Light-Mediated Atom Transfer Radical Polymerization of Semi-Fluorinated (Meth)acrylates: Facile Access to Functional Materials

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S *Supporting Information*

ABSTRACT: A highly efficient photomediated atom transfer radical polymerization protocol is reported for semi-fluorinated acrylates and methacrylates. Use of the commercially available solvent, 2-trifluoromethyl-2-propanol, optimally balances monomer, polymer, and catalyst solubility while eliminating transesterification as a detrimental side reaction. In the presence of UV irradiation and ppm concentrations of copper(II) bromide and Me₆-TREN (TREN = tris(2-aminoethyl amine)), semi-fluorinated monomers with side chains containing between three and 21 fluorine atoms readily polymerize under controlled conditions. The resulting polymers exhibit narrow molar mass distributions ($Đ \approx 1.1$) and high end group fidelity, even at conversions greater than 95%. This level of control permits the *in situ* generation of chain-end functional homopolymers and diblock copolymers, providing facile access to semi-fluorinated macromolecules using a single methodology with unprecedented monomer scope. The results disclosed herein should create opportunities across a variety of fields that exploit fluorine-containing polymers for tailored bulk, interfacial, and solution properties.
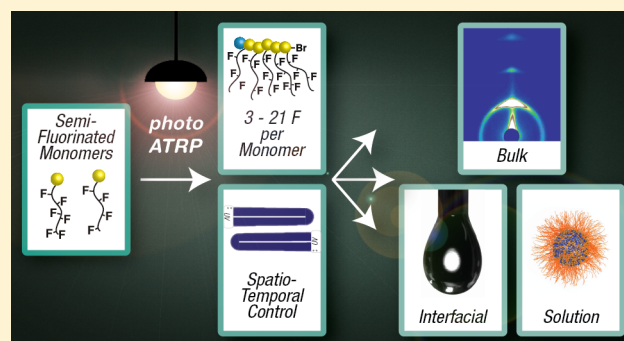
INTRODUCTION

Light-mediated controlled radical polymerization has emerged as a powerful strategy in polymer chemistry, enabling spatial and temporal control over reaction kinetics, macromolecular sequence, composition, and connectivity[1−15] via external regulation of the equilibrium governing active and dormant species. For example, with photoinduced atom transfer radical polymerization (ATRP), light-promoted reduction of the Cu(II) deactivator complex to Cu(I) by nitrogen-containing ligands leads to the transient generation of active catalyst. Although these and other proof-of-principle methodologies integrating light have recently been discovered (e.g., reversible addition chain transfer (RAFT) and metal-free ATRP), most reports to date utilize traditional, non-functional monomers (e.g., simple styrene and (meth)acrylate derivatives). Extrapolation of existing synthetic conditions to more complicated monomer families introduces new challenges, including starting material incompatibility and reactivity differences. More robust strategies are thus required to evolve light-mediated polymerizations into an enabling platform applicable to the widest selection of monomers.

Fluorinated and semi-fluorinated polymers exemplify useful macromolecular systems with limited accessibility via contemporary controlled polymerization processes. Broad interest in these materials arises due to unique properties including high hydrophobicity and tunable lipophilic character.[16−18] For instance, the mutual immiscibility of hydrocarbons, polar media, and many fluorinated molecules accentuates the unusual intermolecular interactions characteristic of C−F bonds.[19,20] In addition, fluorinated materials often exhibit anomalously low refractive indices (ca. 1.3) and high thermal, chemical, and electrochemical stability relative to hydrogenous analogues. These beneficial attributes are widely leveraged in conjunction with the intrinsically low surface energy[21,22] imparted by fluorine
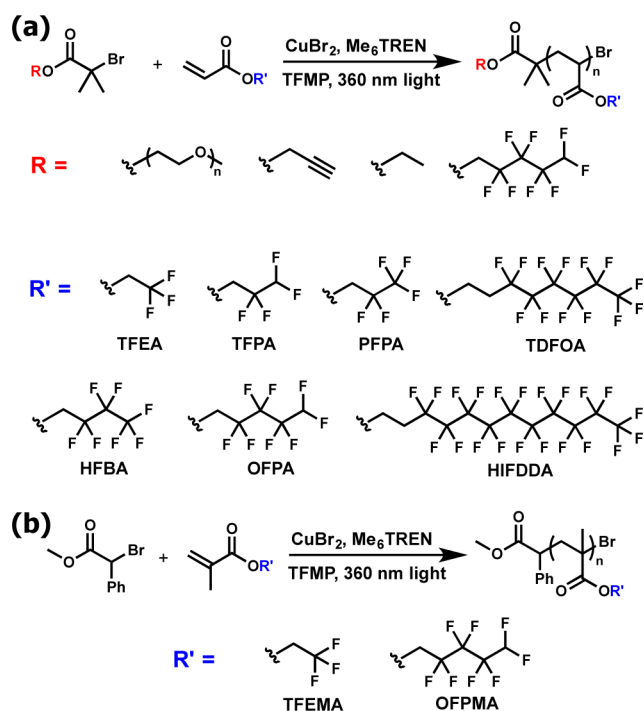
Figure 1. Semi-fluorinated (a) poly(acrylates) and (b) poly(methacrylates) controllably polymerized herein.

