

# Mainchain Semifluorinated Polymers with Ultra High Molecular Weight *via* Reaction-enhanced Reactivity of Intermediate (RERI) Mechanism

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 Electronic Supplementary Information

**Abstract** Achieving the linear polymers with high molecular weight *via* step-growth polymerization of  $A_2$  and  $B_2$  monomers is significantly limited by the requirement of strict stoichiometry of two monomers when the reactivity of A and B groups are not changed during the polymerization. Herein, a unique step-growth polymerization based on copper-catalyzed azide-alkyne cycloaddition (CuAAC) with reaction-enhanced reactivity of intermediate (RERI) mechanism was developed for the preparation of mainchain semifluorinated polymers with high molecular weight. The CuAAC polymerization of bis-alkynyl-terminated fluorinated monomers ( $A_2$ ) and 2,2-bis(azidomethyl)propane-1,3-diyl bis(2-methylpropanoate) (BiAz,  $B_2$ ) with RERI effect at different stoichiometric ratio was systematically investigated. The results indicated that the semifluorinated polymers with ultrahigh molecular weight,  $M_{w, MALLS} > 10^6$  g/mol, could be efficiently synthesized by using excess molar of BiAz monomers. The resultant high-molecular-weight semifluorinated polymers show good thermostability and high hydrophobicity. In addition, the glass transition temperature ( $T_g$ ) of these mainchain semifluorinated polymers could be tuned conveniently due to the bis-alkynyl-terminated comonomers could be consumed completely when excessive BiAz monomers were used in this step-growth polymerization.

**Keywords** Semifluorinated polymers; Click polymerization; Step-growth polymerization

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## INTRODUCTION

Fluorinated and semifluorinated polymers have many unique properties, including outstanding thermal and chemical stability, excellent weatherability, and resistance to oxidation as well as low surface energy, low dielectric constant, permittivity, and water absorptivity. These properties give the fluorinated polymers lots of high-end applications spanning from solid polymer electrolytes to biomedical materials.<sup>[1–3]</sup> Meanwhile, the properties of polymeric materials are critically determined by the molecular weight. High-molecular-weight (HMW), especially for ultra-high-molecular-weight (UHMW), can endow polymers outstanding mechanical properties, good thermal stability and advanced application.<sup>[4]</sup> Therefore, the development of synthetic techniques for the preparation of functional fluorinated and (semi)fluorinated polymers with precise structure and (ultra)high molecular weight is of significant interest.<sup>[5–13]</sup> So far, chain-growth polymerization

based on reversible-deactivation radical polymerization (RDRP) of vinyl monomer is among the most popularly used method for the synthesis of UHMW polymers.<sup>[14–18]</sup> For instance, Chen *et al.* reported the precise synthesis of UHMW semifluorinated polymers using a chain transfer agent (CTA) differentiation approach by photo-mediated RDRPs.<sup>[6]</sup> Nevertheless, a fundamental limitation of polymers prepared by radical polymerization strategy is their lack of facile degradability because their backbone is made up of C–C bonds, limiting their utility in a range of applications.

The step-growth polymerization of  $A_2$  and  $B_2$  monomers is the most common strategy for the preparation of various polymer materials, especially for the high-performance polymer materials because they can readily incorporate functionalities along the polymer backbone by using proper monomers. However, to achieve the linear polymer with high molecular weight *via* step-growth polymerization of  $A_2$  and  $B_2$  monomers is significantly limited by the requirement of strictly balanced stoichiometry of  $A_2$  and  $B_2$  monomers when the reactivity of A and B groups are not changed during the polymerization. So far, several step-growth polymerizations have been developed that could achieve high molecular weight under nonstoichiometric conditions, in which one of

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participating monomer has a reaction-enhanced reactivity of intermediate (RERI) effect.<sup>[19–29]</sup> For instance, Zhang *et al.* reported the synthesis of polymers with high molecular weight *via* step-growth polymerization of A<sub>2</sub> and B<sub>2</sub> monomers based on double-strain-promoted azide-alkyne click reaction (DSPAAC) reaction, in which the cyclic sym-dibenzo-1,5-cyclooctadiene-3,7-diyne (DIBOD) monomer showing a RERI effect.<sup>[24,25,28,29]</sup> Although several reactions with RERI effect have been used in the step-growth polymerization to prepare polymers with a high molecular weight, only a few of reports have detailed the synthesis of UHMW polymers *via* step-growth polymerization of A<sub>2</sub> and B<sub>2</sub> monomers under non-stoichiometric conditions.<sup>[24,30,31]</sup> However, the difficulties in scalability of monomers or a harshly catalytic conditions in these polymerizations render general use in functional polymer synthesis challenging. Moreover, the preparation of UHMW semifluorinated polymers through a step-growth polymerization of A<sub>2</sub> and B<sub>2</sub> has not been reported as far as we know.

