Research Article

Synthesis of Fluorinated Amphiphilic Block Copolymers Based on PEGMA, HEMA, and MMA via ATRP and CuAAC Click Chemistry

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Synthesis of fluorinated amphiphilic block copolymers via atom transfer radical polymerization (ATRP) and Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) was demonstrated. First, a PEGMA and MMA based block copolymer carrying multiple side-chain acetylene moieties on the hydrophobic segment for postfunctionalization was carried out. This involves the synthesis of a series of P(HEMA-co-MMA) random copolymers to be employed as macroinitiators in the controlled synthesis of P(HEMA-co-MMA)-*block*-PPEGMA block copolymers by using ATRP, followed by a modification step on the hydroxyl side groups of HEMA via Steglich esterification to afford propargyl side-functional polymer, alkyne-P(HEMA-co-MMA)-*block*-PPEGMA. Finally, click coupling between side-chain acetylene functionalities and 2,3,4,5,6-pentafluorobenzyl azide yielded fluorinated amphiphilic block copolymers. The obtained polymers were structurally characterized by ¹H-NMR, ¹⁹F-NMR, FT-IR, and GPC. Their thermal characterizations were performed using DSC and TGA.

1. Introduction

The perfluoroalkyl moieties in amphiphilic molecules provide distinct properties, such as hydrophobicity and lipophobicity, high thermal and chemical stability, excellent mechanical properties at extreme temperatures, low refractive index, and a strong tendency to self-assemble [1–6]. A great deal of attention has been paid to the incorporation of fluorinated groups into synthetic materials, which combine the advantages of both fluorinated groups and other polymers [7–10]. Controlled radical polymerization (CRP) can serve as a powerful synthetic tool in the production of well-defined fluorinated polymers with various architectures having predetermined chain lengths and low polydispersities. Fluorinated

block copolymers have been synthesized previously via CRPs, involving nitroxide mediated radical polymerization (NMP) [11, 12], reversible addition fragmentation chain transfer polymerization (RAFT) [13, 14], and atom transfer radical polymerization (ATRP) [15–19].

Amphiphilic block copolymers consisting of hydrophobic fluorinated blocks and hydrophilic poly[poly(ethylene glycol)methyl ether methacrylate] (P(PEGMA)) have been synthesized [20–23]. P(PEGMA) block, prepared by CRPs, is a versatile polymer in fine-tuning hydrophobic/hydrophilic balance of the amphiphile since lengths of both P(PEGMA) and PEG side-chains can be altered. Besides, P(PEGMA) segments may introduce favorable characteristics to the copolymers including water solubility, low toxicity, and high

biocompatibility [24–26]. 2,3,4,5,6-Pentafluorobenzyl containing segments have been employed as the hydrophobic part in several studies and have accounted for the above-mentioned properties stemming from perfluoroalkyl moieties [27–29]. The overall macromolecules have potential in applications involving nonlinear optics, rheology modifiers, and antifouling coatings.

Quite recently, click reactions have attracted considerable attention in synthetic polymer chemistry owing to their high specificity, high tolerance of functional groups, and quantitative reaction yields. Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC), which occurs between an azide and an alkyne to give 1,2,3-triazole ring [30, 31], has emerged as a powerful tool in the preparation of versatile macromolecular structures when used in conjunction with controlled/living radical polymerization techniques [9, 32].

Herein, we report the synthesis of a fluorinated amphiphilic block copolymer on the basis of combined ATRP and Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) methods. To the best of our knowledge, this is the first study to report the preparation of perfluoroalkylated amphiphilic block copolymer brushes by this approach. Furthermore, the method allows for facile adaptation of a variety of other click moieties and fine-tunes their concentration without altering the size of hydrophobic segment.

2. Experimental

2.1. Materials. Methyl methacrylate (MMA, 99%, Aldrich) and 2-hydroxyethyl methacrylate (HEMA, 99%, Aldrich) were distilled before use. Poly(ethylene glycol) methyl ether acrylate (PEGMA, $M_n = 480$ g/mol, Aldrich) was passed through basic alumina column to remove the inhibitor Ethyl α -bromoisobutyrate (EBIB, 98%, Aldrich), 2,3,4,5,6-pentafluorobenzyl chloride (Aldrich 99%), CuCl ($\geq 99.99\%$, Aldrich), CuBr (98%, Aldrich), sodium azide (NaN_3 , Sigma-Aldrich), 2,2-bipyridine (bpy, 99%, Fluka), N, N, N', N'', N''' -pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), methanol (≥ 99.9 , Aldrich), N, N' -dicyclohexylcarbodiimide (DCC, 99%, Aldrich), 4-(dimethylamino) pyridine (DMAP, $\geq 99.99\%$, Aldrich), propiolic acid (99%, Aldrich), and N, N -dimethylformamide (DMF, 99%, Aldrich) were used as received.