Figure 2. Influence of solvent on monomer stability under ATRP conditions. ^{1}H NMR spectra demonstrating (a) transesterification between a fluorinated monomer and 2,2,2-trifluoroethanol (primary alcohol) in the presence of Me_6-TREN, and (b) lack of transesterification with 2-trifluoromethyl-2-propanol (tertiary alcohol) in the presence of Me_6-TREN.

to drive segregation of specific moieties to low dielectric interfaces (e.g., air or vacuum). Semi-fluorinated polymers are therefore attractive materials for a variety of bulk, interfacial, and solution applications spanning optics,[19] self-assembly,[23] membranes, lubricants, coatings,[24] surfactants, lithography, magnetic resonance imaging,[25] and drug delivery.[19,26]

Given these favorable properties and real-world applications, the development of synthetic techniques for the preparation of well-defined fluorine-containing polymers is of significant interest. Two generic strategies are typically employed: (1) postpolymerization functionalization of non-fluorinated polymers[19,27−29] and (2) polymerization of fluorinated monomers.[30,31] While the former route is in principle compatible with many polymer backbones, the strategy requires reactive pendant functionality and efficient coupling chemistry. Additionally, all starting materials and intermediate products must remain soluble in the reaction mixture. These requirements increase overall synthetic complexity, often with diminishing control over final product composition. In contrast, the polymerization of fluorinated monomers circumvents these limitations by directly producing the desired fluorinated materials but typically requires modified polymerization procedures with inherent limitations that minimize the breadth of accessible products.[32]

A number of reports have detailed the synthesis of semi-fluorinated methacrylates via living anionic polymerization,[32−35] a technique that is both synthetically difficult and limited in monomer scope/sequence. Operationally simpler and less-restrictive alternatives have also been investigated,[30] primarily RAFT,[36,37] nitroxide-mediated polymerization,[38] and ATRP.[39,40] Classical ATRP procedures for the preparation of semi-fluorinated polymers (i.e., non-light-mediated mechanisms) include pioneering work by DeSimone and co-workers, who polymerized semi-fluorinated macromolecules using fluorinated ligands in supercritical CO_2 as the solvent.[41−44] Hvilsted and Haddleton also utilized ATRP to homopolymerize semi-fluorinated methacrylates
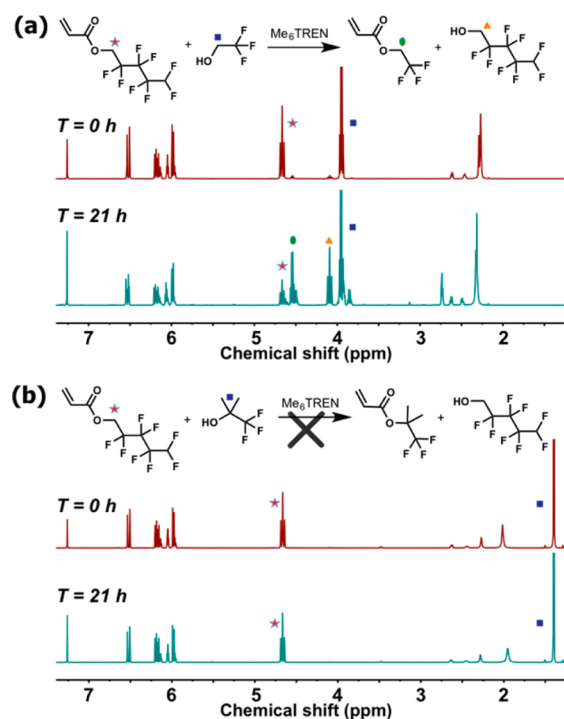
in toluene, although a number of monomers underwent phase separation leading to uncontrolled molar mass dispersities (Đ).[45,46] These examples illustrate the promise of well-defined fluorinated materials, yet also highlight many remaining synthetic obstacles including poor solubility, compromised Đ at high conversions, the need for complex fluorinated ligands, and the prevalence of undesired side reactions (e.g., transesterification).[32,47] As a result, the controlled synthesis of semi-fluorinated homopolymers and block copolymers remains a significant challenge.