The copper-catalyzed azide-alkyne cycloaddition (CuAAC) click reaction has been broadly applied in polymer synthesis and post-modification due to the easy preparation of monomers and high efficiency.<sup>[32–42]</sup> The RERI effect of 1,3-diazide compounds, namely 2,2-bis-(azidomethyl)propane-1,3-diol was first identified by Finn and co-worker when they studied the mechanistic of ligand-free CuAAC reactions, in which the reaction of one azido group spontaneously increases the reactivity of the other azido group on the monoreacted intermediate due to the complexation of *in situ* formed triazole and Cu catalyst.<sup>[43,44]</sup> Gao group reported the synthesis of hyperbranched polymers with high degree of branching and molecular bottlebrushes with ultrahigh grafting density based on the derivative of this 1,3-diazide compound.<sup>[45–51]</sup> Both cases confirmed that the derivative of 1, 3-diazide compound has a desirable RERI effect.

Herein, the RERI effect of 1,3-diazide compounds was first applied to develop a step-growth polymerization based on CuAAC click reaction for achieving the efficient synthesis of mainchain semifluorinated polymers with high molecular weight. Firstly, a 1,3-diazide compound derivative (B<sub>2</sub>), namely 2,2-bis-(azidomethyl)propane-1,3-diol bis(2-methylpropanoate) (BiAz) that has a desirable RERI effect and three bis-alkynyl-terminated fluorine-containing monomers (A<sub>2</sub>) were synthesized, as shown in Scheme 1. Then, a series of (ultra)high-molecular-weight semifluorinated polyether and polyester, have been synthesized *via* this step-growth polymerization using a slightly excessive BiAz to bi-alkynyl monomers. In addition, the physical properties of these main-chain semifluorinated polymers were also investigated and tuned.

## EXPERIMENTAL

The materials and instrumentation used in current research, and the detailed synthesis of monomers can be found in the electronic supplementary information (ESI).

### Synthesis of PolyM1, PolyM2 and PolyM3

Typical procedures in the CuAAC polymerization of M1 and BiAz at molar ratio of [M1]<sub>0</sub>: [BiAz]<sub>0</sub>: [CuSO<sub>4</sub>·5H<sub>2</sub>O]<sub>0</sub>: [ascorbic acid]<sub>0</sub>=

0.91:1:0.091:0.46 are as follows. M1 (100.0 mg, 0.3 mmol), BiAz (108.0 mg, 0.33 mmol), CuSO<sub>4</sub>·5H<sub>2</sub>O (7.5 mg, 0.03 mmol) and DMF (3 mL, [M1]<sub>0</sub>=0.1 mol·L<sup>-1</sup>) were charged in a 10 mL Schlenk flask equipped with a magnetic stir bar. The flask was sealed with glass stopper and deoxygenated by three freeze-pump-thaw cycles before ascorbic acid (26.4 mg, 0.15 mmol) was added into the flask. The polymerization was initiated at 45 °C. After polymerization, 2 equiv. of PMDETA ligand was added to exact the Cu catalyst out of the polymer, the polymers in DCM were then passed through a flash alumina column before being precipitated in diethyl ether three times. The final dried product was colorless with a yield around 80%.

The procedures for synthesizing polyM1, polyM2 and polyM3 at varied feed ratios were similar as above.

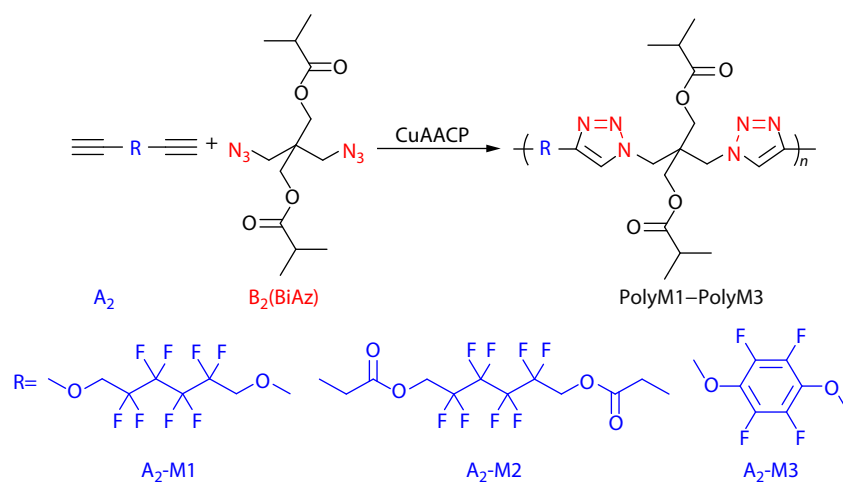
### Synthesis of Poly(M1-co-M3)

Typical procedures in the CuAAC copolymerization of M1 and M3 with BiAz at molar ratio of [M1+M3]<sub>0</sub>: [BiAz]<sub>0</sub>: [CuSO<sub>4</sub>·5H<sub>2</sub>O]<sub>0</sub>: [ascorbic acid]<sub>0</sub>=0.91:1:0.091:0.46 ([M1]<sub>0</sub>: [M3]<sub>0</sub>=8:2) are as follows: M1 (67.6 mg, 0.2 mmol), M3 (12.9 mg, 0.05 mmol), BiAz (89.8 mg, 0.28 mmol), CuSO<sub>4</sub>·5H<sub>2</sub>O (5.8 mg, 0.023 mmol) and DMF (2.5 mL, ([M1]<sub>0</sub>+ [M3]<sub>0</sub>)=0.1 mol·L<sup>-1</sup>) were charged in a 10 mL Schlenk flask equipped with a magnetic stir bar. The flask was sealed with glass stopper and deoxygenated by three freeze-pump-thaw cycles before ascorbic acid (20.0 mg, 0.12 mmol) was added into the flask. The polymerization was initiated at 45 °C. After polymerization, 2 equiv. of PMDETA ligand was added to exact the Cu catalyst out of the polymer, the polymers in DCM were then passed through a flash alumina column before being precipitated in diethyl ether for three times. The final dried product was colorless with a yield around 80%.

