# Cycloalkenyl-Functionalized Polymers and Block Copolymers: Syntheses via Selective RAFT Polymerizations and Demonstration of Their Versatile Reactivity

**Jun Ma,[†] Chong Cheng,[‡] and Karen L. Wooley*[,†]**

*Department of Chemistry and Department of Radiology, Washington University, Saint Louis, Missouri 63130-4899, and Department of Chemical and Biological Engineering, The State University of New York at Buffalo, Buffalo, New York 14260*

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ABSTRACT: A facile synthetic strategy for the preparation of well-defined polymers bearing cycloalkenyl side groups has been established via selective reversible addition−fragmentation chain transfer (RAFT) polymerization of cycloalkene-functionalized asymmetrical divinyl monomers. Two representative monomers, 4-(6′-methylcyclohex-3′-enylmethoxy)-2,3,5,6-tetrafluorostyrene and 4-(cyclohex-3′-enylmethoxy)-2,3,5,6-tetrafluorostyrene, were synthesized. RAFT polymerizations of these bifunctional monomers, using *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate as the chain transfer agent and 2,2′-azobis(isobutyronitrile) (AIBN) as the thermal initiator, exhibited superb selectivity toward the substituted styrenyl vinylic unit relative to the cyclohexenyl unit, even at high monomer conversions (>80%). The resulting polymers retained quantitative cyclohexenyl groups, while having predetermined molecular weights and narrow molecular weight distributions (PDI = 1.09−1.15). Well-defined block copolymers with pendent cyclohexenyl groups were also prepared by sequential RAFT chain extension polymerizations. A variety of functional polymers were further obtained by functional group transformations using the cyclohexene-functionalized polymers as precursors.

## Introduction

The design and synthesis of well-defined polymers with multiple pendent functionalities is an important research topic in modern polymer chemistry.[1−4] The incorporation of functional groups into polymer structures can modify their properties greatly, such as hydrophilicity, hydrophobicity, biocompatibility, thermal property, adhesion, degradability etc., thereby, providing polymers with useful characteristics. Moreover, through highly efficient orthogonal chemical reactions, performed upon the incorporated reactive groups, the polymers serve as templates for (regioselective) functionalization,[5−9] grafting, and cross-linking and as building blocks for the preparation of advanced polymeric architectures. For example, incorporation of carbonyl groups (e.g., ketone[10−14] and aldehyde[15]) enhanced the photodegradability[10] and also allowed for efficient grafting via well-established carbonyl chemistries.[11,14,16−18]

Alkene-functionalized polymers have attracted considerable attention because the olefin groups undergo transformations by robust, selective, and mild olefin chemistries via thiol−ene UV reaction,[19−23] aldehyde−alkene photoreaction,[24] ring-opening metathesis (ROM)[25−29] and cross-metathesis (CM) reactions,[30−34] electrophilic addition,[35,36] radical polymerization,[37] and so on. Relative to postpolymerization functionalization, selective living polymerization of asymmetrical divinyl monomers has provided well-defined polymers with pendent alkenyl groups directly from alkene-functionalized monomers. Typically, anionic polymerization or ring-opening polymerization has been employed to achieve selective polymerization.[22,36,38,39] It should also be noted that, no matter which method is used, most of the alkene-functionalized polymers in the literature have open-chain alkenyl side groups, and few examples of polymers with pendent cycloalkenyl functionalities have been reported.[40]

Compared to anionic polymerization and ring-opening polymerization, controlled/living radical polymerization requires mild reaction conditions, has relatively high functional group tolerance, and therefore, has been used widely for the synthesis of polymers with both well-defined macromolecular architectures and diverse functionalities.[3,4,41−43] As an important controlled polymerization technique, reversible addition−fragmentation chain transfer (RAFT) polymerization[44,45] provides homogeneous and metal-free reaction systems for the polymerization of a wide range of monomers. Recently, we have reported a facile approach to synthesize well-defined (co)polymers with pendent open-chain alkenyl groups via selective RAFT polymerization of asymmetrical divinyl monomers.[46] Using 4-(3′-buten-1′-yloxy)-2,3,5,6-tetrafluorostyrene as a representative monomer, polymerization with high selectivity toward the substituted styrenyl group was achieved until moderate monomer conversions (∼50%), yielding (co)polymers having butenyl side groups. However, the polymerization selectivity decreased noticeably when high molar ratios of butenyl group to the substituted styrenyl group were reached at high monomer conversions.

As a special class of alkenes, cyclic alkenes have appreciable distinctions in reactivity under various reaction conditions. Relative to monosubstituted alkenes, cyclic alkenes, such as *cis*-cyclohexene and *cis*-cyclopentene, exhibit remarkably low reactivity in radical polymerization. Their lack of a highly strained ring structure provides considerable thermodynamic stability, and their 1,2-dialkyl substituents induce steric hindrance toward attack upon the vinyl bonds.[47] No radical homopolymerization and only few radical copolymerizations with these cycloalkenes have been reported.[48−51] In each of the copolymerizations, a comonomer with a highly polar vinyl group, such as maleic anhydride or *N*-phenylmaleimide, was employed to activate the copolymerization system, owing to the contrasting polarities of the comonomers.[37] Therefore, we hypothesized that, by avoiding strong polarity activation effects through judicious monomer design, monocycloalkene-functionalized asymmetrical divinyl monomers may have very high selectivity in radical polymerization. As a result, RAFT polymerization of these monomers was expected to yield well-

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* Corresponding author: e-mail klwooley@wustl.edu, Tel (314) 935-7136, Fax (314) 935-9844.

[†] Washington University.

[‡] The State University of New York at Buffalo.

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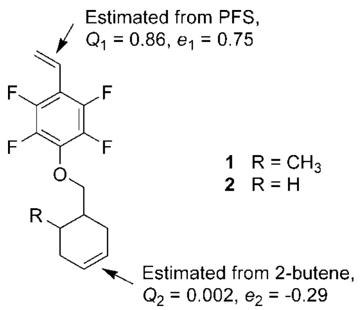


**Figure 1.** Structural design of asymmetrical divinyl monomers **1** and **2** for selective RAFT polymerizations to afford cyclohexenyl-functionalized polymers and block copolymers.

defined polymers with pendent cycloalkenyl groups over a wide range of monomer conversions.

## Results and Discussion

**Design and Synthesis of Cyclohexene-Functionalized Asymmetrical Divinyl Monomers.** 4-[(6′-Methylcyclohex-3′-enylmethoxy)methyl]-2,3,5,6-tetrafluorostyrene (**1**; R = $-CH_3$) and 4-(cyclohex-3′-enylmethoxy)-2,3,5,6-tetrafluorostyrene (**2**; R = −H) were designed as the cycloalkene-functionalized asymmetrical divinyl monomers for selective RAFT polymerization (Figure 1) due to the expected high contrast of radical polymerization reactivity of their two vinyl groups and their synthetic feasibilities. Because there is no literature that reported $Q$ and $e$ values for 4-alkoxy-2,3,5,6-tetrafluorostyrene and cyclohexene (CHE), the reactivities of the substituted styrenyl groups and CHE groups in **1** and **2** were estimated through 2,3,4,5,6-pentafluorostyrene (PFS, $Q_1 = 0.86$, $e_1 = 0.75$) and 2-butene, a model compound of 1,2-dialkyl-substituted vinyl monomer ($Q_2 = 0.002$, $e_2 = -0.29$), respectively. To predict polymerization selectivity, polymerization of an asymmetrical divinyl monomer can be considered as a copolymerization of the two types of vinyl groups. Relative to $Q_2$ of almost zero, $Q_1$ of 0.86 indicates the incomparably high intrinsic reactivity of the substituted styrenyl group; only moderate difference between $e_1$ and $e_2$ further excludes strong polarity activation effects that would be required for the participation of CHE group in copolymerization. Quantitative analysis using Alfrey−Price equations[47] gave estimated reactivity ratios $r_1$ of about 200 and $r_2$ of less than 0.002. These values indicate that the styrenyl groups have significantly higher reactivities than do the CHE groups and further suggest that the polymerizations of **1** and **2** can be considered essentially as homopolymerizations of their substituted styrenyl groups.