Herein we describe a versatile light-mediated ATRP protocol that enables facile access to a wide array of well-defined, semi-fluorinated polymers. The judicious selection of commercially available 2-trifluoromethyl-2-propanol (TFMP) as the solvent is a key discovery, which simultaneously solubilizes all reagents (monomer, catalyst, and ligand) while preventing phase separation and deleterious transesterification side-reactions. Importantly, this platform cleanly polymerizes a wide range of semi-fluorinated (meth)acrylates to near quantitative conversions (Figure 1) and is also compatible with non-fluorinated acrylic monomers. The resulting polymers exhibit low Đ and high end-group fidelity as characterized by size exclusion chromatography (SEC), matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-ToF-MS), ^{1}H NMR, and quantitative in situ chain extension. Semi-fluorinated homopolymers and block copolymers synthesized via this technique exhibit material properties directly related to the level of fluorine incorporation. Unparalleled control over the polymerization of semi-fluorinated monomers using a single protocol should create new possibilities for synthesizing functional materials.

RESULTS AND DISCUSSION

Inspired by literature reports detailing the use of 2,2,2-trifluoroethanol (TFE) as a solvent for polymerizations,[47−49] our initial studies utilized TFE with copper(II) bromide, Me$_6$-TREN, and UV irradiation (360 nm light).[50] Low dispersities at quantitative conversions were obtained for trifluoroethyl acrylate (TFEA), with very high end-group fidelity as evidenced by SEC and MALDI-ToF-MS (Figure S1). However, when monomers containing a longer fluorinated chain, e.g., tridecafluorooctyl acrylate (TDFOA, Figure S2), were polymerized under otherwise identical conditions, MALDI-ToF-MS analysis revealed multiple molar mass distributions. Considering the presence of base in solution, we confirmed that transesterification of the side-chain ester group was occurring. These pernicious side-reactions thus compromise the integrity of most semi-fluorinated monomer polymerizations, yielding statistically random copolymers instead of the desired homopolymers. Recognizing that transesterification is only problematic when the alcohol solvent is chemically distinct from the corresponding ester moiety, simply
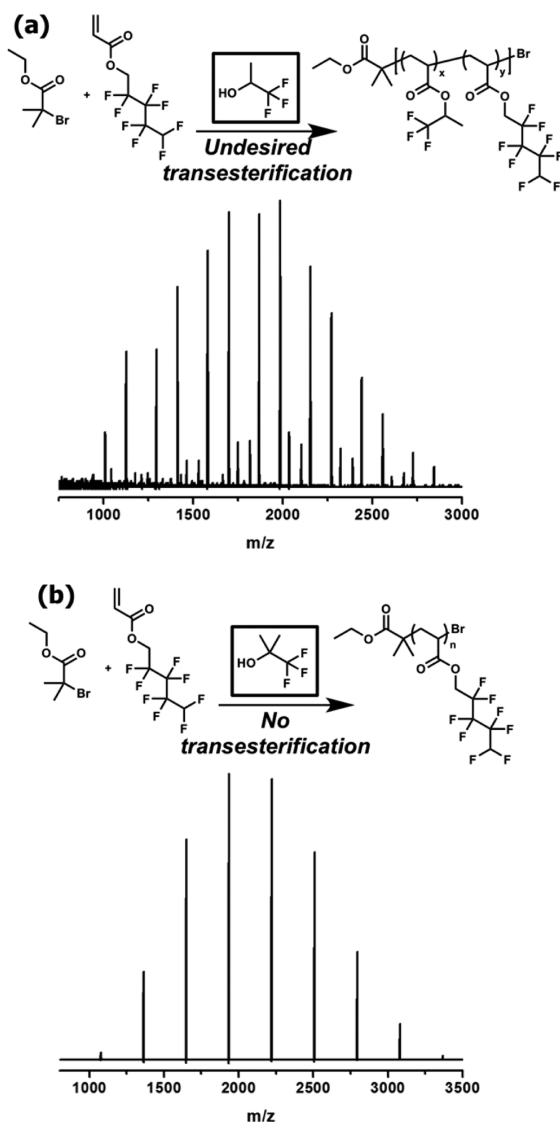