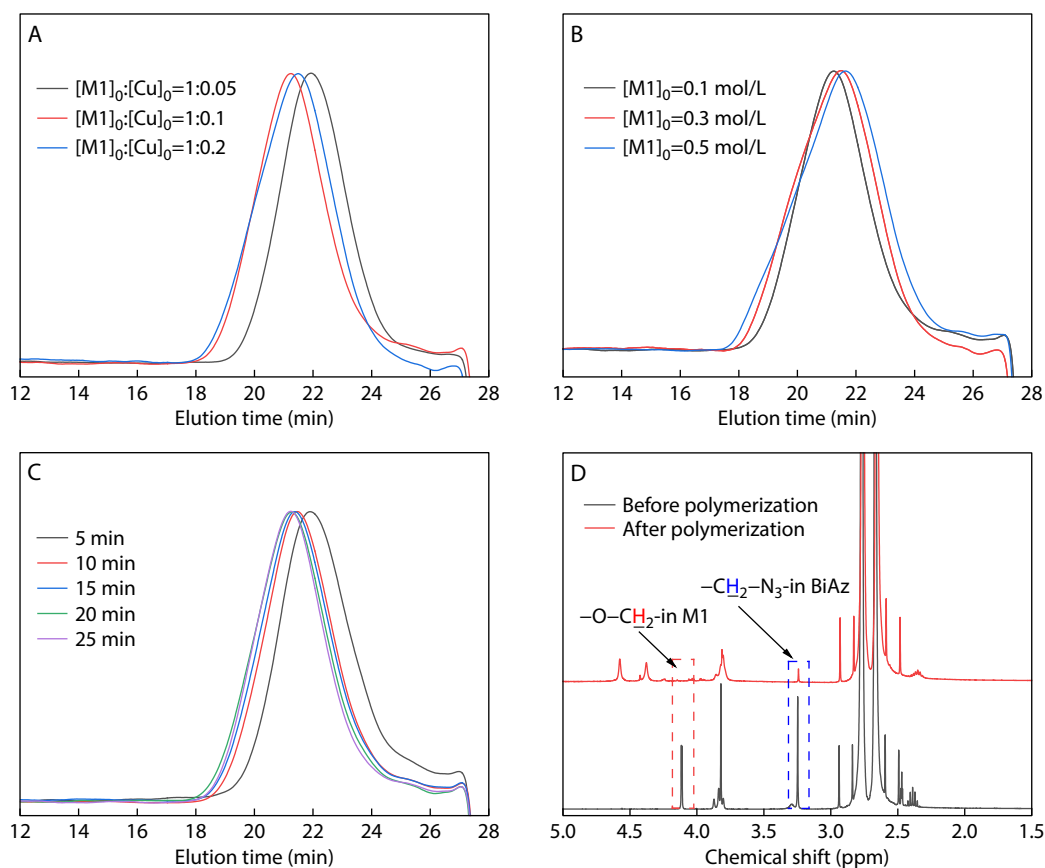
The procedures for synthesizing copolymers with other feed ratios of [M1]: [M3] were similar as above.

## RESULTS AND DISCUSSION

To demonstrate this step-growth CuAAC polymerization with RERI mechanism, BiAz (B<sub>2</sub>) with a desirable RERI effect was facilely synthesized according to the literature report with overall yield of 90%.<sup>[47,52]</sup> Meanwhile, three A<sub>2</sub> types of bis-alkynyl-terminated fluorinated monomers, M1, M2 and M3, were synthesized by facile esterification or etherification reaction with yields over 95% except M3 with yield about 30%. The molecular structure of these A<sub>2</sub> and BiAz monomers were confirmed by NMR, as shown in Scheme 1 and Figs. S1–S4 (in ESI). Then the conditions of CuAAC polymerization were explored and optimized using BiAz and M1 as model monomers, respectively. The feeding ratio and concentration of catalysts and monomers were first investigated. A series of CuAAC polymerizations between BiAz and M1 with varied M1/Cu catalyst ratios ([M1]<sub>0</sub>: [CuSO<sub>4</sub>·5H<sub>2</sub>O]<sub>0</sub>: [ascorbic acid]<sub>0</sub>= 1: x: 5x, x=0.05, 0.1 and 0.2) and concentration of M1 ([M1]<sub>0</sub>=0.1, 0.2 and 0.3 mol/L) were carried out in DMF at feed ratios of [M1]<sub>0</sub>: [BiAz]<sub>0</sub>=0.91, an excessive of BiAz relatively to M1, at 45 °C. In order to ensure a high extent of reaction, the CuAAC polymerization reaction time was first fixed for 12 h. Fig. 1(A) gives the SEC traces of the *in situ* polymerization for polyM1 at varied M1/Cu catalyst ratios and the concentration of [M1]<sub>0</sub>=0.1 mol/L, a highest M<sub>n,SEC</sub> value of 270.3 kg/mol with a dispersivity of



**Scheme 1** Synthesis of semifluorinated polymers with high molecular weight using step-growth polymerization with RERI mechanism based on CuAAC click reaction.