Monomers **1** and **2** were synthesized readily by the nucleophilic aromatic substitution reaction of PFS with a CHE-containing alcohol (6-methylcyclohex-3-enylmethanol for **1**; cyclohex-3-enylmethanol for **2**), in the presence of NaH in tetrahydrofuran heated at 50 °C for 3 h. The yields for **1** and **2** were 84 and 85%, respectively. Confirmation of their structures was made by $^1H$ NMR spectroscopy (Figure 2a,c). Upon coupling of the cyclohexenyl alcohols onto PFS, the exocyclic methylene proton resonances shifted downfield, from ca. 3.5 ppm to signals centered at 4.14 and 4.10 for **1** and **2**, respectively. The resonances of these methylene protons in **1** at 4.35−4.07 ppm exhibit a complex peak pattern due to the mixture of stereoisomers, while the resonance of the $-OCH_2-$ protons in **2** had a doublet splitting pattern centered at 4.10 ppm. For both **1** and **2**, the resonance intensity ratios of these methylene protons vs the CHE vinylic protons (at 5.68 ppm for both monomers) vs the styrenyl vinylic protons (at 5.62, 6.02, and 6.62 ppm) were in excellent agreement with their proton number ratios of 2:2:3.

**Syntheses and Characterization of Well-Defined Cyclohexenyl-Functionalized Polymers.** Well-defined homopolymers bearing cyclohexenyl side groups, **3** and **4**, were synthesized by RAFT polymerizations of monomers **1** and **2** using *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (DDMAT)[52] as the chain transfer agent and 2,2′-azobis(isobutyronitrile) (AIBN) as the thermal initiator at 69 °C for 12−16 h (Scheme 1). The feed ratio of $[M]_0$:$[DDMAT]_0$:$[AIBN]_0$ was 50:1:0.1 or 100:1:0.1. The polymerization solvent was 30 vol % of 2-butanone or 1,4-dioxane. All of the synthetic conditions and their results are summarized in Table 1.

For each of the trials, at time intervals during polymerization, small aliquots were withdrawn from the polymerization solution and analyzed by $^1H$ NMR spectroscopy for the determination of monomer conversions and by GPC for the determination of molecular weights and polydispersities of the resulting polymers. Continuous increase of conversion of the substituted styrenyl group was verified by $^1H$ NMR spectroscopy, based upon comparison of the resonance intensities of the substituted styrenyl protons at 6.62 and 6.02 ppm with the resonance intensities of methylene protons ($-OCH_2-$) at 4.35−3.78 and 4.20−3.80 ppm for polymerizations of **1** and **2**, respectively. The resonance intensities of the protons of the CHE groups remained consistent during the polymerizations, indicating that, essentially, only the styrenyl groups were polymerized. As monitored by GPC, with increase of the polymerization times and monomer conversions, the molecular weights (MW) of the resulting polymers increased (Figure 2). Narrow and monomodal MW distributions (PDI < 1.20) were observed even at late stages of the polymerizations. The final polymers **3a**, **3b**, and **4**, obtained at 82−84% monomer conversions, had number-average molecular weights ($M_n$) that were in agreement with the theoretical values and low PDI values (1.09−1.15). $^1H$ NMR spectroscopy was also used to determine the $M_n$ values of **3a**, **3b**, and **4**, based on the intensity integration ratios of the resonances for the $-OCH_2-$ protons on their monomer repeat units to the resonance of the $-SCH_2-$ protons on their terminal RAFT agent functionality. All of the above results supported the controlled characteristics of the RAFT polymerizations of **1** and **2** with a specificity toward the styrenyl group relative to the CHE group.

One important advantage of controlled/living polymerizations, relative to nonliving polymerization, is that well-defined block structures can be obtained readily by sequential polymerization of different monomers. Thus, we investigated the chain extension of the CHE-functionalized homopolymer, bearing a terminal trithiocarbonate chain transfer functionality, by RAFT polymerization of a new monomer. Chain extension of styrene was conducted to prepare regio-functionalized block copolymers, containing the cyclohexenyl side-chain functionalities along only the first segment of the resulting diblock copolymer. Using **3a** as the macro-chain transfer agent (macro-CTA), RAFT polymerization of styrene ($[St]_0/[macro\text{-}CTA]_0/[AIBN]_0 = 510/1.0/0.2$, Scheme 2a) was performed at 70 °C in 2-butanone (60 vol %). The polymerization was allowed to proceed for 3 h, during which 14% conversion of styrene was obtained, as measured by $^1H$ NMR spectroscopy. The low monomer conversion was intentionally targeted to avoid a significant occurrence of unfavorable side reactions related to the cyclohexenyl groups. The formation of diblock copolymer **5** ($M_n^{GPC} = 21.8$ kDa, PDI = 1.21) by chain extension from **3a** was verified by progressive increases in molecular weight, as observed by GPC. The $M_n$ and low PDI of **5** indicated no considerable occurrence of side reactions of the CHE groups that were highly concentrated on the macro-CTA.

In another experiment, chain extension from a functional macro-CTA allowed for demonstration of the fidelity of the

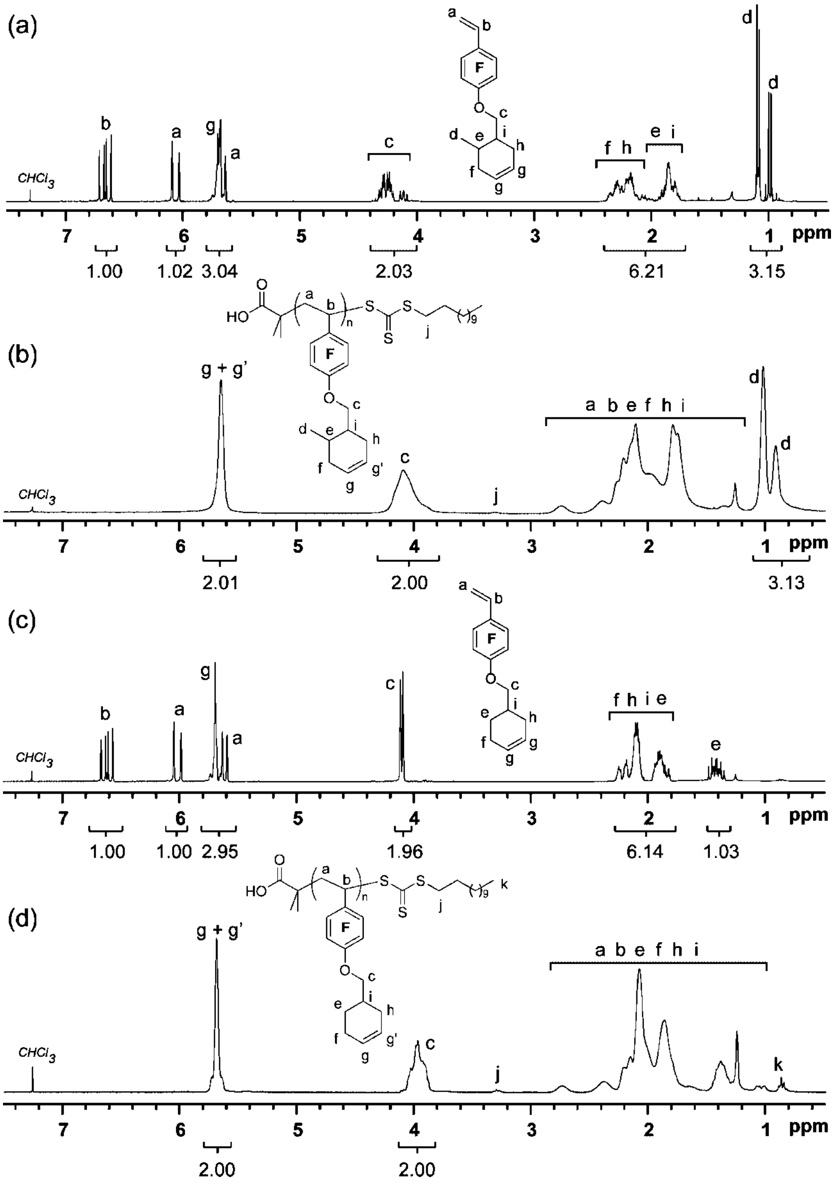
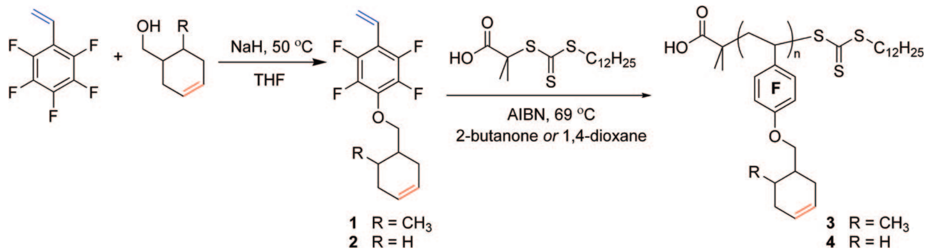