Figure 3. Polymerization of octafluoropentyl acrylate (OFPA) using (a) TRFP solvent results in undesired transesterification and multiple molar mass distributions, and (b) TFMP solvent generates a single distribution corresponding to the expected chain-ends.
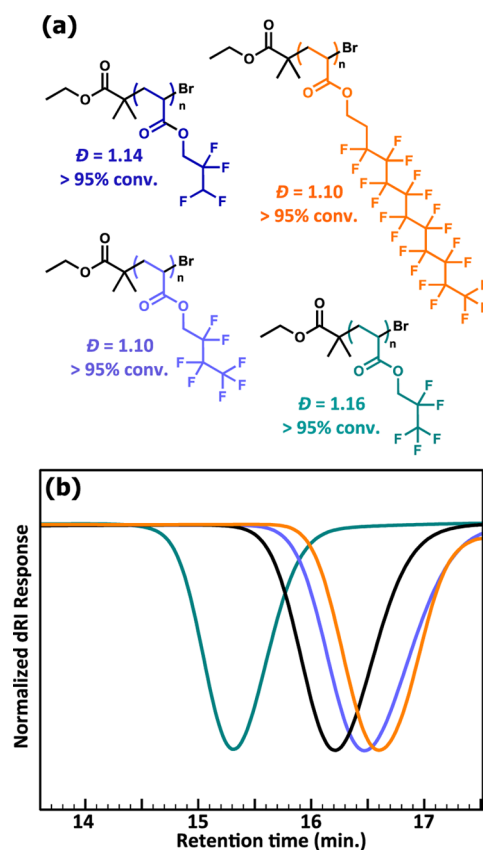

Figure 4. (a) Examples of high conversions and low dispersities for various semi-fluorinated homopolymers obtained using optimized reaction conditions. (b) Corresponding normalized SEC differential refractive index traces.

using identical functionality should render transesterification inconsequential. For instance, control experiments indicate the polymerization of tetrafluoropropyl acrylate (TFPA) in 2,2,3,3-tetrafluoro-1-propanol (TFP) results in one set of molecular ions as characterized by MALDI-ToF-MS with no additional peaks appearing by ^{1}H NMR (Figure S3). Although insightful for the manipulation of reaction conditions, use of a different fluorinated alcohol for every distinct semi-fluorinated monomer is impractical and especially ineffective for synthesizing diblock copolymers composed of two different semi-fluorinated blocks. In order to address this limitation, we sought to find an alternative, more versatile solvent that would retain the delicate balance necessary to solvate Cu catalyst, monomer, and polymer while preventing *in situ* monomer transesterification. Octafluoropentyl acrylate (OFPA) was selected as a model system to screen the extent of transesterification in a range of primary, secondary, and tertiary alcohol solvents including TFE, TFP, TFMP, and 1,1,1-trifluoro-2-propanol (TRFP). The primary alcohols TFE and TFP induce significant monomer transesterification in the presence of Me$_6$TREN (Figures 2a and S4). Methacrylate analogues are unfortunately also prone to transesterification (Figure S4). Polymerization of OFPA in primary and secondary alcohol solvents accordingly generated multiple polymer molar mass distributions attributed to varying degrees of solvent transesterification (Figure 3a).