2.2. Typical Procedure for the Random Copolymerization of HEMA with MMA via ATRP (1a–d). Molar ratio of MMA and HEMA was varied to get random copolymers with different HEMA contents. For instance, to obtain P(HEMA(20)-co-MMA(80)), in which the numbers in parenthesis refer to v/v percentages, reagents at the molar ratio of [HEMA]/[MMA]/[EBIB]/[CuCl]/[bpy]: 18/82/1/1/2.5 were added. HEMA (1.72 g, 1.60 mL, 13 mmol), MMA (6.01 g, 6.40 mL, 60 mmol), CuCl (0.072 g, 0.72 mmol), ethyl α -bromoisobutyrate (EBIB, 0.142 g, 0.72 mmol), and bipyridine (bpy, 0.145 g, 0.093 mmol) were mixed in a Schlenk tube equipped with a magnetic stirring bar, to which 5.3 mL of methanol ([monomer]/solvent = 1.5:1 v/v) was added. The tube was degassed by three freeze-pump-thaw cycles.

The polymerization flask was placed on a magnetic stirrer and kept there for a given period at room temperature, after which the reaction was terminated by dipping the tube into liquid nitrogen. The mixture was diluted with THF and passed through a silica gel column to remove the complex salts. The solution was then concentrated and precipitated into 10-fold excess hexane. The precipitate was collected by filtration and dried in a vacuum oven at 30°C overnight. (68 % conv., $^1\text{H-NMR}$ (CDCl_3 , ppm): $\delta = 0.88\text{--}1.36$ (s, $\alpha\text{-CH}_3$, MMA and HEMA), 1.5–2.1 (s, -CH_2 , MMA and HEMA), 3.55 (s, -OCH_3 , MMA), 3.78 (t, $\text{-CH}_2\text{OH}$, HEMA), 4.05 (t, -OCH_2 , HEMA). FT-IR (cm^{-1}): 3540 (-OH stretching), 2957 (-CH aliphatic stretching), 1726 (-C=O stretching), and 1151 (-C-O-C- stretching).

2.3. Block Copolymerization of PEGMA Using Poly(HEMA-co-MMA) Macroinitiator via ATRP (2b, 2d). In a typical procedure, P(HEMA(20)-co-MMA(80)) (1b) macroinitiator (0.41 g, 0.045 mmol), PEGMA (8.72 g, 18 mmol) monomer, CuBr (0.007 g, 0.045 mmol), and PMDETA (0.016 g, 0.09 mmol) were dissolved in methanol/water mixture ($\text{MeOH/water} = 2:1$ v/v) in a Schlenk tube equipped with a magnetic stirring bar. The reaction mixture was degassed by three freeze-pump-thaw cycles, backfilled with nitrogen, and kept in a magnetic stirrer at room temperature. After the given period, the Schlenk tube was immersed into liquid nitrogen to terminate the reaction. Upon reaching room temperature, the mixture was diluted with THF and passed through a silica gel column to remove the copper salt. The solution was completely dried in a rotary evaporator and then subjected to dialysis against regularly replaced distilled water to remove PEGMA monomer (spectra/Por membranes, cut-off 1,000 Da). The solution was again evaporated to dryness in a rotary evaporator. The residue was dissolved in THF and precipitated into 10-fold excess hexane. The precipitate was collected by filtration and dried *in vacuo* overnight. Yield: 75%. $^1\text{H-NMR}$ (CDCl_3 , ppm): $\delta = 0.84\text{--}1.4$ (s, $\alpha\text{-CH}_3$, MMA and HEMA), 1.8–2.1 (s, -CH_2 , MMA and HEMA), 2.3–2.5 (d, -CH_2 , PEGMA), 3.38 (s, $\text{CH}_3\text{O-}$, PEGMA), 3.55 (s, $\text{CH}_3\text{O-}$, MMA), 3.65 (t, $\text{-CH}_2\text{O-}$, PEGMA), 3.84 (t, $\text{-OCH}_2\text{-}$, HEMA), 4.1–4.2 (t, $\text{-CH}_2\text{OH}$ and $\text{-CH}_2\text{CH}_2\text{O}$, HEMA and PEGMA). FT-IR (cm^{-1}): 3550 (-OH stretching), 2870 (-CH aliphatic stretching), 1733 (-C=O stretching), and 1095 (-C-O-C- stretching).