**Figure 2.** $^1$H NMR spectra (300 MHz, $CDCl_3$) of asymmetrical divinyl monomers and their corresponding homopolymers prepared by RAFT polymerization: (a) monomer **1**; (b) poly(**1**), i.e., **3a**; (c) monomer **2**; (d) poly(**2**), i.e., **4**.

**Scheme 1. Syntheses and Selective RAFT Polymerizations of Asymmetrical Divinyl Monomers Bearing a Pendent CHE Group**



selective polymerization of the styrenyl unit of the divinylic-based monomers and also produced block copolymers having distinctive chemically reactive groups segregated into each of the two block segments. Chain extension from poly(St-*alt*-MAn)$_n$, a well-defined macro-CTA agent,[46] by RAFT polymerization of monomer **2** ([**2**]$_0$/[macro-CTA]$_0$/[AIBN]$_0$ = 103/1.0/0.1, Scheme 2b) at 58 °C in 2-butanone (60 vol %) yielded diblock copolymer **6** poly(St-*alt*-MAn)$_n$-*b*-poly(**2**)$_m$ ($M_n^{GPC}$ = 16.6 kDa, PDI = 1.25). These results further supported the high efficiency of the RAFT chain extension reaction and the intrinsic stability of the CHE groups under radical polymerization conditions. Amphiphilic diblock copolymers with CHE-functionalized hydrophobic segments may be subsequently prepared by transformation of the maleic anhydride units on copolymer **6** into hydrophilic structures.[46]

Thermogravimetric analyses were conducted from 25 to 550 at 10 °C/min under a nitrogen atmosphere to evaluate the thermal stabilities of these homo- and block fluoropolymers with pendent CHE groups. All homopolymers **3a**, **3b**, and **4** showed little mass loss (<5%) before 300 °C (Figure 5a,b). Homopolymer **3a** ($M_n^{GPC}$ = 14.0 kDa, $M_n^{NMR}$ = 13.6 kDa) exhibited an initial decomposition onset temperature ($T_d$) at 335 °C, followed

**Table 1. Conditions and Results for the Homopolymerizations**[a]

| entry | M | $[M]_0/[CTA]_0/[AIBN]_0$ | solvent | *t* (h) | conv (%)[b] | $M_n^{calc}$ (kDa)[c] | $M_n^{NMR}$ (kDa)[d] | $M_n^{GPC}$ (kDa)[e] | PDI | polymer |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **1** | 50/1/0.1 | 2-butanone | 12 | 82 | 12.7 | 13.6 | 14.0 | 1.15 | poly(**1**), **3a** |
| 2 | **1** | 100/1/0.1 | 2-butanone | 16 | 82 | 25.9 | 26.6 | 22.8 | 1.15 | poly(**1**), **3b** |
| 3 | **2** | 50/1/0.1 | 1,4-dioxane | 12 | 84 | 12.4 | 13.2 | 11.1 | 1.09 | poly(**2**), **4** |

[a] Polymerization conditions: 69 °C, 30 vol % of solvent. [b] Conversions were obtained by $^1$H NMR spectroscopy. [c] $M_n^{calc}$ was calculated based on the equation $M_n^{calc} = \{(\text{MW of monomer}) \times ([M]_0/[CTA]_0) \times \text{conv }\%\} + 364$. [d] $M_n^{NMR}$ was determined by $^1$H NMR spectroscopy (600 MHz, $CDCl_3$), based on the equation $M_n^{NMR} = \{(\text{MW of monomer}) \times [I(-OCH_2-)/I(-SCH_2-)]\} + 364$, where *I* represents the intensities of characteristic resonance. [e] Molecular weights determined by GPC are relative to polystyrene (PS) standards.

**Scheme 2. Regio-Functionalized Diblock Copolymers Prepared by RAFT Block Copolymerizations**

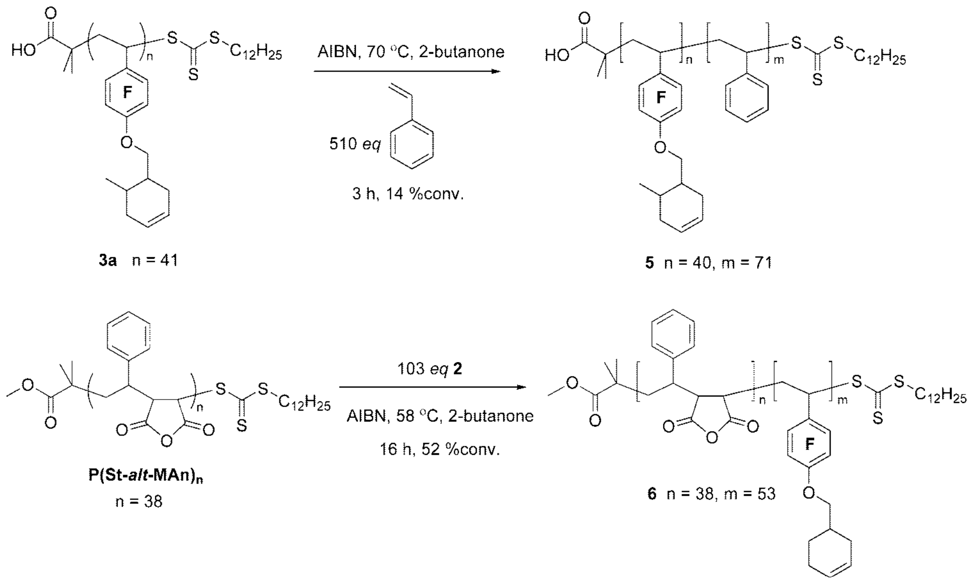


**Table 2. Synthesis of CHE-Functionalized Diblock Copolymers by Selective Sequential RAFT Polymerization**[a]

| entry | reaction conditions | *T* (°C) | *t* (h) | conv (%)[b] | $M_n^{calc}$ (kDa)[c] | $M_n^{NMR}$ (kDa)[c] | $M_n^{GPC}$ (kDa) | PDI | copolymer[d] |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $[St]_0/[\mathbf{3a}]_0/[AIBN]_0 = 510/1.0/0.2$ | 70 | 3 | 14 | 20.1 | 22.9 | 21.8 | 1.21 | poly(**1**)$_n$-*b*-PSt$_m$, **5** |
| 2 | $[\mathbf{2}]_0/[\text{P(St-}alt\text{-MAn)}]_0/[AIBN]_0 = 103/1.0/0.1$ | 58 | 16 | 52 | 23.4 | 22.2 | 16.6 | 1.25 | poly(St-*alt*-MAn)$_n$-*b*-poly(**2**)$_m$, **6** |