In contrast, use of the tertiary alcohol solvent TFMP resulted in no monomer (Figure 2b) or polymer (Figure 3b) transesterification, even after prolonged reaction/polymerization times (21 h). To demonstrate the utility of TFMP for controlled

polymerization of additional semi-fluorinated monomers, we investigated homopolymerizations of TFPA, pentafluoropropyl acrylate (PFPA), heptafluorobutyl acrylate (HFBA), TDFOA, and heneicosafluorododecyl acrylate (HIFDDA). Initially, low molar mass polymers were targeted (to permit facile characterization) by subjecting monomers to the same polymerization conditions as described above (irradiation with 360 nm light in TFMP). The resulting homopolymers were characterized by SEC equipped with a differential refractive index detector using chloroform as an eluent (Figure 4b), MALDI-ToF-MS (Figures 5 and S5), differential scanning calorimetry (DSC) and ^{1}H and ^{19}F NMR (Figures S6–S8). Each reaction resulted in near quantitative conversion (>95%), low dispersity, and well-defined molar mass, indicating well-controlled polymerizations. The negative dRI signals observed by SEC are characteristic of fluorinated polymers with a smaller refractive index than the eluent ($n_{polymer} < n_{chloroform} = 1.4459$). MALDI-ToF-MS also clearly demonstrates excellent molar mass dispersity and chain-end fidelity for each polymer. For example, the polymerization of TFPA leads to peaks separated by 186 m/z, corresponding to a single monomer unit, and absolute m/z values match the expected initiator and bromine chain-ends (Figure 5a). High end group fidelity was also observed in the synthesis of PTDFOA, a highly fluorinated derivative containing 13 fluorine atoms (~60 wt %) per repeat unit (Figure 5b). The molar masses presented in Table 1 were calculated relative to polystyrene standards. Nevertheless, measured molar masses correlate with the nominal values predicted from polymerization feed equivalents (c.f., 4 vs 5, 6 vs 7, and 8 vs 9). Note that we believe even larger molar masses may be possible, but solubility issues preclude definitive and exhaustive analysis via typical characterization techniques (Figure S9). Purified polymers are reasonably stable in bulk and solution, e.g., PFPA homopolymer is unreactive toward excess primary amine (Figure S10) and primary alcohols without added base (Figure S5).

Table 1. Characterization of Fluorinated Homopolymers (see SI for Experimental Details)

entry	polymer	N^c	conversion (%)	M_n (g/mol) theor	M_n (g/mol) exp^d	$Đ^e$
1^a	PTFPA	100	93	17300	17900	1.06
2	PTFEA	100	>95	18600	20500	1.04
3^b	PTFPA	80	>95	14300	15000	1.08
4	PPFPA	8	>95	1600	1700	1.16
5	PPFPA	60	>95	11800	9400	1.07
6	PHFBA	8	>95	2000	2300	1.14
7	PHFBA	50	90	11400	11300	1.10
8	POFPA	6	>95	1700	1600	1.17
9^b	POFPA	40	91	10400	10600	1.07
10	PTDFOA	4	>95	1700	2000	1.24
11^b	PHIFDDA	4	>95	2500	1500^f	1.10

^{a}Synthesized using TFP as solvent. ^{b}Contains DMSO (10% v/v). ^{c}N values are nominal based on polymerization feed ratios. ^{d}$M_{n,exp}$ determined using ^{1}H NMR unless otherwise noted. ^{e}Đ determined by SEC. ^{f}$M_{n,exp}$ determined by SEC.