**Fig. 1** DMF SEC evolution of M1 and BiAz at the feed ratio of  $[M1]_0:[BiAz]_0=0.91$  at  $45\text{ }^\circ\text{C}$  in DMF under different conditions: (A)  $[M1]:[Cu]$  ratio, (B) the concentration of M1, and (C) the reaction time; (D)  $^1\text{H-NMR}$  spectra of before and after polymerization at the feed ratio of  $[M1]_0:[CuSO_4\cdot 5H_2O]_0:[ascorbic\ acid]_0=1:0.1:0.5$  and the concentration of  $[M1]_0$  was  $0.1\text{ mol/L}$ .

$M_w/M_n=1.62$  was determined at the Cu catalyst of  $0.1\text{ equiv.}$  Moreover, Fig. 1(D) gives the *in situ*  $^1\text{H-NMR}$  spectra of before and after polymerization at the Cu catalyst of  $0.1\text{ equiv.}$ , the methylene protons ( $4.11\text{ ppm}$ ) adjacent to alkynyl group of M1 monomer completely disappeared, indicating a quantitative consumption of M1 monomers. These results indicated that the CuAAC polymerization underwent effectively and achieved a

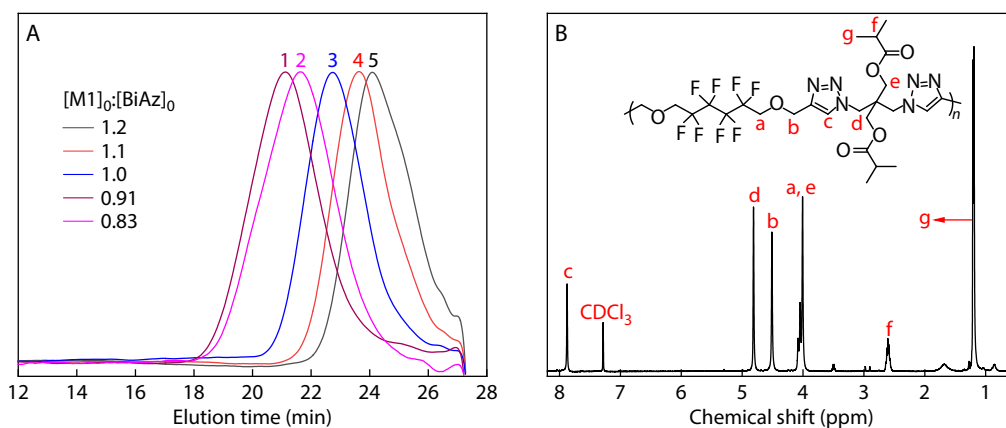
high-molecular-weight polymer with low dispersity. Then, the effect of M1 concentration on the CuAAC polymerization were investigated at feed ratio of  $[M1]_0:[CuSO_4\cdot 5H_2O]_0:[ascorbic\ acid]_0=1:0.1:0.5$ . As shown in Fig. 1(B), when the concentration of  $[M1]_0$  increased from  $0.1\text{ mol/L}$  to  $0.3\text{ mol/L}$  and  $0.5\text{ mol/L}$ , the resulted polymers with similar molecular weight were obtained and the SEC traces became slightly broad probably because of

the high viscosity of polymerization at 0.3 and 0.5 mol/L. The molecular weight and dispersity of the resultant polymers are summarized in Table S1 (in ESI). Subsequently, the polymerization time of CuAAC polymerization was investigated at feed ratio of  $[M1]_0:[CuSO_4 \cdot 5H_2O]_0:[ascorbic\ acid]_0=1:0.1:0.5$  and the concentration of  $[M1]_0$  was 0.1 mol/mL. The SEC evolution of CuAAC polymerization at different reaction time in Fig. 1(C) shows an overlapped SEC curves after 20 min, indicated that this CuAAC polymerization was fast and could be finished in 20 min. Therefore, all of the subsequent CuAAC polymerization were carried out at feed ratio of  $[M1]_0:[BiAz]_0:[CuSO_4 \cdot 5H_2O]_0:[ascorbic\ acid]_0=x:1:0.1x:0.5x$  and the concentration of  $[M1]_0$  was 0.1 mol/mL.

