpolymerization functionalization, covalent modification of surfaces, and cross-linking. Iodine can be efficiently displaced with thioacetate (25) to give polymer 26 (Figure 5A). Removal of the acetate groups yielded thiol-containing polymer 27, which could undergo Michael addition

Figure 5. (A) Functionalization and cross-linking methods using thiols. (B) TGA analysis of thioacetate polymer 26 and cross-linked polymers 28 and 30. (C) Differential scanning calorimetry of thioacetate polymer 26 and cross-linked polymers 28 and 30 with Tg onset midpoints indicated. (D) The addition of azide to the polymer backbone and reaction with alkynes to yield cross-linked or fluorescent polymers (see Figure S19 for complete structure of cyclooctyne fluorophore). (E) Drop-cast films of 11a and 32 before and after treatment with cyclooctyne 34. Films were prepared by drop-casting 5 mg/mL polymer solutions in THF and annealing at 85 °C for 10 min. Films of 11a and 32 were placed in a 0.6 mg/mL solution of 34 in methanol for 14 h. Films were then sequentially washed with water and methanol to remove excess 34 and then placed under 365 nm light for photographs.
with acrylamide to produce 31 or oxidation to give cross-linked network 28. Cross-linked polymer 28 represents a redox-active material, providing opportunities for responsive, dynamic fluoruous scaffolds. Irreversibly cross-linked materials could also be prepared by treatment of 11a with ethanedithiol or photo-cross-linking 26 via thiol–ene chemistry with 1,9-decadiene (9) to give polymers 29 and 30, respectively. Permanently cross-linked fluoruous materials are advantageous for reducing creep. All polymer cross-links were confirmed by TGA, DSC, and infrared (IR) spectroscopy (Figures S5B,C, S16, and S17, and Table S1, respectively).

Thiols are not the only nucleophile that can displace the iodo atoms on the polymer backbone. We found that azide groups could also be appended to the fluoropolymers to yield polymer 32 (Figure 5D). In this instance, competing elimination was observed, resulting in 50% of iodo being replaced with an azide. The azide incorporation allowed for cross-linking of the polymers via Cu-catalyzed azide alkyne cycloaddition (33, Figures 5D and S18). The azide also represents an opportunity to covalently conjugate to surfaces coated with the semifluorinated polymers, as demonstrated through the attachment of monofluorinated cyclododecene (34) (Figure S19) to films of 32 to yield fluorescent polymer 35 (Figure S5E).

Finally, we looked to exploit the homolytic reactivity of the C–I bond for postpolymerization modification and cross-linking. By treatment of 11a with AIBN and allyl ethyl sulfone (36), we were able to install allyl functionality onto the polymer backbone with a 45% conversion (Figure 6A), producing polymer 37. This unique postpolymerization modification opens many avenues for further modification and cross-linking. We demonstrated the introduction of additional fluoruous character by performing another iodo–ene reaction on 37 to produce 38. Next, we exploited the homolytic reactivity of the C–I bond for direct photo-cross-linking of the iodo–ene polymers. We prepared 20 mg/mL samples of polymer 13 in toluene with or without 15 wt % photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA). The solutions were placed under a 365 nm UV lamp, and gelation began within 5 min if DMPA was present (Figure 6B). After 30 min had passed, no gelation was evident in the DMPA-free control (Figure S20). Thus, we are able to photo-cross-link the iodo–ene polymers in a DMPA-dependent manner. To determine the cause of gelation, small molecule 39 was synthesized and submitted to light and DMPA (Figure 6C). 1H NMR and 19F NMR supported that the reaction proceeded to complete loss of iodine in 10 min with 2 equiv. of DMPA (Figure S21). High-resolution gas chromatography–mass spectrometry (HR-GCMS) provided evidence of dimerization to compound 39 (Figure S22), which was further supported by DEPT90 13C NMR (Figure S23). An authentic HR-GCMS standard of 40 was prepared by oxidative coupling chemistry of 39 and confirmed the presence of 40 in the photo-cross-linking conditions. On inspection of the crude reaction mixture, we also observed minor amounts of reduced product 41, eliminated iodine product 42, and DMPA adducts (Figure S24); however, subjecting 42 to photo-cross-linking conditions did not yield any dimer formation. On the basis of these data, we hypothesize covalent cross-linking is achieved via recombination of radicals generated after homolytic cleavage of the C–I bond. Interestingly, similar radicals are generated throughout the polymerization mechanism, yet we do not detect cross-linked polymer. This may be due to