Encouraged by the retention of bromo chain-ends at near quantitative conversions, we prepared various semi-fluorinated diblock copolymers by sequential monomer addition and *in situ* chain extension. Initial studies involved the confirmation of controlled polymerization for non-fluorinated acrylates using the aforementioned conditions optimized with semi-fluorinated systems. The addition of DMSO (10% v/v) as a cosolvent for both hydrophilic and hydrophobic monomers proved to mitigate solubility issues without compromising conversion or polymerization control. This is exemplified by the polymerization of *tert*-butyl acrylate (*t*BA), which resulted in near quantitative conversion and low dispersity (Đ = 1.09). Subsequent *in situ* chain extension with OFPA produced P*t*BA-*b*-POFPA diblock copolymers with SEC characterization revealing the expected
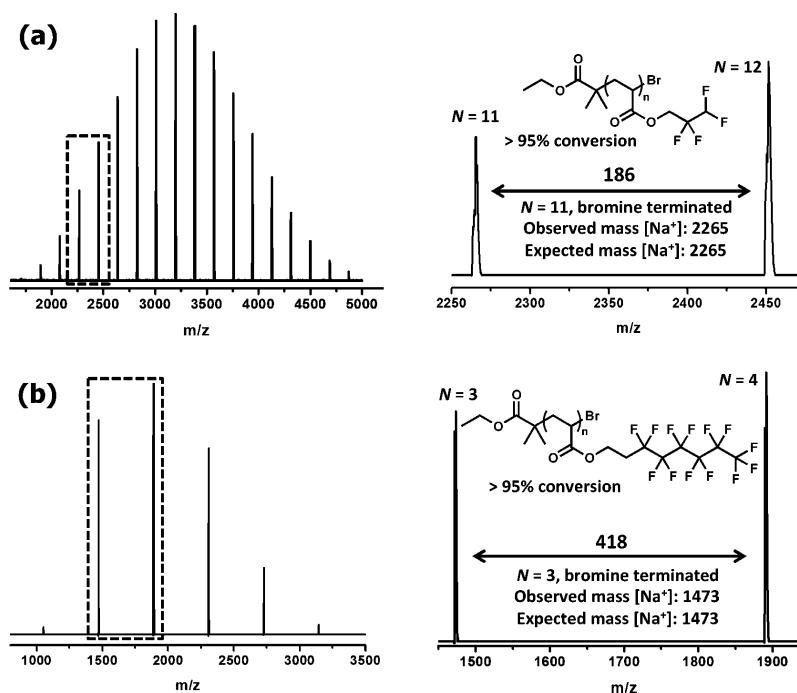

Figure 5. MALDI-ToF-MS analysis indicates a single molar mass distribution corresponding to Br-terminated (a) PTFPA and (b) PTDFOA. Magnified regions confirm the expected monomer spacing.
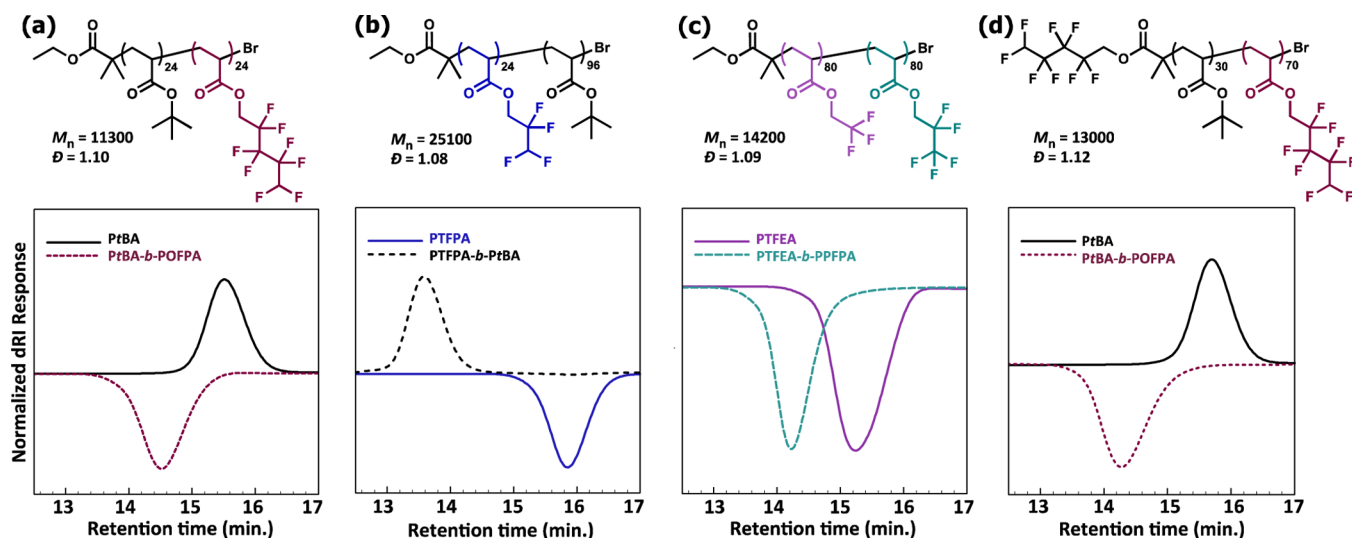
Figure 6. Diblock copolymerization of (a) (non-fluorinated)-*b*-(semi-fluorinated), (b) (semi-fluorinated)-*b*-(non-fluorinated), (c) (semi-fluorinated)-*b*-(semi-fluorinated), and (d) (non-fluorinated)-*b*-(semi-fluorinated) using a semi-fluorinated initiator.
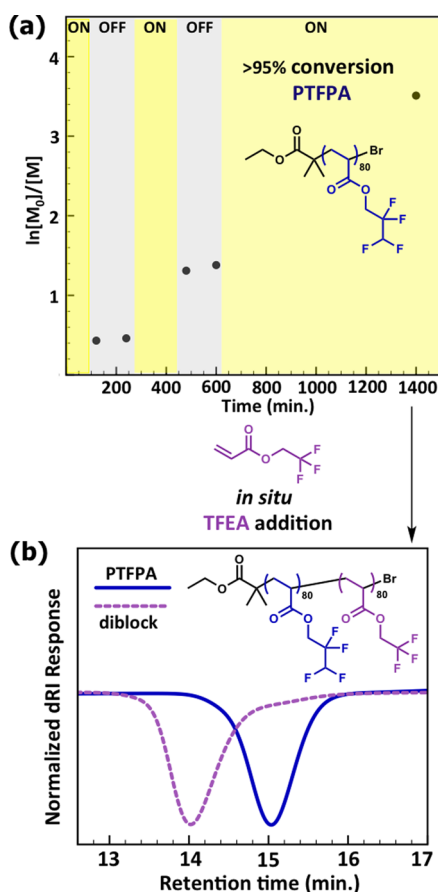