Under the optimal polymerization condition, the effect of the stoichiometric ratio on the CuAAC polymerization between M and BiAz was systematically investigated using M1 as model monomer at feed ratios of  $[M1]_0:[BiAz]_0:[CuSO_4 \cdot 5H_2O]_0:[ascorbic\ acid]_0=x:1:0.1x:0.5x$ , ( $x=1.2, 1.0, 0.91$  and  $0.83$ ) and fixed concentration of  $[M1]_0=0.1$  mol/L. The CuAAC polymerization of M1 and BiAz at a feed ratio of  $[M1]_0:[BiAz]_0=1:1$  was first carried out. Fig. S5(a) (in ESI) gives the Fourier transform infrared spectroscopy (FTIR) curves of the *in situ* polymerization for polyM1 after polymerization (blue curve), the absorption peak of azido at  $2100\text{ cm}^{-1}$  completely disappeared, indicating a complete consumption of BiAz monomers and a high extent of reaction. An  $M_{n,SEC}$  value of 78.1 kg/mol with a dispersity of  $M_w/M_n=1.59$  was determined for the resultant polymer, defined as polyM1-1.0, as shown in Fig. 2(A) (curve 3). When the feed ratio of  $[M1]_0:[BiAz]_0$  decreased to 0.91 and 0.83, namely the excessive BiAz was used, the molecular weight of the resultant PolyM1 was much higher than that of the feed ratio of  $[M1]_0:[BiAz]_0=1$ , as shown in Fig. 2(A) (curves 1 and 2). For instance, when  $x=0.91$  and  $0.83$ , the  $M_{n,SEC}$  value of 270.3 and 246.7 kg/mol were determined for polyM1-0.91 and polyM1-0.83, respectively, indicating that the usage of slightly excessive BiAz compounds could achieve a high molecular weight. The  $M_n$  value of polyM1-0.83 was slightly lower than polyM1-0.91 correlated well with the previously literature reported.<sup>[19]</sup> After polymerization, the Cu catalyst in the polymers could be easily removed by the addition of two equivalents of PM-DETA, a strong ligand of Cu, which gave a colorless polyM1. A

purified polyM1-0.91 was obtained with over 85% yield and the molecular structure was confirmed by  $^1\text{H-NMR}$  spectroscopy, as shown in Fig. 2(B). The absolute molecular weight ( $M_{w,MALLS}$ ) of polyM1-0.91 was determined by SEC with multi-angle laser light scattering (MALLS) and an  $M_{w,MALLS}$  value of 1072.2 kg/mol was calculated using its own  $dn/dc=0.0549$  mL/g, indicating that the semifluorinated polymer with ultrahigh molecular weight was successfully synthesized. However, when the feed ratio of  $[M1]_0:[BiAz]_0$  increased to 1.1 and 1.2, the BiAz was consumed completely during polymerization due to the usage of excessive M1 monomer, this was confirmed by the *in situ* FTIR spectrum (Fig. S5a in ESI) and  $^1\text{H-NMR}$  spectrum (Fig. S5b in ESI). As shown in Fig. 2(A), the elution time of the resultant polyM1 increases with increasing the feed ratio of  $[M1]_0:[BiAz]_0$  from 1.0 to 1.2, indicated that the excessive M1 monomers decrease the molecular weight of the resultant polyM1. For instance, when  $x=1.1$  or  $1.2$ , the  $M_{n,SEC}$  value of 49.1 and 33.5 kg/mol was determined for polyM1-1.1 and polyM1-1.2, respectively, indicated that this CuAAC based step-growth polymerization followed the classical kinetics theory in the presence of excess alkynyl groups, in which the usage of excess alkynyl to azido groups seriously decreased the molecular weight of the resultant polyM1. These results indicated that this step-growth polymerization based on CuAAC reaction of BiAz showed the stoichiometric imbalance-promoted property, in which the high-molecular-weight polymers could be produced in the presence of slightly excess BiAz due to its desirable RERI effect. The molecular weight and dispersity of polyM1 at varied feed ratios were summarized in Table 1. It is worth noting that the terminal group of the resultant polymers in this step-growth polymerization should be entirely determined by the concentration of BiAz due to the higher reactivity of half-reacted BiAz intermediate. There is no half-reacted BiAz intermediate when the excessive bis-alkynyl-terminated monomers were used, thus the resultant polymers are all terminated with alkynyl group. When more BiAz monomers were used, the alkynyl-terminated oligomer and polymers could further react with BiAz until the complete consumption of alkynyl group, thus the resultant polymers are all terminated with azido group.

To explore the versatility of this novel step-growth poly-



**Fig. 2** (A) SEC traces of *in situ* polymerization of M1 with BiAz at varied feed ratios of  $[M1]_0:[BiAz]_0$  and the concentration of  $[M1]_0=0.1$  mol/L at  $45\text{ }^\circ\text{C}$  and (B)  $^1\text{H-NMR}$  spectra of purified polyM1-0.91.

