Synthesis of Telechelic Fluoropolymers with Well-Defined Functional End Groups for Cross-Linked Networks and Nanocomposites

Kun Li, Siwei Liang, Yingying Lu, and Qing Wang*

Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802

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Introduction. Fluoropolymers, i.e., polymers having a fluorinated backbone, exhibit many interesting properties not found in their hydrocarbon analogues.[1] These properties include unique piezoelectric and pyroelectric properties, high thermal stability, and excellent chemical resistance. However, low surface energy and coefficient of friction of these polymers have limited their applications, particularly those in which surface adhesion and miscibility with other functional components are paramount.[1b] Thus, a number of synthetic methods have been developed to enhance their compatibility by incorporating functional groups into fluoropolymer chains.[2] Telechelic structures in which functional groups are introduced at polymer chain ends are of great interest.[3] This chain-end functionalization approach would keep the main-chain structures of fluoropolymers intact and thus preserve their distinctive physical properties to a large degree. Telechelic structures have also been used as building blocks to construct complex macromolecular architectures and composites with predetermined compositions and structures.[4] Unfortunately, literature procedures to produce telechelic fluoropolymers are very sparse.[5] Current synthetic methods do not allow for polymerization of fluorinated alkenes by living anionic/cationic polymerization[3,6] or pseudo-living radical polymerization,[7] the methods commonly adopted in chain-end functionalization of hydrocarbon polymers. Many studies utilize transfer agents in telomerization to generate low molecular mass fluorinated telomers with halogen end groups.[8] For example, iodine transfer polymerization has been developed to prepare iodine-terminated fluoropolymers.[9] The drawback of this method is that the terminal iodine groups cannot be transformed to other reactive functional groups facilely.

While functional azo-initiators have been used in free radical polymerization to produce early examples of end-functionalized polydienes and polystyrenes under the "dead-end" conditions,[3,10] this route could be particularly appealing for the synthesis of telechelic fluoropolymers. It has been suggested that the termination in radical polymerization of fluorinated alkenes proceeds predominately through the radical coupling reaction.[11] Hence, one would expect a fluoropolymer to possess functional groups at both termini when obtained from the polymerization reaction where the initiator carries the desirable functional group. Ameduri et al. examined the use of hydrogen peroxide as an initiator to prepare VDF/HFP (vinylidene fluoride/hexafluoropropene) elastomers containing hydroxyl terminal groups.[5c] However, the final product contains not only hydroxyl terminal groups but also a substantial amount of carboxylic acids as well as unsaturated bonds from the side reactions. Herein, we report the synthesis of fluoropolymers containing well-defined reactive functional end groups such as hydroxy, carboxylic acid, phenol, and amine. On this basis, we demonstrate the preparation of cross-linked fluorinated polymer networks and nanocomposites with high thermal stability and uniform dispersibility under mild conditions.

* To whom correspondence should be addressed. E-mail: wang@matse.psu.edu.

Results and Discussion. Benzoyl peroxide (BPO) has proven to be an efficient initiator for the polymerization of a broad range of fluorinated alkenes.[12] As shown in Scheme 1, a series of BPO-based functional initiators were readily prepared by the acylation of Li_2O_2 with benzoyl chloride substituted by the corresponding functional group. The BPO derivatives were also obtained through the reaction of functional group substituted benzoic acid with H_2O_2 in the presence of *N*,*N*′-dicyclohexylcarbodiimide (DCC). The rate constants and half-lives of the peroxides measured by iodometric titration as well as the synthetic details are given in the Supporting Information.