Figure 7. (a) Intermittent exposure (on/off) during TFPA polymerization. After ca. 1400 min (>95% conversion), TFEA monomer was added *in situ* to yield (b) a semi-fluorinated diblock copolymer.
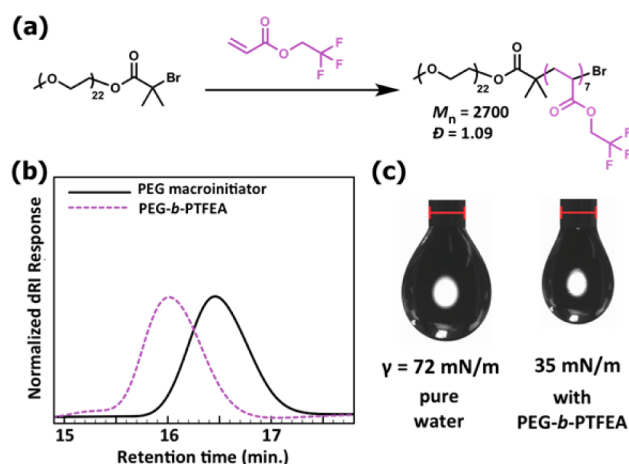

Figure 8. (a) Synthesis of potential fluorinated surfactant with a PEG macroinitiator and (b) corresponding SEC overlay depicting resulting shift. (c) Pendant drop data demonstrating a decrease in the surface tension of water.

(POFPA-*b*-P*t*BA)—^{1}H NMR analysis indicates diagnostic peaks for both blocks and integration confirms the degree of control over macromolecular composition (Figures S11 and S12). Significantly, successful chain extension was also achieved with other semi-fluorinated monomers, yielding higher molar masses and diverse block pairs (Figure 6). For example, the *in situ* synthesis of a diblock copolymer containing two different semi-fluorinated blocks is enabled by the concurrent compatibility of the TFMP solvent with multiple semi-fluorinated monomers.