[a] Using 60 vol % 2-butanone as the solvent. [b] Conversions were measured by $^1$H NMR spectroscopy. [c] $M_n^{calc}$ was calculated based on the equation $M_n^{calc} = (M_n \text{ of macro-CTA}) + \{(\text{MW of monomer}) \times [M]_0/[\text{macro-CTA}]_0 \times \text{conv }\%\}$. [d] $M_n^{NMR}$ was calculated based on the equation $M_n^{NMR} = (M_n \text{ of macro-CTA}) \times (1 + r)$, where *r* is the block mass ratio of the newly grown second block vs the macro-CTA, which derives from $^1$H NMR spectroscopy, by the comparison of the resonance intensities of aromatic protons (6.00−7.50 ppm) (PSt block in **5** or P(St-*alt*-MAn) block in **6**) to methylene protons ($-OCH_2-$) (poly(**1**) block in **5** and poly(**2**) block in **6**).

by a distinct thermal decomposition range from 335 to 495 °C with 60% of mass loss (Figure 5a). The weight percentage of the residue of **3a** was measured to be 33% at 550 °C. Interestingly, relative to **3a**, **3b** with a higher $M_n$ ($M_n^{GPC} = 22.8$ kDa; $M_n^{NMR} = 26.6$ kDa) showed a thermolytic profile (Figure 5b) having a higher initial $T_d$ onset at 350 °C and a higher residue mass of 53% at 550 °C, indicative of greater thermal stability. Polymer **4** ($M_n^{GPC} = 11.1$ kDa; $M_n^{NMR} = 13.2$ kDa) exhibited a thermolytic profile similar to that of **3** and had a residue mass of 29% at 550 °C. Because linear poly(PFS) showed complete mass loss at 550 °C under similar conditions,[53] the higher residue mass of **3** and **4** suggested that their mass losses were retarded through thermal cross-linking via their cycloalkenyl pendent groups. Thermogravimetric analysis of diblock copolymers **5** and **6** showed a major mass loss in the temperature range of 270−460 °C. At 550 °C, residue mass percentages were 13% and 26% for **5** and **6**, respectively. Relative to homopolymers **3** and **4**, the lower residue mass percentages of diblock copolymers **5** and **6** were ascribed to their low concentrations of cycloalkenyl groups.

**Postpolymerization Functional Group Transformation.** On the basis of a variety of well-established organic reactions to convert alkene groups into other types of functionalities, polymers bearing CHE groups may be utilized as precursors for the preparation of new functional polymers. Choosing homopolymer **3b** as the model CHE-functionalized polymer, we performed a series of reactions, including epoxidation, dihydroxylation, and thiol−ene photoreactions, to demonstrate the reactivity of the CHE groups in functional group transformation (Scheme 3). For epoxidation, a $CHCl_3$ solution of polymer **3b** was treated with an excess amount of *m*-chloroperbenzoic acid (*m*-CPBA) at 0 °C for 3 h, and the quantitative consumption of the CHE units was observed from the disappearance of their unique $^1$H NMR resonances at 5.68 ppm. The resulting polymer **7**, obtained after precipitation in hexane, showed $^1$H NMR resonances of epoxide protons at ~3.2 ppm ($^1$H NMR, Figure 6a), which is in good agreement with the characteristic resonances of small molecule epoxides. Dihydroxylation of the CHE groups via osmylation[38,40] by treating a solution of polymer **3b** with *N*-methylmorpholine-*N*-oxide (NMO) and a catalytic amount of $OsO_4$ gave polymer **8** with diol-containing repeat units, as verified by $^1$H NMR analysis. The complete disappearance of CHE proton signals and the generation of 1,2-diol units with resonances at 3.10−4.30 ppm (Figure 6b) was observed in DMSO-$d_6$. The good solubility of **8** in ethanol also supports the transformation of the CHE groups into vicinal diols. A typical thiol−ene reaction of the CHE pendent groups was carried out by using $C_{12}H_{25}SH$ as the thiol reagent, in the

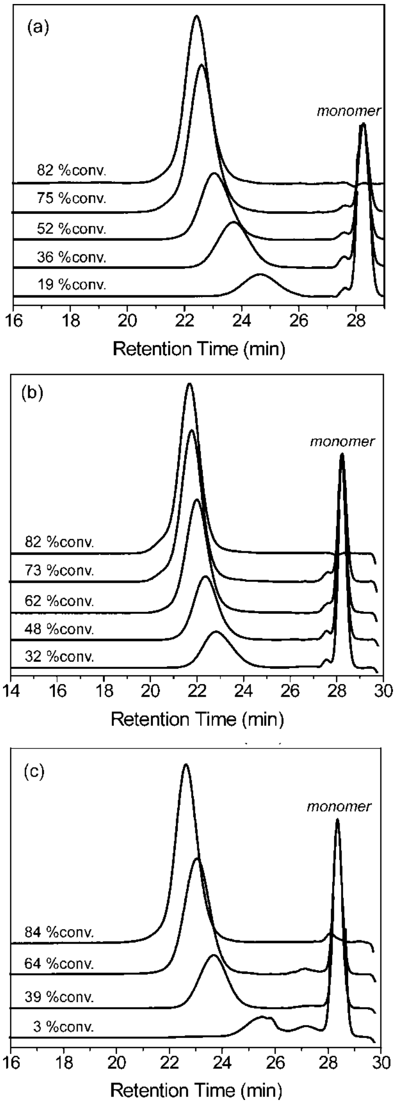


**Figure 3.** GPC chromatograms collected as a function of monomer conversion during the RAFT polymerizations of bifunctional monomers **1** and **2**: (a) Table 1, entry 1; (b) Table 1, entry 2; (c) Table 1, entry 3. For each composite of chromatograms, the sample at the highest monomer conversion is shown after purification by precipitation.

presence of 2 mol % 2,2′-dimethoxy-2-phenylacetophenone (DMAP) as the radical initiator with minimum amount of THF as solvent.[23] The reaction mixture was irradiated under UV for 30 min without stirring, to convert nearly 85% of the CHE groups into thioethers, as indicated by $^1$H NMR resonance intensities of unreacted CHE protons at 5.68 ppm vs methylene protons at 3.80−4.20 ppm. The incorporation of $-SC_{12}H_{25}$ into the polymer side chain was further confirmed by additional resonances in the $^1$H NMR spectrum of polymer **9** (Figure 6c), including the appearance of methane and methylene protons ($\rangle C\mathit{H}SC\mathit{H}_2-$) at 2.4−2.6 ppm, the aliphatic protons ($-SCH_2$-$C_{10}\mathit{H}_{20}CH_3$) at 1.2 ppm, and the methyl protons ($-CH_2C\mathit{H}_3$) at 0.8 ppm.

## Conclusions

Using cyclohexene (CHE) as a representative cycloalkenyl group, we have established selective RAFT polymerization of asymmetrical monomers having both styrenyl and cycloalkenyl groups as a facile synthetic method for the preparation of well-defined cycloalkenyl-functionalized polymers. By virtue of a convenient synthetic approach to access such bifunctional monomers, fluorocarbon units were also incorporated into the monomer and polymer structures. With quantitative RAFT functionality at the chain ends, these functional polymers were further employed for the synthesis of regio-functionalized block copolymers by sequential RAFT chain extension reactions. These CHE-functionalized fluoropolymers exhibited retarded mass losses during pyrolysis under nitrogen. A series of functional group transformation reactions, including epoxidation, dihydroxylation, and thiol−ene reactions, were conducted to obtain a variety of new functional polymers. These systems may also serve as templates for the preparation of polymers having more advanced architectures, cross-linked or grafted polymer conjugates, etc., each of which may use to advantage the CHE side-chain units and their diverse olefin chemistry. Such strategies are currently being investigated in our laboratory.