The prepared functional BPOs are capable of initiating the homopolymerization of vinylidene fluoride (VDF) as well as co- and terpolymerization of VDF with hexafluoropropene (HFP), chlorotrifluoroethylene (CTFE), and trifluoroethylene (TrFE). The polymerizations were carried out in acetonitrile in the presence of 0.2 mol % functional initiator at 90 °C. Gaseous fluorinated monomers were transferred and condensed through a dual-manifold Schlenk line into an autoclave equipped with a magnetic stirrer. The typical reaction time was about 6−8 h. As exemplified in Figure 1, the ^{1}H NMR spectrum of the copolymer P(VDF-*co*-CTFE) prepared using **R1** as the initiator clearly shows the signals at 1.58 and 8.10 ppm corresponding to the protons from *tert*-butyl and phenyl groups, respectively. Removal of the protecting *tert*-butyl groups in the copolymer using iodotrimethylsilane yielded the fluoropolymer with carboxylic acid end groups, evidenced by complete disappearance of the peaks from *tert*-butyl protons at 1.58 ppm in the ^{1}H NMR spectrum and appearance of new absorption bands at 1736 cm^{-1} attributed to carbonyl groups from carboxylic acids in the infrared spectrum. A small triplet centered at 6.3 ppm is also observed. These peaks are associated with $-CF_2H$ group resulting from a short chain-branching process, which involves an intramolecular 1−5 hydrogen shift analogous to similar radical reactions reported in low-density polyethylene.[13] The presence of a triplet centered at 4.7 ppm is assigned to the extreme methylene group that is linked with the ester group from the initiator. End-group analysis based on the ^{1}H and ^{19}F NMR spectra revealed a number-average molecular weight (M_n) of 50 300 g/mol for the P(VDF-*co*-CTFE), while triple-detection gel permeation chromatography (GPC) measurements in DMF gave a M_n of 48 000 g/mol (see Supporting Information). The average degree of functionality[10c] was thus calculated to about 1.9, near the expected theoretical values of 2. Remarkably, the ^{1}H and ^{19}F NMR spectra do not show any resonances of unsaturated bonds resulting from disproportionation reactions at 5.5 to 6.5 and −120 to −130 ppm, respectively. Therefore, growing radicals are only consumed by recombination or termination with primary radicals, which is corroborated by M_w/M_n values of 1.5−1.6 revealed in the GPC measurements. This is in direct contrast to free radical polymerization of hydrocarbon alkenes, in which termination often occurs by a combination of coupling and disproportionation. The achieved high efficiency in the carboxylic acid-terminated P(VDF-*co*-CTFE) proves the principle of the design, which may also be a consequence of a high rate of incorporation of the primary radical into the

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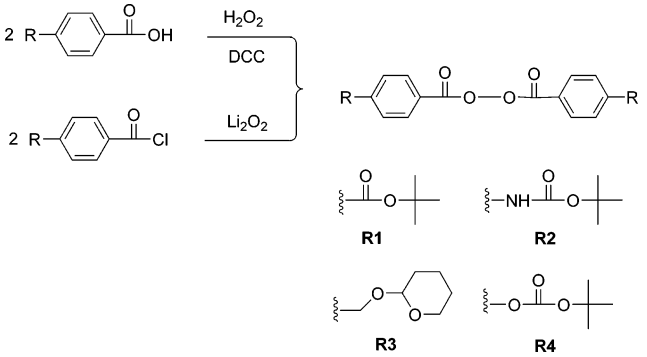
Scheme 1. Synthesis and Chemical Structures of the BPO-Based Functional Initiators



polymers.[14] Although about 8% phenyl radicals estimated from the ^{1}H NMR spectra were generated during the polymerization, the decarboxylation of the functional BPOs does not affect the average degree of chain-end functionality.