Temporal modulation of polymerization kinetics was subsequently investigated using intermittent light and dark exposure. Irradiation of TFPA in TFMP for 2 h induced approximately 35% monomer conversion. Upon cessation of light exposure, propagation stalled and this on/off process could be repeated multiple times, ultimately yielding near quantitative conversion (>95%) after sufficient illumination. To demonstrate high chain-end fidelity despite these consecutive on/off cycles, *in situ* chain extension using TFEA was performed to yield well-defined diblock copolymers comprising two semi-fluorinated blocks (Figure 7).

shift to lower retention time and complete inversion of the dRI signal (Figure 6a). This inversion arises from the positive dn/dc of P*t*BA and the aforementioned negative dn/dc of many fluorinated polymers, e.g., POFPA. Invoking a simple weight-averaged mixing rule suggests that $(dn/dc)_{BCP}$ is dominated by POFPA with n_{BCP} smaller than $n_{solvent}$. The flexibility of our conditions also enables access to the reverse diblock sequence

Our synthetic protocol is also fully compatible with well-established functional initiators originally developed for traditional ATRP. These include initiators containing a pendant alkyne (Figure S13), hydrophilic PEG chain (Figures 8a and S14), and semi-fluorinated macroinitiator (Figures 6d and S15). Additionally, switching from ethyl-α-bromoisobutyrate (EBiB) to methyl bromophenyl acetate (MBPA) under otherwise identical conditions successfully controls the polymerization of semi-fluorinated methacrylates, such as TFEMA (Figure S16) and OFPMA (Figure S17). With both monomers, TFMP enables high conversion (>95%) without compromising molar mass dispersity ($Đ \approx 1.15$).

Finally, a series of experiments was performed to showcase the physical properties of semi-fluorinated diblock copolymers. Aqueous solutions containing PEG-*b*-PTFEA (Figure 8c) exhibit a significantly reduced surface tension relative to pure water (elucidated by pendant drop measurements), as expected for interfacial segregation of low surface energy fluorinated moieties. Moreover, the synthetic versatility of this system allows for systematic variation of fluorine content to produce a library of surfactants and multifunctional diblock copolymers. Examples include P*t*BA-*b*-PTFPA (nominally $N_A = N_B = 96$) which when annealed at 150 °C under vacuum for 12 h (Figures 9a and S18)
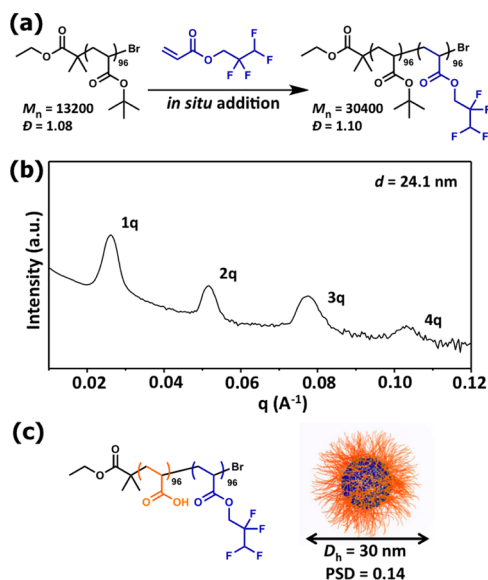

Figure 9. (a) Synthetic scheme for P*t*BA-*b*-PTFPA and (b) corresponding SAXS data confirming microphase separation (lamellae). (c) Deprotection of the P*t*BA block to poly(acrylic acid) and dilution with water induces micellization as characterized by DLS.

reveals small-angle X-ray scattering (SAXS) Bragg reflections consistent with well-ordered lamellae (Figure 9b). Deprotection (Figures S19 and S20) of the same diblock copolymer generates amphiphilic poly(acrylic acid)-*b*-PTFPA that forms micelles in aqueous solution. Dynamic light scattering (DLS) indicates diameters ca. 30 nm (Figures 9c and S21) and a zeta potential of −26 mV. These types of materials (or derivatives thereof) may find utility in a variety of applications that currently leverage or could benefit from block copolymers containing fluorine, for example antifouling coatings,[51−53] surface-active additives for lithography,[54] and high-χ oligomers.[55−58]

CONCLUSIONS

We have developed a versatile protocol for the photomediated ATRP of semi-fluorinated acrylates and methacrylates. Excellent chain-end fidelity is retained at near quantitative conversions with low molar mass dispersity, permitting *in situ* chain extension and the formation of a diverse library of diblock copolymers with no observed sequence constraints. The synthetic advances described herein expand the accessibility of well-defined functional polymers, providing improved access to tailored macromolecules containing prescribed levels of fluorine incorporation at specific molecular locations.

ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b01694.

Experimental procedures for preparation of all compounds and characterization data for all compounds, including Figures S1−S21 (PDF)

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Notes
The authors declare no competing financial interest.

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