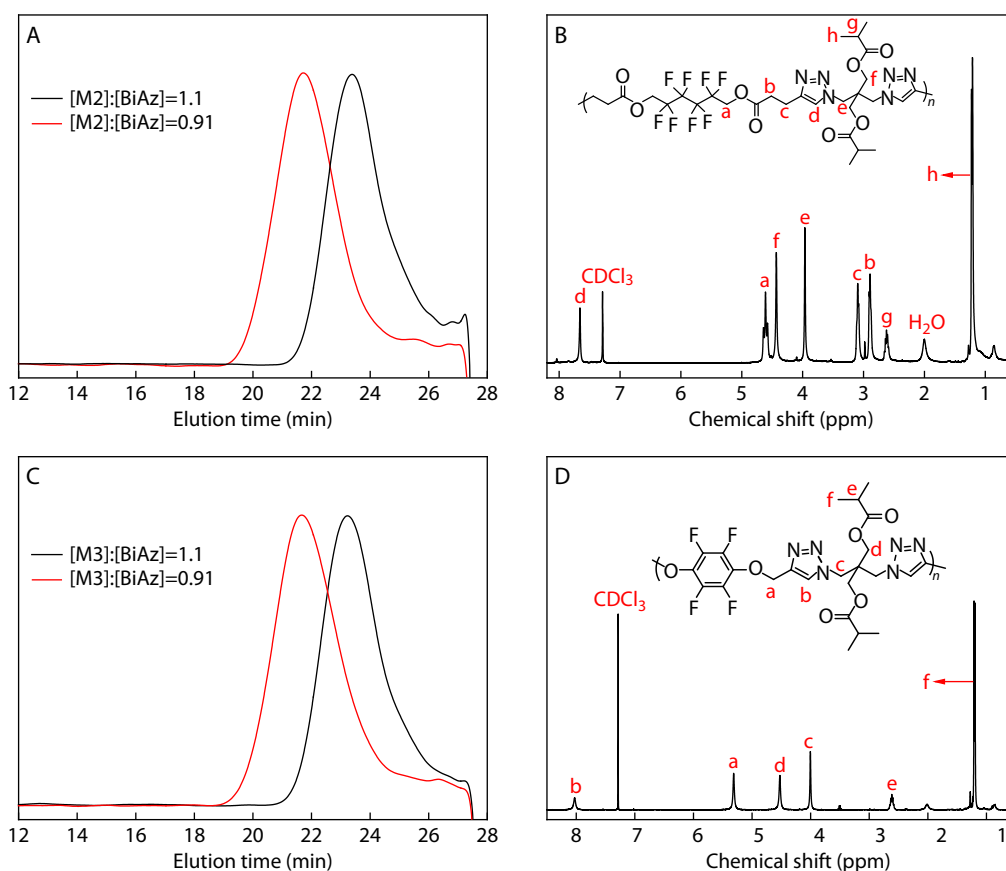
**Table 1** Synthesis and characterization of PolyM1, PolyM2 and PolyM3.

Sample <sup>a</sup>	$x^b$	$M_{n,theo.}^c$ (kg/mol)	$M_{n,SEC}^d$ (kg/mol)	$M_w/M_n^d$	$M_{w,MALLS}^e$ (kg/mol)	$T_g$ (°C)	$dn/dc$ (mL/g)	CA (deg)
PolyM1-1.2	1.2	7.6	33.5	1.42	—	—	—	—
PolyM1-1.1	1.1	14.7	49.1	1.48	—	—	—	78.4
PolyM1-1.0	1.0	∞	78.1	1.59	—	—	—	—
PolyM1-0.91	0.91	14.7	270.3	1.62	1072.2	15.8	0.0549	84.4
PolyM1-0.83	0.82	7.6	246.7	1.65	—	—	—	—
PolyM2-0.91	0.91	16.5	202.7	1.52	905.4	14.3	0.0446	85.1
PolyM3-0.91	0.91	12.4	161.2	1.62	62.6	66.7	0.1440	103.7

<sup>a</sup> The polymerization was carried out at feed ratios of  $[M]_0:[BiAz]_0:[CuSO_4 \cdot 5H_2O]_0:[ascorbic\ acid]_0 = x:1:0.1x:0.5x$ , ( $x=1.2, 1.1, 1.0, 0.91$  or  $0.83$ ) and the  $[M]_0=0.1$  mol/L in DMF at 45 °C; <sup>b</sup> Initial molar ratio of bis-alkynyl terminated monomers and BiAz ( $[M]_0/[BiAz]_0$ ); <sup>c</sup> Calculated from the equation of  $(1+r)/(1+r-2p)$  with  $p=1$ ; <sup>d</sup> The apparent number-average molecular weight ( $M_{n,SEC}$ ) and dispersity ( $M_w/M_n$ ) measured by SEC with an RI detector, calibrated with linear PS standards; <sup>e</sup> The weight-average molecular weight measured by SEC with a MALLS detector.

merization with RERI effect and achieve high-molecular-weight functional polymers, two more bis-alkynyl-terminated fluorinated monomers, M2 and M3 (see Scheme 1), were also applied to synthesize semifluorinated polymers with high molecular weight. M2 monomer containing ester groups that can endow the polymers with degradability and M3 containing an aromatic ring that can endow the polymers with high rigidity. The CuAAC polymerization of M2 or M3 with BiAz was performed under similar condition at the varied feed ratio of  $[M2 \text{ or } M3]_0:[BiAz]_0$  and  $[M2 \text{ or } M3]_0=0.1$  mol/L. The SEC trace of the resultant polyM2 and polyM3 at varied feed ratios of  $[M2 \text{ or } M3]_0:[BiAz]_0$  in Figs. 3(A) and 3(C) show the monomodal peak with low dispersity ( $M_w/M_n$ ) about 1.6, further con-