## Experimental Section

**Materials and Methods.** All chemicals and reagents were purchased from Aldrich Chemical Co. and used as received unless otherwise noted. Styrene was distilled over $CaH_2$ prior to polymerization. The RAFT agent, *S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (DDMAT), was prepared following literature method.[52] Poly(styrene-*alt*-maleic anhydride)$_n$ macro-CTA ($M_n^{NMR}$ = 7.8 kDa, $M_n^{GPC}$ = 8.1 kDa, PDI = 1.16, $n$ = 38) was prepared as reported previously.[46] A F300S UV system (Fusion UV Systems, Inc.) was used for the irradiation of samples for the thiol−ene chemistry. The UV system consists of a P300MT power supply and an I300MB irradiator with an H bulb (13 mm, 300 W/in.) which emits UV light in a range from 200 to 600 nm with peaks at 265, 315, 405, 435, 545, and 575 nm.

**Characterization Methods.** $^1$H NMR spectra were recorded at 300 or 600 MHz on solutions in $CDCl_3$, $CD_2Cl_2$, acetone-$d_6$, or DMSO-$d_6$ on a Varian Mercury 300 or Varian Unity 600 spectrometer, respectively, with the solvent proton signal as standard. $^{13}$C NMR spectra were recorded at 75 MHz on a Varian Mercury 300 spectrometer with the solvent carbon signal as standard. $^{19}$F NMR spectra were recorded at 282.2 MHz on a Varian Mercury 300 spectrometer with external $CFCl_3$ as standard. Infrared spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR system using diffuse reflectance sampling accessories and were analyzed using FT-IR Spectrum v. 2.00 software (Perkin-Elmer Corp., Beaconsfield, Bucks, England). Gel permeation chromatography (GPC) was conducted on a Waters 1515 HPLC (Waters Chromatography, Inc.), equipped with a Waters 2414 differential refractometer and a three-column series PL gel 5 $\mu$m Mixed C, 500 Å, and $10^4$ Å, 300 × 7.5 mm columns (Polymer Laboratories, Inc.). The system was equilibrated at 35 °C in THF, which served as the polymer solvent and eluent with a flow rate of 1.0 mL/min. Polymer solutions were prepared at a known concentration (ca. 3 mg/mL), and an injection volume of 200 $\mu$L was used. Data collection and analysis were performed respectively with Precision Acquire software and Discovery 32 software (Precision Detectors, Inc.). Molecular weight and molecular weight distributions were determined based on calibration of the GPC system with polystyrene standards. Thermogravimetric analysis (TGA) was performed on a TGA/SDTA851e instrument (Mettler-Toledo, Inc.) measuring the total mass loss on ~10 mg samples from 25 to 550 °C at a heating rate of 10 °C/min in a nitrogen flow of 50 mL/min.

**Synthesis of 4-(6′-Methylcyclohex-3′-enylmethoxy)-2,3,5,6-tetrafluorostyrene (1, Mixture of Isomers).** (6-Methylcyclohex-3-enyl)methanol (12.0 g, 95.1 mmol) was diluted with dry THF (250 mL) and deprotonated by the addition of NaH (2.64 g, 109 mmol) over 20 min at 0 °C. After $H_2$ was released completely, pentafluorostyrene (15.7 g, 81.0 mmol) in dry THF (50 mL) was added over 10 min. The reaction mixture was heated at 50 °C for 3 h, allowed to cool to room temperature, and concentrated under reduced pressure. Then, a saturated $NH_4Cl_{(aq)}$ solution (150 mL) was added slowly, and the organic products were extracted with $CH_2Cl_2$ (70 mL × 3). The organic phase was washed with water (70 mL), dried over $MgSO_4$, and concentrated. The resulting crude product was further purified by flash chromatography using ethyl

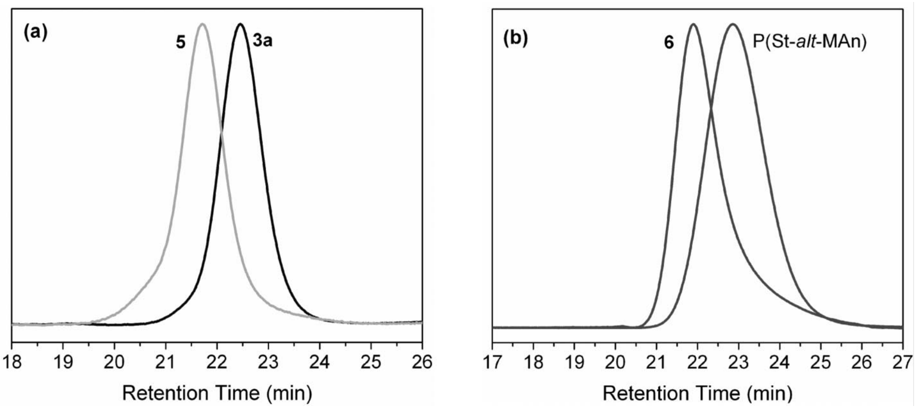


**Figure 4.** GPC chromatograms of (a) diblock copolymer **5** by chain extension from homopolymer **3a** by RAFT polymerization of styrene and (b) diblock copolymer **6** by chain extension from poly(St-*alt*-MAn) by RAFT polymerization of **2**.

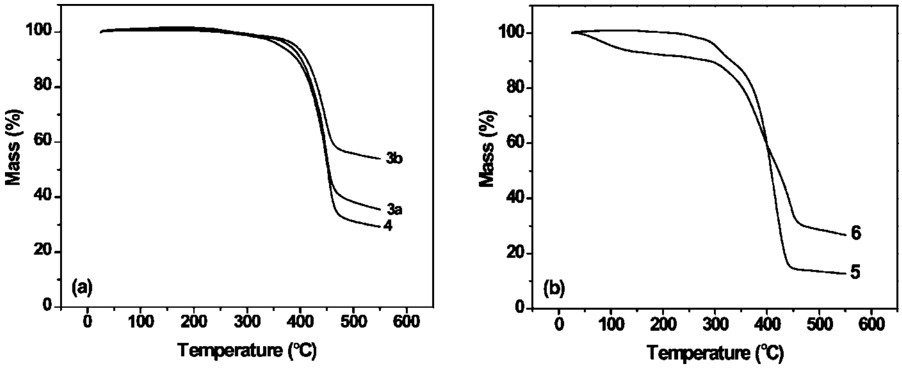
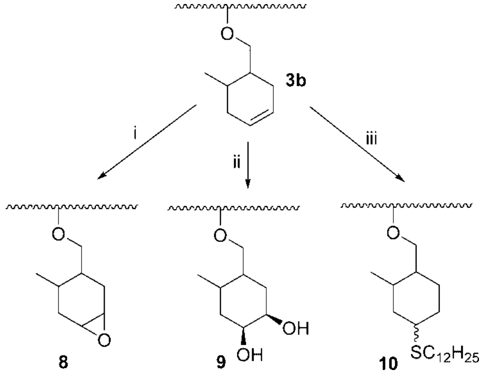


**Figure 5.** (a) Thermolytic profiles of cyclohexene-functionalized fluoropolymers **3a**, **3b**, and **4**. (b) Thermolytic profiles of diblock copolymers **5** and **6** (heating rate: 10 °C/min; nitrogen atmosphere).