Similar results have been obtained from the polymerization using **R2**−**4** as the initiators. The presence of terminal amino, hydroxyl, and phenol groups in the fluorinated polymers was confirmed by NMR spectroscopy (see Supporting Information). All the ^{1}H NMR spectra display the presence of the characteristic multiplet centered at 2.9 ppm assigned to the methylene groups of $-CF_2CH_2-CF_2CH_2-CF_2CH_2-$ resulting from the normal head-to-tail (H−T) VDF addition, which agrees with the signal at −93.0 and −95.2 ppm in the ^{19}F NMR spectra attributed to the difluoromethylene groups in $-CH_2CF_2-CH_2CF_2-CH_2-CF_2-$ and $-CH_2CF_2-CF_2CH_2-CH_2CF_2-CH_2CF_2-$, respectively. Additionally, the ^{19}F NMR spectra exhibited expected multiplets centered at −114.3 and −116.1 ppm, corresponding to the head-to-head (H−H) VDF sequence in the polymer chain. The mole fraction of H−T sequence assessed from the integrals of the characteristic peaks is typically around 95%, as observed in commercially available PVDF.

The utilization of the terminal functional groups in the telechelic fluoropolymers was demonstrated in the formation of cross-linked networks, which can be accomplished both thermally and chemically via condensation with a curing agent having complementary multiple functional groups. For example, thermally induced amidation reaction was initiated by adding trimesic acid (1−2 wt %) to a concentrated DMF solution of the amine-terminated P(VDF-*co*-CTFE) that was prepared using **R2** as the initiator and iodotrimethylsilane as a deprotection agent. After heating the cast thin film at 100 °C for about 6 h under vacuum, an insoluble material was observed. Cross-linking was chemically induced by combining trimesic acid trichloride with the amine-terminated P(VDF-*co*-CTFE)s at room temperature. Spectroscopic evidence for the cross-linking reaction was obtained using infrared spectroscopy where a new amide II peak (N−H mixed mode) appears at 1630 cm^{-1} at the expense of a dramatically attenuated absorbance at 1726 cm^{-1} owing to the carbonyl groups in the acids. The distribution of amide linkages in the cross-linked thin films was mapped by FTIR reflectance-transmission microspectroscopy (FTIR-RTM) (see Supporting Information). Further evidence for the cross-linking reaction was provided through thermal analysis, as shown in Figure 2. In addition to a broader melting transition, the crystallization temperature was found to decrease by nearly 11 °C relative to its telechelic form. These results indicate that the formation of cross-linking structures inhibits the recrystallization and leads to reduction in crystal sizes, which is in accord with those reported in the electron-irradiated PVDF films.[15]

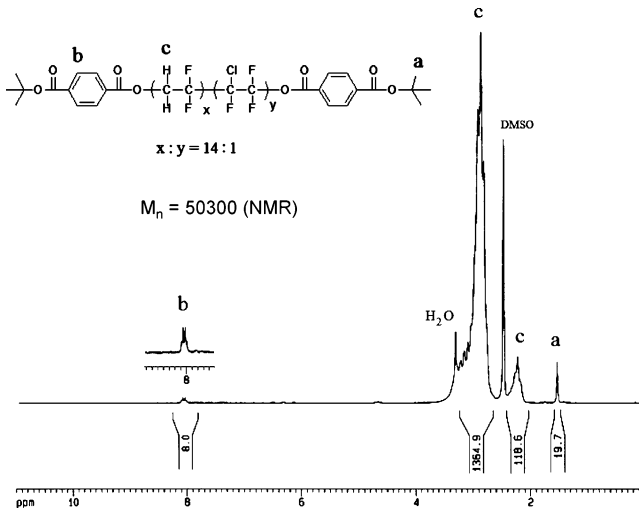


Figure 1. ^{1}H NMR spectrum of P(VDF-*co*-CTFE) with *tert*-butyl ester as terminal groups.