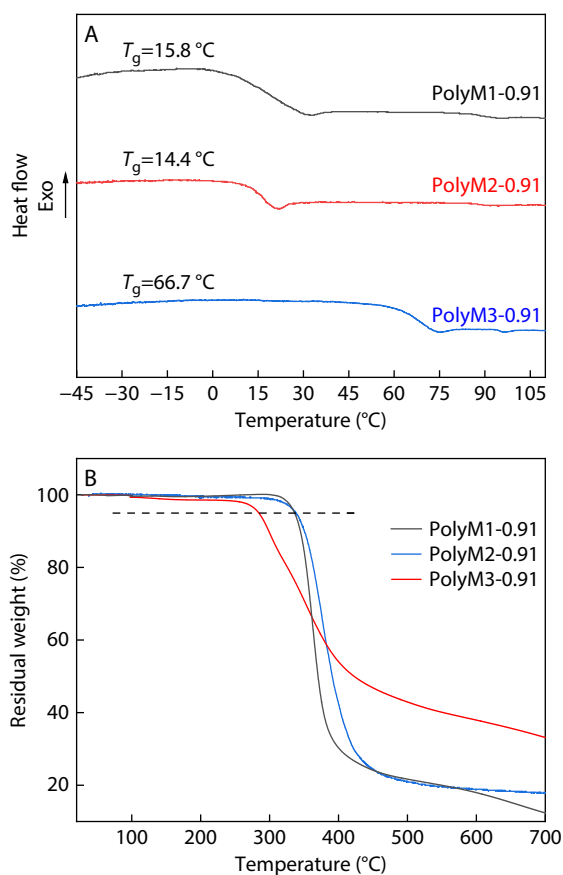
firmed the usage of slightly excessive BiAz compounds could achieve a high molecular weight, no matter what bi-alkynyl-terminated monomers. The  $M_{w,MALLS}$  values of 905.4 and 62.6 kg/mol were determined for polyM2-0.91 ( $dn/dc=0.0446$  mL/g) and polyM3-0.91 ( $dn/dc=0.144$  mL/g), respectively. It is noted that the polyM3-0.91 had a much lower  $M_{w,MALLS}$  value of 62.6 kg/mol, the possible reason is that the large steric hindrance of M3 could decrease the reaction efficiency of the first azide-alkyne cycloaddition. The molecular weight ( $M_n$ ) and dispersity ( $M_w/M_n$ ) of polyM2-0.91 and polyM3-0.91 are summarized in Table 1. The molecular structures of polyM2-0.91 and polyM3-0.91 were confirmed by <sup>1</sup>H-NMR spectroscopy, as shown in Figs. 3(B) and 3(D). As a result, this step-



**Fig. 3** (A, C) SEC traces of *in situ* polymerization of M2 or M3 with BiAz at varied feed ratios of  $[M2 \text{ or } M3]_0:[BiAz]_0$  (1.1 and 0.91) and the concentration of  $[M2 \text{ or } M3]_0=0.1$  mol/L at 45 °C; (B, D) <sup>1</sup>H-NMR spectra of purified polyM2-0.91 and polyM3-0.91.

growth polymerization with RERI effect was indeed a versatile method to prepare varied mainchain semifluorinated polymers with high molecular weights.

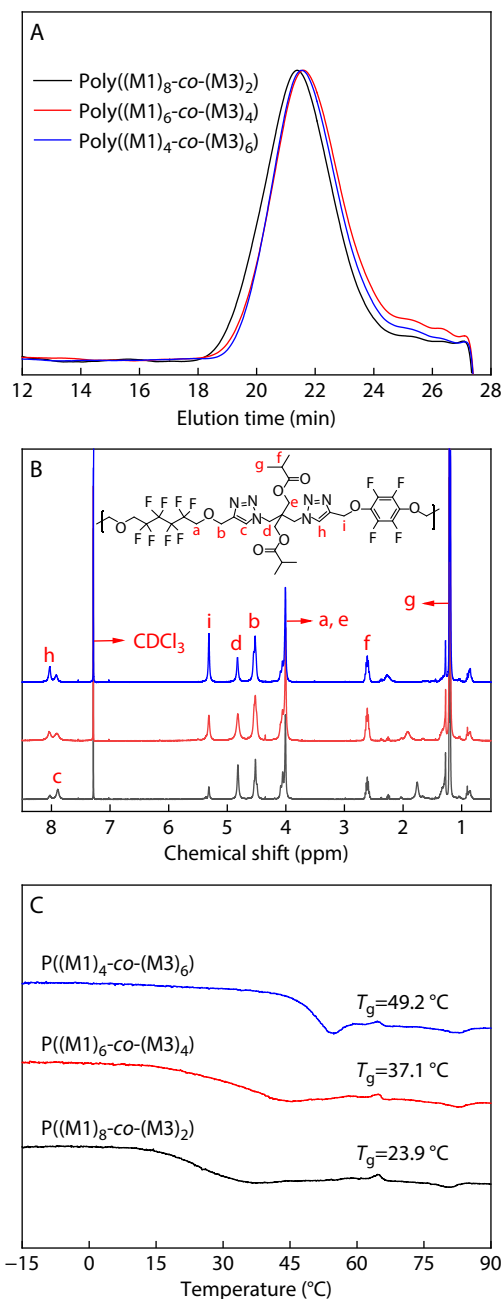
Next, the thermal properties of these mainchain semifluorinated polymers were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass transition temperature ( $T_g$ ) was measured as 15.8, 14.4 and 66.7 °C for polyM1-0.91, polyM2-0.91 and polyM3-0.91, respectively, as shown in Fig. 4(A). These semifluorinated polymers were found to be amorphous, which makes them easier to process than commercial fluoropolymers, such as poly(tetrafluoroethylene) (PTFE) and poly(vinylidene fluoride) (PVDF). The decomposition temperature ( $T_d$ ) at 5% weight loss was 336, 336 and 284 °C for polyM1-0.91, polyM2-0.91 and polyM3-0.91, respectively, indicating a good thermostability, as shown in Fig. 4(B). It is noted that the  $T_d$  of polyM3-0.91 is much lower than that of the polyM1-0.91 and polyM2-0.91, maybe because of a low molecular weight of polyM3-0.91 and a less stable fluorinated phenyl ether bonds. In addition, the wettability of these mainchain semifluorinated polymers were also investigated by measuring their water contact angles (CA). The CA values of polyM1-1.1 and polyM1-0.91 were 78.4° and 84.4°, respectively, indicating a better hydrophobicity of high-molecular-weight semifluorinated polymers. For the polyM3-0.91, the CA value was 103.7°, which is higher than that of polyM1-0.91 and polyM2-0.91 (85.1°), indicated that the aromatic semifluorinated polymers had a