**Scheme 3. Functional Group Transformation Reactions of CHE-Functionalized Fluoropolymer 3b**[a]



[a] Conditions: (i) 1.5 equiv of *m*-CPBA, CHCl$_3$, 0 °C, 4 h; (ii) 2 equiv of NMO, 5 wt % KOsO$_4$, THF/acetone/*t*-BuOH/H$_2$O, 12 h; (iii) 3 equiv of C$_{12}$H$_{25}$SH, 2 mol % of DMAP, UV irradiation for 30 min.

acetate/hexane (1/19) as eluent to yield 20.4 g (84%) of product as a colorless liquid. IR (NaCl, cm$^{-1}$): 3030−2850, 1646, 1502, 1488, 1429, 1407, 1384, 1151, 1121, 1080, 968, 930, 660, 582. $^1$H NMR (CDCl$_3$, 7.27 ppm): δ 0.98 (d, *J* = 6.5 Hz, −CH$_3$), 1.08 (d, *J* = 6.5 Hz, −CH$_3$), 1.84 (m, 2H, CH$_3$CH⟨ and −OCH$_2$CH⟨), 1.96−2.40 (m, 4H, −CH$_2$CH═CHCH$_2$−), and −OCHH$_2$CH⟨), 4.07−4.35 (m, 2H, −OCHH$_2$−), 5.62 (d, *J* = 12.0 Hz, 1H, *cis* CHH═CHAr), 5.67 (s, 2H, −CH$_2$CH═CHCH$_2$−), 6.02 (d, *J* = 18.0 Hz, 1H, *trans* CHH═CHAr), 6.62 ppm (dd, *J* = 12.0 and 18.0 Hz, 1H, CH$_2$═CHAr). $^{13}$C NMR (CDCl$_3$, 77.2 ppm): δ 14.9, 19.3, 25.7, 28.1, 29.7, 32.7, 33.6, 37.9, 40.6, 77.8, 78.0, 110.9, 122.1, 125.1, 125.9, 137.3, 140.0, 143.2, 143.9, 147.2. $^{19}$F NMR (CDCl$_3$): δ −160.1 (m, 2F, *meta-F*), −146.9 ppm (m, 2F, *ortho-F*). MS (ESI, M$^{\cdot+}$): [C$_{16}$H$_{16}$OF$_4$ + H$^+$], calcd: 301.1210; found: 301.1216.

**Synthesis of 4-(Cyclohex-3′-enylmethoxy)-2,3,5,6-tetrafluorostyrene (2).** A similar procedure for the synthesis of **1** was followed. Cyclohex-3-enylmethanol (10.0 g, 89.2 mmol) was diluted with dry THF (250 mL) and deprotonated by the addition of NaH (2.47 g, 103 mmol) over 20 min at 0 °C. After H$_2$ was released completely, pentafluorostyrene (14.7 g, 75.8 mmol) in dry THF (50 mL) was added in over 10 min. The reaction mixture was heated at 50 °C for 3 h, allowed to cool to room temperature, and concentrated under reduced pressure. Then, a saturated NH$_4$Cl$_{(aq)}$ solution (150 mL) was added slowly, and the organic products were extracted with CH$_2$Cl$_2$. The organic phase was washed with water, dried over MgSO$_4$, and concentrated. The resulting crude product was further purified by flash chromatography using ethyl acetate/hexane (1/19) as eluent to yield **2** as a colorless liquid. Yield: 19.2 g (85%). IR (NaCl, cm$^{-1}$): 3040−2830, 1646, 1501, 1488, 1429, 1407, 1384, 1295, 1197, 1151, 1122, 1080, 968, 930, 668, 660, 582. $^1$H NMR (CDCl$_3$, 7.27 ppm): δ 1.42 (m, 1H, −CHH-CH$_2$CH═CH−), 1.80−1.99 (m, 2H, −OCH$_2$CH⟨ and −CHH-CH$_2$CH═CHCH$_2$−), 2.06−2.28 (m, 4H, −CH$_2$CH═CHCH$_2$−), and −CHCHHCH═CH−), 4.10 (d, 2H, *J* = 4.5 Hz, −OCH$_2$−), 5.62 (d, *J* = 12.0 Hz, 1H, *cis* CHH═CHAr), 5.69 (s, 2H, −CH$_2$-CH═CHCH$_2$−), 6.02 (d, *J* = 18.0 Hz, 1H, *trans* CHH═CHAr), 6.62 (dd, *J* = 12.0 and 18.0 Hz, 1H, CH$_2$═CHAr). $^{13}$C NMR (CDCl$_3$, 77.2 ppm): δ 24.7, 25.3, 28.2, 34.8, 79.9, 110.8, 122.1, 125.7, 127.3, 137.2, 140.1, 143.3, 143.8, 147.3. $^{19}$F NMR (CDCl$_3$): δ −159.7 (m, 2*F*, *meta*-F), −145.7 ppm (m, 2F, *ortho-F*). MS (ESI, M$^{\cdot+}$): [C$_{15}$H$_{14}$OF$_4$ + H$^+$], calcd: 287.1054; found: 287.1035.

**General Procedure for the Preparation of CHE-Functionalized Polymers by RAFT Homopolymerizations.** A 10 mL Schlenk flask equipped with a stir bar was charged with **1** (for synthesis of polymer **3**) or **2** (for synthesis of polymer **4**), DDMAT, AIBN, and 2-butanone or 1,4-dioxane (as the solvents) and then

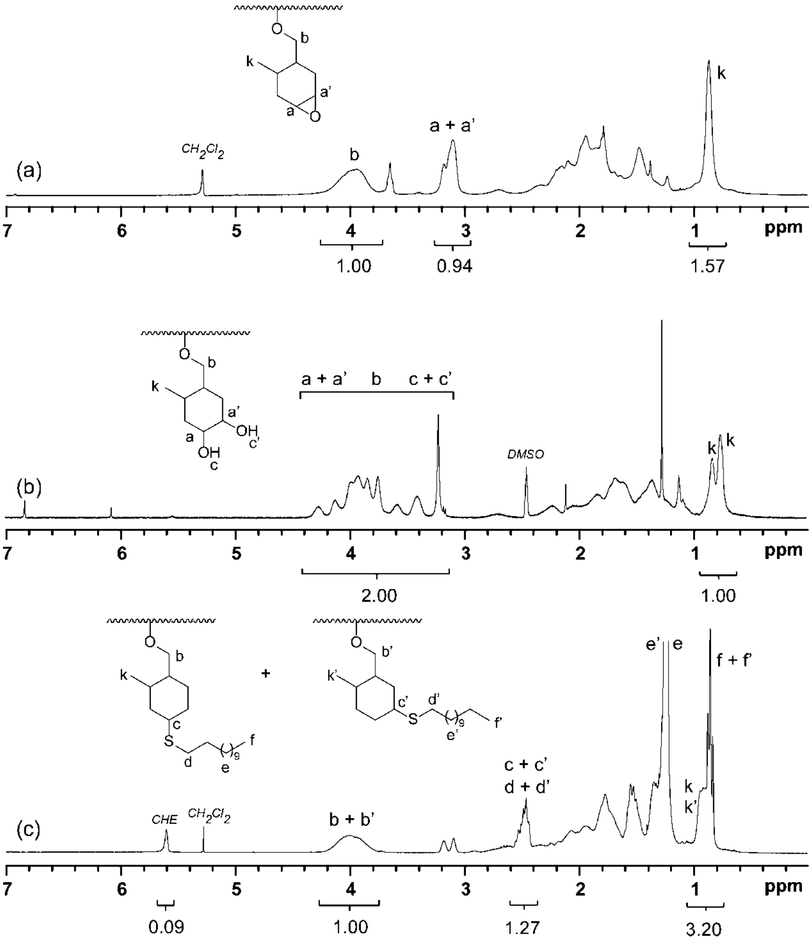


**Figure 6.** $^1H$ NMR spectra (300 MHz) of products resulting from functional group chemical transformation of CHE-functionalized polymer **3b**: (a) the epoxidation product (polymer **7**); (b) osmylation product (polymer **8**), and (c) thiol−ene reaction product (polymer **9**).

sealed with a rubber septum. After five cycles of freeze−pump−thaw, the flask was placed into an oil bath at 69 °C to allow for polymerization. During polymerization, small aliquots (~0.1 mL) of the polymerization solution were withdrawn with a $N_2$-washed syringe and were analyzed by $^1H$ NMR spectroscopy and GPC for the determination of conversions of monomer and the molecular weights of the polymers formed. After the reaction time of 12−16 h, the reaction mixture was allowed to cool to room temperature, diluted with THF, and precipitated into a large amount of methanol. The polymer was recovered by filtration and was dried in vacuo.