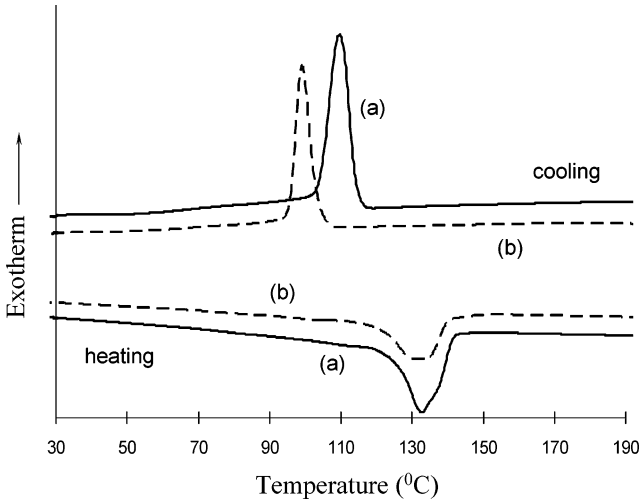


Figure 2. DSC thermograms of the amine-terminated P(VDF-*co*-CTFE) copolymer film (a) before and (b) after cross-linking.

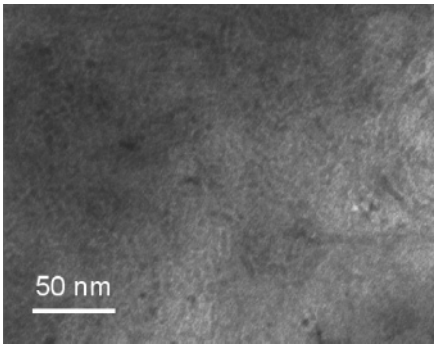


Figure 3. Transmission electron micrograph of the thin film prepared by cross-linking amine-terminated P(VDF-*co*-CTFE) with carboxylic acid-covered TiO_2 nanoparticles.

To further the applications of the telechelic fluoropolymers, hybrid materials composed of fluoropolymers and inorganic nanoparticles were prepared. Oleic acid-capped titanium oxide (TiO_2) nanoparticles with a mean length of 18 ± 5 nm were synthesized by hydrolysis of titanium(IV) isopropoxide in the presence of aqueous trimethylamine *N*-oxide (TMAO) and oleic acid according to literature procedures.[16] Oleic acid was then replaced with 11-phosphonoundecanoic acid by ligand exchange in THF to yield TiO_2 covered by carboxylic acids. The surface

coverage on the TiO_2 nanoparticles was confirmed by the presence of resonances characteristic of the phosphine oxide in the ^{31}P NMR and FTIR spectra. The surface-modified TiO_2 are readily dispersed in organic media such as THF and DMF. Thin films of nanocomposites were formed by casting the dispersion of amine-terminated P(VDF-*co*-CTFE) copolymer and carboxylic acid-coated TiO_2 (20 wt %) in DMF on glass substrate and then baking at 100 °C for several hours under vacuum. Analysis of the composite thin films by transmission electron microscopy (TEM) reveals the uniform nature of the films (Figure 3). The formation of amide bonds renders great stability of the films. For example, the prepared thin films have been heated at 200 °C overnight while the melting point of the original amine-terminated P(VDF-*co*-CTFE) is around 120 °C. The films were found to remain intact without any significant changes observed in film thickness.

In conclusion, we successfully synthesized, for the first time, a family of telechelic fluoropolymers containing well-defined functional terminal groups by tailoring the chemical structures of the initiator. Unlike a growing alkyl radical chain, the fluoroalkyl radical chain is not subject to disproportionation. Consequently, this functional initiator approach leads to high fidelity of functional groups presenting at fluoropolymer chain ends. Interestingly, this work suggests a mild and effective route to cross-linked fluoropolymer networks with controlled molecular structures. This overcomes the problems yielded from dehydrofluorination or irradiation reactions that are currently utilized in fluoropolymer vulcanization, including formation of excessive unsaturated structures, chain scission (degradation), and uncontrolled cross-linking density.[17] This general functional approach also opens new possibilities for self- and directed-assembly of inorganic nanoparticles in fluoropolymer matrix to form novel composite materials with uniform dispersibility and high thermal stability.

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Supporting Information Available: Experimental details for the synthesis and characterization. This material is available free of charge via the Internet at http://pub.acs.org.

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