2.4. Synthesis of Alkyne-P(HEMA-co-MMA)-block-PPEGMA (3b, 3d). The reagents were used according to the following molar ratios: [side-chain OH]/[DCC]/[DMAP]/[propionic acid]: 1/1.6/0.16/1.5. To obtain alkyne-P(HEMA-co-MMA)-block-PPEGMA (3b, 3d), P(HEMA-co-MMA)-block-PPEGMA (2b, 2d) (0.5 g, 0.008 mmol), DCC (0.053 g, 0.256 mmol), DMAP (0.003 g, 0.0256 mmol), and propionic acid (0.017 g, 0.24 mmol) were added in a round-bottom flask and dissolved in 50 mL CH_2Cl_2 under stirring at room temperature. Then, the mixture was concentrated in the rotary evaporator and precipitated in 10-fold excess hexane. Yield: 87 %. $^1\text{H-NMR}$ (CDCl_3 , ppm): $\delta = 0.84\text{--}1.4$ (s, $\alpha\text{-CH}_3$, MMA and HEMA), 1.8–2.1 (s, -CH_2 , MMA and HEMA),

FIGURE 1: Schematic illustration of click coupling between PEGMA based amphiphilic block copolymers bearing pendant clickable sites and azide-functional group.

2.3-2.4 (d, $-\text{CH}_2$, PEGMA), 2.57 (s, $-\text{OC}\equiv\text{CH}$) 3.38 (s, $\text{CH}_3\text{O}-$, PEGMA), 3.55 (s, $\text{CH}_3\text{O}-$, MMA), 3.63 (t, $-\text{CH}_2\text{O}$, PEGMA), 3.82 (t, $-\text{OCH}_2$, HEMA), 4.1-4.2 (t, $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{O}$, HEMA and PEGMA). FT-IR (cm^{-1}): 3320 ($-\text{C}\equiv\text{CH}$ stretching), 2875 ($-\text{CH}$ aliphatic stretching), 2350 ($-\text{C}\equiv\text{CH}$ stretching), 1735 ($-\text{C}=\text{O}$ stretching), and 1099 ($-\text{C}-\text{O}-\text{C}-$ eter stretching).

2.5. Synthesis of 2,3,4,5,6-Pentafluorobenzyl Azide. NaN_3 (0.65 g, 0.01 mol) and 2,3,4,5,6-pentafluorobenzyl chloride (2 g, 0.008 mol) were dissolved in 50 mL *N,N*-dimethylformamide in a round-bottomed flask equipped with a magnetic stirrer. The reaction solution was stirred for 24 h at room temperature [33–36]. Then, DMF was removed under reduced pressure in a rotary evaporator and the remaining solid was dissolved in CH_2Cl_2 . The mixture was washed thoroughly with water. The organic layer was removed and recovered solid was dried under vacuum at 25°C . Yield: 80%. $^1\text{H-NMR}$ (CDCl_3 , ppm): δ = 3.67 (s, $-\text{CH}_2$). FT-IR (cm^{-1}): 2110 ($-\text{N}_3$ stretching), 1650–1500 ($-\text{C}=\text{C}-$ stretching), and 1235 ($-\text{CF}$ stretching). $^{19}\text{F-NMR}$ (CDCl_3 , ppm): δ = o: -142 (2F), p: -151 (1F), m: -161 (2F).

2.6. Click Coupling Reaction of Alkyne-*P*(HEMA-*co*-MMA)-*block*-PPEGMA with 2,3,4,5,6-Pentafluorobenzyl Azide (4). The reagents were used according to the following molar ratios: [side-chain acetylene]/ $[-\text{N}_3]$ /[CuBr]/[PMDETA]: 1/1/2.5/2.5. Alkyne-*P*(HEMA-*co*-MMA)-*block*-PPEGMA (0.3 g, 0.005 mmol) (**3b**) was dissolved together with 2,3,4,5,6-pentafluorobenzyl azide (0.016 g, 0.07 mmol) in degassed DMF under nitrogen. To the reaction mixture CuBr (0.025 g, 0.176 mmol) and PMDETA (0.031 g, 0.176 mmol) were added, while the solution was being purged with nitrogen. Then,