**Synthesis of Poly(1), 3a.** Sample **3a** was prepared from the polymerization mixture of **1** (3.01 g, 10.0 mmol), DDMAT (72.8 mg, $2.00 \times 10^{-2}$ mmol), AIBN (3.2 mg, $2.0 \times 10^{-3}$ mmol), and 1.50 mL of 2-butanone as the cosolvent at 69 °C. At 2, 4, 7, 10, and 12 h, the conversions of the monomer were measured to be 19, 36, 52, 75, and 82%, respectively. Finally, the polymerization was quenched after 12 h, and the isolated yield was 2.02 g (82%, based on the final 82% conversion of monomer). IR (KBr, $cm^{-1}$): 3050−2820, 1649, 1493, 1459, 1438, 1384, 1262, 1221, 1147, 1091, 1014, 960, 860, 668. $^1H$ NMR ($CDCl_3$, 7.27 ppm): $\delta$ 0.75−1.10 (br, $-CH_3$ on pendent cyclohexene groups), 1.20−2.90 (br, alkyl protons of the RAFT agent, aliphatic protons of the pendent CHE group, and protons of the polymer backbone), 3.30 (br, $-SCH_2-$ of RAFT agent), 4.09 (br, $-OCH_2-$), 5.65 (br, $-CH{=}CH-$). $^{13}C$ NMR ($CDCl_3$, 77.2 ppm): $\delta$ 14.7, 19.3, 25.3, 27.8, 29.5, 32.5, 33.4, 37.6, 40.3, 76.8, 113.2, 124.9, 125.9, 137.2−143.2, 147.1. $^{19}F$ NMR ($CDCl_3$): $\delta$ −158.6 (m, 2F, *meta-F*), −146.0 to −142.9 ppm (m, 2F, *ortho-F*). $M_n^{calc} = 12.7$ kDa, $M_n^{NMR} = 13.6$ kDa, $M_n^{GPC} = 14.0$ kDa, PDI = 1.15. TGA in $N_2$: 25−335 °C, 3% mass loss; 335−495 °C, 60% mass loss; 495−550 °C, 4% mass loss.

**Synthesis of Poly(1), 3b.** Sample **3b** was prepared from the polymerization mixture of **1** (3.02 g, 10.1 mmol), DDMAT (36.7 mg, $1.01 \times 10^{-2}$ mmol), AIBN (1.6 mg, $1.0 \times 10^{-3}$ mmol), and 1.50 mL of 2-butanone as the cosolvent at 69 °C. At 4, 6, 9, 12, and 16 h, the conversions of the monomer were measured to be 32, 48, 62, 73, and 82%, respectively. Finally, the polymerization was quenched after 16 h, and the isolated yield was 1.80 g (73%, based on the final 82% conversion of monomer). $M_n^{calc} = 25.9$ kDa, $M_n^{NMR} = 26.6$ kDa, $M_n^{GPC} = 22.8$ kDa, PDI = 1.15. TGA in $N_2$: 25−375 °C, 3% mass loss; 355−475 °C, 40% mass loss; 475−550 °C, 4% mass loss.

**Synthesis of Poly(2), 4.** Sample **4** was prepared from the polymerization mixture of **2** (1.45 g, 5.06 mmol), DDMAT (36.9 mg, $1.01 \times 10^{-2}$ mmol), AIBN (1.7 mg, $1.0 \times 10^{-3}$ mmol), and 0.70 mL of 1,4-dioxane as the solvent 69 °C. At 1, 5, 8, and 12 h of the polymerization, the conversions of monomer were measured to be 3, 39, 64, and 84%, respectively. Finally, the polymerization was quenched after 12 h, and the isolated yield of **4** was 1.18 g (94%, based on the final 84% conversion of monomer). $M_n^{calc} = 12.4$ kDa, $M_n^{NMR} = 13.2$ kDa, $M_n^{GPC} = 11.1$ kDa, PDI = 1.09. IR (KBr, $cm^{-1}$): 3050−2820, 1702, 1650, 1561, 1493, 1460, 1438, 1392, 1369, 1266, 1216, 1193, 1146, 1119, 1094, 961, 870, 739, 655. $^1H$ NMR ($CDCl_3$, 7.27 ppm), $\delta$ 0.88 (br, $-CH_3$ of RAFT agent), 1.25 (br, alkyl protons of RAFT agent), 1.30−2.82 (br, alkyl protons of the pendent CHE groups and protons of the polymer backbone), 3.31 (br, $-SCH_2-$ of RAFT agent), 3.99 (br, $-OCH_2-$), 5.69 (br, $-CH{=}CH-$). $^{13}C$ NMR ($CDCl_3$, 77.2 ppm): $\delta$ 25.5, 29.8, 34.4, 39.0−42.0, 76.4, 117.6, 125.9, 127.5, 128.2, 133.8, 139.4−143.3, 146.6. $^{19}F$ NMR ($CDCl_3$): $\delta$ −158.9 (m, 2F, *meta-F*), −145.7 to −142.5 ppm (m, 2F, *ortho-F*). TGA in $N_2$: 25−345 °C, 3% mass loss; 355−480 °C, 64% mass loss; 480−550 °C, 4% mass loss.

**Synthesis of Poly($1_n$-*b*-$St_m$), 5.** A 10 mL Schlenk flask fitted with a stir bar was charged with **3a** as macro-CTA (290 mg, 0.0228 mmol), styrene (1.21 g, 11.6 mmol), AIBN (0.66 mg, $4.0 \times 10^{-4}$

mmol), and 1.00 mL of 2-butanone (as the solvent) and was then sealed with a rubber septum. The reaction mixture was degassed by five cycles of freeze−pump−thaw and then heated with an oil bath at 70 °C. The polymerization was quenched after 3 h when the conversion of styrene reached 14% as measured by $^1$H NMR spectroscopy. The reaction mixture was allowed to cool to room temperature and was then diluted with THF. The polymer solution was precipitated into 100 mL of methanol and dried in vacuo to yield **5** as a pale yellow powder. Yield: 320 mg (70%, based on the final 14% conversion of styrene). $M_n^{calc}$ = 20.1 kDa, $M_n^{NMR}$ = 22.9 kDa, $M_n^{GPC}$ = 21.8 kDa, PDI = 1.21. IR (KBr, cm$^{-1}$): 3100−2800, 1686, 1649, 1601, 1561, 1546, 1493, 1453, 1391, 1368, 1193, 1144, 1072, 1029, 961, 868, 757, 698, 670, 656, 541. $^1$H NMR (CDCl$_3$, 7.27 ppm): $\delta$ 0.92−1.02 (br, −C*H*$_3$ on pendent CHE groups), 1.26 (br, alkyl protons of RAFT agent), 1.30−2.90 (br, alkyl protons on the CHE group and protons of the polymer backbone), 3.30 (br, −SC*H*$_2$− of RAFT agent), 4.05 (br, −OC*H*$_2$−), 5.65 (br, −C*H*═C*H*−), 6.20−7.20 (br, aromatic protons). $^{13}$C NMR (CDCl$_3$, 77.2 ppm): $\delta$ 14.6, 19.9, 26.0, 27.2, 27.9, 29.6, 32.4, 34.3, 37.7, 40.8, 42.2−45.6, 68.0, 77.5, 113.6, 117.2, 124.9, 125.9, 129.4, 133.5, 139.4−143.7, 146.7. $^{19}$F NMR (CDCl$_3$): $\delta$ −158.1 (m, 2F, *meta-F*), −145.2 to −141.8 ppm (m, 2F, *ortho-F*). TGA in N$_2$: 25−300 °C, 3% mass loss; 300−340 °C, 11% mass loss; 340−445 °C, 70% mass loss; 445−550 °C, 2% mass loss.