Figure 6. (A) Addition of allyl groups to the polymer backbone and subsequent iodo–ene reaction with perfluoroheptyl iodide. (B) Gelation of 13 in the presence of 2,2-dimethoxy-2-phenylacetophenone (DMPA). Two solutions of 13 in toluene (20 mg/mL) were prepared, and 15% DMPA was added to the solution on the right. Both solutions were irradiated with 365 nm light for 5 min. Pictures were taken before and after irradiation. (C) Model compound 39 to probe the cross-linking mechanism of 13 with DMPA. (D) Molding and photocuring of polymer 13 into a heart. A solution of compound 13 (100 mg/mL) and DMPA (15%) was placed in a heart mold and irradiated with 365 nm light for 5 min. The resulting gel was removed from the mold and treated with boiling water or 105 °C mineral oil without loss of the heart shape.
The polymerization and the photo-cross-linking. The direct photo-cross-linking of the iodo-ene polymers allows opportunities to fabricate organo and fluorogels. We prepared a 100 mg/mL solution of 13 in toluene and placed it into a heart mold. After 5 min of irradiation, the cross-linked gel was removed from the mold and retained the heart shape (Figure 6D). We found that the gel withstood hot mineral oil and boiling water without shape deformation, although it became smaller in mineral oil because of leaching of the toluene. The mineral oil treated gel could be readily reswollen in toluene or semifluorinated solvents such as trifluorotoluene (Figure S25). As with surfaces containing 13, the stability of the fluoropolymers is much lower when the iodine atoms are present. We were able to increase the thermal stability of the gel by treatment with DBU in toluene for 5 min with no loss of the gel shape (Figures S26 and S27). Thus, we are able to obtain bulk, thermally stable fluorous materials through a combined photo and chemical treatment process.

**CONCLUSION**

We have developed a facile polymerization of dienes and diiodoperfluorozalkanes that allows access to an array of fluorinated polymers up to 128 kDa. Further size control can be performed through the addition of end-caps. The fluorous nature of the polymer can be easily tuned through strategic selection of monomers and postpolymerization modifications. The mild polymerization conditions enable sensitive monomers to be polymerized and yields fluorinated polymers that degrade into segments that do not bioaccumulate. Iodine incorporation along the polymer backbone gives an exquisite degrade into segments that do not bioaccumulate. Iodine mers to be polymerized and yields of polytetrafluoroethylene: Effect of melt treatment on tensile deformation mechanism. J. Appl. Polym. Sci. 2012, 132, 1667−1674. (4) Olabisi, O., Adewale, K., Eds. Handbook of thermoplastics, 2nd ed.; CRC Press: Boca Raton, FL, 2015. (5) Shi, X; Wu, C; Rong, M; Czizany, T; Ruan, W; Zhang, M. Improvement of creep resistance of polytetrafluoroethylene films by nano-incclusions. Chin. J. Polym. Sci. 2013, 31, 377−387. (6) Sun, H; Cooke, S; Bates, D; Wynne, J. Supercritical CO2 processing and annealing of polytetrafluoroethylene (PTFE) and modified PTFE for enhancement of crystallinity and creep resistance. Polymer 2005, 46, 8872−8882. (7) Krafft, M; Riess, J. Per- and polyfluorinated substances (PFAs): Environmental challenges. Curr. Opin. Colloid Interface Sci. 2015, 20, 192−212. (8) Tervoort, T; Visjager, J; Smith, P. Melt-processable poly(tetrafluoroethylene)—compounding, fillers and dyes. J. Fluorine Chem. 2002, 114, 133−137. (9) Mark, H; Bikales, N; Overberger, C; Menges, G; Kroschwitz, J. Encyclopedia of polymer science and engineering, 2nd ed.; Interscience: New York, 1986; Vol. 6. (10) Scheirs, F. Modern fluoropolymers: High performance polymers for diverse applications, 1st ed.; John Wiley & Sons, Chichester, 1997. (11) Inderherbergh, J. Polynvinylidene fluoride (PVDF) appearance, general properties and processing. Ferroelectrics 1991, 115, 295−302. (12) Asandei, A. Photomediated controlled radical polymerization and block copolymerization of vinylidene fluoride. Chem. Rev. 2016, 116, 2244−2274. (13) Ameduri, B. From vinylidene fluoride (VDF) to the applications of VDF-containing polymers and copolymers: Recent developments and future trends. Chem. Rev. 2009, 109, 6632−6686. (14) Hinterz, K; Carlson, D; Schmiegel, W. Fluoropolymers, Organic. Ullmann’s encyclopedia of industrial chemistry, 6th ed.; Wiley-VCH: Weinheim, Germany, 2002. (15) Zhao, H; Zhang, J; Wu, N; Zhang, WU; Crowley, K; Weber, S. Transport of organic solutes through amorphous Teflon-AF films. J. Am. Chem. Soc. 2005, 127, 15112−1511. (16) Hung, M. The chemistry of fluorinated diooxes and dioxolanes. S. Structure-property relationship of fluorinated dioxole polymers. Macromolecules 1993, 26, 5829−5834. (17) See Chemours Web site for pricing details (https://www. chemours.com/Teflon_I ndustrial/en_US/products/index.html). (18) Oshima, A; Washio, M. Chemical and radiation cross-linking of polytetrafluoroethylene by containing fluorinated compound. In Polymer Durability and Radiation Effects; Celina, M. C; Assink, R. A., Eds.; ACS Symposium Series; American Chemical Society, 2007; pp 204−217.
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