**Fig. 4** (A) DSC and (B) TGA curves of polyM1-0.91, polyM2-0.91 and polyM3-0.91.

better hydrophobicity relative to aliphatic semifluorinated polymers. The  $T_g$  and CA values of these semifluorinated polymers are summarized in Table 1.

We were also interested in demonstrating the possibility of copolymerization of two bis-alkynyl-terminated monomers with BiAz in this step-growth polymerization for tuning properties of the resultant polymers. The bis-alkynyl-terminated comonomers could be consumed completely when excessive BiAz monomers were used, thus the comonomer could be quantitatively introduced in copolymers. To demonstrate the tunability of polymer properties for this step-growth polymerization with RERI effect, the copolymerization of M1 and M3



**Fig. 5** (A) SEC traces, (B) <sup>1</sup>H-NMR spectra and (C) DSC curves of poly((M1)<sub>8</sub>-co-(M3)<sub>2</sub>), poly((M1)<sub>6</sub>-co-(M3)<sub>4</sub>) and poly((M1)<sub>4</sub>-co-(M3)<sub>6</sub>).

with BiAz were performed for tuning the  $T_g$  of the resultant copolymers. The step-growth copolymerization was carried out at feed ratio of  $[M1+M3]_0:[BiAz]_0:[CuSO_4 \cdot 5H_2O]_0:[ascorbic\ acid]_0=0.91:1:0.91:0.46$  and keeping the concentration of  $[M1+M3]_0=0.1$  mol/L, in which the molar ratio of  $[M1]_0:[M3]_0=8:2, 6:4$  and  $4:6$ . The SEC traces of obtained copolymers show monomodal peak and low  $M_w/M_n$ , as shown in Fig. 5(A). The  $M_{w,MALLS}$  of these copolymers decreased with the increasing the fraction of polyM3 segments due to the low reaction efficiency of M3, as shown in Table S2 (in ESI). The  $^1H$ -NMR spectra of the resultant copolymers are given in Fig. 5(B), there are typical peaks at 5.22–5.43 ppm, the methylene protons adjacent to fluorinated aromatic ring in M3 segment, and 4.44–4.66 ppm, the methylene protons in M1 segment. The chemical composition of these copolymers was determined by the integral area of peak i and peak b, they are consistent with the theoretical values. The DSC characterization showed that the overall  $T_g$  of copolymers increased with increasing the mole fraction of polyM3 segment due to the rigidity of polyM3 segment, as shown in Fig. 5(C). For instance, the overall  $T_g$  increased from 23.9 °C to 49.2 °C when molar fraction of polyM3 segment increased from 0.2 to 0.6. These results indicated that the physical properties of these mainchain semifluorinated polymers could be tuned conveniently by copolymerization. The molecular weight ( $M_n$ ) and dispersity ( $M_w/M_n$ ) as well as their  $T_g$  values of these semifluorinated copolymers were summarized in Table S2 (in ESI).

## CONCLUSIONS

In summary, a rapid and highly efficient step-growth polymerization with RERI mechanism based on CuAAC reaction was developed to synthesize mainchain semifluorinated polymers with (ultra)high molecular weight. This novel step-growth polymerization with RERI mechanism could overcome the requirement of the traditional step-growth polymerization for the strict equivalence of functional groups, and realizes the synthesis of high molecular weight polymers in a stoichiometric imbalance condition using a slightly excessive BiAz to bi-alkynyl monomers. Meanwhile, the bis-alkynyl-terminated monomers in this step-growth polymerization could be consumed completely when excessive BiAz monomers were used, this provides the possibility to precisely tune polymer properties. Considering the easy preparation of monomers and high efficiency of CuAAC reaction, this step-growth polymerization with RERI effect based on CuAAC reaction is expected to be of broad interest in both polymer chemistry and materials science for the synthesis of high-molecular-weight polymers.

## NOTES

The authors declare no competing financial interest.

## Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-023-2919-1>.

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