**Synthesis of Poly(St-*alt*-MAn)$_n$-*b*-poly(2)$_m$, 6.** A 10 mL Schlenk flask fitted with a stir bar was charged with poly(St-*alt*-MAn)$_n$ macro-CTA (501 mg, 0.0619 mmol), **2** (1.81 g, 6.33 mmol), AIBN (1.0 mg, 6.0 × 10$^{-3}$ mmol), and 2.0 mL of 2-butanone (as the solvent) and was then sealed with a rubber septum. The reaction mixture was degassed by three cycles of freeze−pump−thaw and then heated with an oil bath at 58 °C. The polymerization was quenched after 16 h when the conversion of **2** reached 52% measured by $^1$H NMR spectroscopy. The reaction was quenched by being allowed to cool to room temperature and then opening the flask to air. The polymer solution was precipitated into 200 mL of pentane and dried in vacuo to yield **6** as a pale yellow powder. Yield: 1.06 g (74%, based on the final 52% conversion of **2**). $M_n^{calc}$ = 23.4 kDa, $M_n^{NMR}$ = 22.2 kDa, $M_n^{GPC}$ = 16.6 kDa, PDI = 1.25. IR (KBr, cm$^{-1}$): 3050−2800, 1858, 1782, 1711, 1650, 1604, 1584, 1562, 1493, 1456, 1439, 1414, 1392, 1368, 1222, 1147, 1092, 960, 871, 763, 703, 655. $^1$H NMR (acetone-*d*$_6$, 2.05 ppm): $\delta$ 0.86 (br, −C*H*$_3$ of RAFT agent), 1.26 (br, alkyl protons of the RAFT agent), 1.30−2.82 (br, aliphatic protons of the pendent CHE group and protons of the polymer backbone), 2.82−3.85 (br, backbone protons of maleic anhydride units), 4.00 (br, −OC*H*$_2$−), 5.65 (br, −C*H*═C*H*−), 6.00−7.40 (br, aromatic protons). $^{13}$C NMR (acetone-*d*$_6$, 29.5 ppm) $\delta$ 27.5, 29.6, 30.2−33.6, 39.1−41.5, 43.1−48.2, 75.8, 113.5, 118.1, 124.3, 137.9−145.0, 147.2, 171.4−175.0. $^{19}$F NMR: $\delta$ −159.1 (br, 2F, *meta-F*), −145.0 to −141.9 (br, 2F, *ortho-F*). TGA in N$_2$: 25−300 °C, 11% mass loss; 300−460 °C, 59% mass loss; 460−550 °C, 4% mass loss.

**Synthesis of 7.** In a 25 mL round-bottom flask, polymer **3b** (150 mg, 0.492 mmol of CHE units) was dissolved in 12 mL of CHCl$_3$, and the solution was stirred for 1 h at room temperature. *m*-Chloroperbenzoic acid (*m*-CPBA, 182 mg, 0.738 mmol) was added into the polymer solution in one portion at 0 °C. The reaction was allowed to stir at 0 °C for 4 h under N$_2$. The solution was then concentrated to ∼3 mL and precipitated into 30 mL of cold hexane. The solid was collected by centrifuge and redissolved in 3 mL of THF and precipitated again into 30 mL of hexane. The solid was collected and dried in vacuo to yield the final product **7** as a white solid. Yield: 98 mg (62%). IR (KBr, cm$^{-1}$): 3100−2800, 1718, 1650, 1598, 1492, 1402, 1358, 1262, 1146, 1085, 958, 864, 809, 755, 678. $^1$H NMR (CD$_2$Cl$_2$, 5.33 ppm): $\delta$ 0.91 (br, −C*H*$_3$ of pendent cyclohexane group), 1.20−2.90 (br, polymer backbone protons and protons on the cyclohexane group, except the epoxide protons), 3.14−3.20 (br, epoxide protons), 3.97 (br, −OC*H*$_2$−). $^{19}$F NMR (CD$_2$Cl$_2$): $\delta$ −156.4 (m, 2F, *meta-F*), −146.7 to −141.0 ppm (m, 2F, *ortho-F*).

**Synthesis of 8.** Polymer **3b** (100 mg, 0.328 mmol of CHE units) was dissolved in mixed solvents of THF (16 mL, 78 vol %), acetone (2.0 mL, 10 vol %), H$_2$O (2.0 mL, 10 vol %), and *tert*-butyl alcohol (0.40 mL, 2 vol %), and the solution was stirred for 1 h at RT. Then, 0.20 mL (0.8 mg, 3 × 10$^{-3}$ mmol) of KOsO$_4$ solution (4.0 wt %) and 77.0 mg of *N*-methylmorpholine-*N*-oxide (NMO, 0.656 mmol) were added. The reaction was allowed to stir at RT for 20 h under N$_2$. An excess amount of sodium sulfite (Na$_2$SO$_3$) was then added into the reaction flask to reduce OsO$_4$, and the byproduct was removed as a precipitate. The solution was concentrated and was diluted by 5 mL of ethanol. The polymer solution was allowed to dialyze against DI water (MWCO = 3500 Da) for 3 days. Water was evaporated, and the final product was dried in vacuo to yield **8** as a white solid. Yield: 55 mg (49%). IR (KBr, cm$^{-1}$): 3700−3100, 3050−2850, 1651, 1497, 1388, 1259, 1145, 1085, 1019, 963, 868, 811, 749, 663, 553. $^1$H NMR (DMSO-*d*$_6$, 2.50 ppm) $\delta$ 0.80−0.95 (br, −C*H*$_3$ of pendent cyclohexane group), 1.15−3.02 (br, protons of the polymer backbone, protons on the cyclohexane group, except for the ⟩C*H*O*H* protons), 3.26−4.15 (br, m, ⟩C*H*O*H* and −OC*H*$_2$−). $^{19}$F NMR (DMSO-*d*$_6$): $\delta$ −158.5 (m, 2F, *meta-F*), −147.3 to −143.8, ppm (m, 2F, *ortho-F*).

**Synthesis of 9.** Polymer **3b** (89 mg, 0.30 mmol of CHE units), 2,2′-dimethoxy-2-phenylacetophenone (DMPA, 1.5 mg, 0.0060 mmol), C$_{12}$H$_{25}$SH (123 mg, 0.610 mmol), and 100 $\mu$L of THF were loaded into a 3 mL vial and sealed with a cap. The vial was shaken for 10 min to thoroughly mix the contents and then irradiated without stirring for 30 min using an F300S UV system at room temperature. The contents were subsequently dissolved in a small amount of THF and precipitated three times into methanol. The final product as a white wax was dried in vacuo. The conversion of the cyclohexene group was measured to be 85% by $^1$H NMR spectroscopy. Yield: 97 mg (68%). IR (NaCl, cm$^{-1}$): 3100−2850, 1687, 1491, 1458, 1451, 1393, 1367, 1273, 1158, 1151, 1036, 847, 753, 667. $^1$H NMR (CD$_2$Cl$_2$, 5.33 ppm) $\delta$ 0.78−1.00 (br, −C*H*$_3$ on the 6-membered rings and −C*H*$_3$ group of the dodecyl units), 1.15−1.41 (br, aliphatic protons of the dodecyl units), 1.41−2.40 (br, protons of the polymer backbone and the 6-membered rings, except for the ⟩C*H*SC*H*$_2$− protons and the remaining alkenyl protons), 2.44 (br, ⟩C*H*SC*H*$_2$−), 3.93 (br, −OC*H*$_2$−), 5.67 (s, remaining −C*H*═C*H*−). $^{19}$F NMR (CD$_2$Cl$_2$): $\delta$ −158.8 (m, 2F, *meta-F*), −146.8−142.2, ppm (m, 2F, *ortho-F*).

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