it was stirred for 48 h at room temperature, after which, the mixture was diluted with THF and passed through a silica gel column to remove the copper salt [34–36]. Finally, excess solvent was removed in a rotary-evaporator and the resultant solution was poured into 10-fold excess hexane for precipitation. The solid was collected by filtration and dried *in vacuo* overnight. (For 2,3,4,5,6-pentafluorobenzyl functional *P*(HEMA-*co*-MMA)-*block*-PPEGMA, yield: 83%, $^1\text{H-NMR}$ (CDCl_3 , ppm): δ = 0.84–1.58 (s, $\alpha\text{-CH}_3$, MMA and HEMA), 1.83 (s, $-\text{CH}_2$, MMA and HEMA), 2.30 (d, $-\text{CH}_2$, PEGMA), 3.38 (s, $\text{CH}_3\text{O}-$, PEGMA), 3.56 (s, $\text{CH}_3\text{O}-$, MMA), 3.65 (t, $-\text{CH}_2\text{O}$, PEGMA), 3.90 (t, $-\text{OCH}_2$, HEMA), 4.0–4.17 (t, $-\text{CH}_2\text{CH}_2$ and $-\text{CH}_2\text{CH}_2\text{O}$, HEMA and PEGMA), 4.47 (s, $-\text{CH}_2-\text{N}_3$), 7.64 (s, $-\text{CH}$, from triazole ring), FT-IR (cm^{-1}): 2870 ($-\text{CH}$ aliphatic stretching), 1733 ($-\text{C}=\text{O}$ stretching), and 1095 ($-\text{C}-\text{O}-\text{C}-$ stretching)).

2.7. Characterizations. FT-IR spectra were recorded using a Bruker Alpha-P in ATR in the range of 4000–400 cm^{-1} . $^1\text{H-NMR}$ spectra were recorded using a 400 MHz Bruker Avance spectrometer in CDCl_3 . Chemical shifts are reported in ppm relative to TMS as internal standard.

Thermal stabilities of the membranes were analyzed by a PerkinElmer STA 6000 Thermal Analyzer. The samples (~ 10 mg) were heated between $30\text{--}750^\circ\text{C}$ under N_2 atmosphere at a scanning rate of $10^\circ\text{C}/\text{min}$. PerkinElmer JADE Differential Scanning Calorimetry (DSC) was used to investigate the thermal transitions of the samples. The samples (~ 10 mg) were put into aluminum pans and then heated to the desired temperature at a rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

Gel-permeation chromatography (GPC) measurements were performed on THF solutions of the polymers using an Agilent GPC 1100 instrument. The measurements were standardized against THF solutions of polystyrene standards.

FIGURE 2: Synthesis of alkyne-P(HEMA-co-MMA)-block-PPEGMA (3) and its click coupling reaction (4).

3. Results and Discussion

A novel approach combining ATRP with Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) in the preparation of a fluorinated amphiphilic block copolymer has been demonstrated (Figure 1). Synthesis of polymers based on MMA and PEGMA carrying clickable moieties for further

functionalization was carried out in a three-step strategy, as depicted in Figure 2. First, a series of precursor random copolymers (**1a–1d**) P(HEMA-co-MMA) were prepared via ATRP of MMA and HEMA. In the second step, the obtained polymer was employed as a macroinitiator in ATRP of PEGMA to afford the block copolymer (**2b**, **2d**), P(HEMA-co-MMA)-block-PPEGMA.

TABLE 1: Conditions^a and results for the synthesis of P(HEMA-*co*-MMA).

Entry	Comonomers in feed (% volume)	Polymer	Time (h)	^b Conv. (%)	^c $M_{n,GPC}$	^d $M_{n,theo}$	^e PDI
1	HEMA(5)-MMA(95)	(1a)	17	91	9300	9420	1.39
2	HEMA(20)-MMA(80)	(1b)	12	68	5850	7360	1.29
3	HEMA(30)-MMA(70)	(1c)	10	60	5500	6690	1.29
4	HEMA(50)-MMA(50)	(1d)	7	43	4384	5100	1.23

^a[Monomer]/solvent = 1.5:1 v/v, [M]/[I]/[CuCl]/[bpy]: 100/1/1/2.5, ethyl α -bromoisobutyrate was used as an initiator, and temperature: r.t. ^bdetermined gravimetrically. ^cdetermined from GPC measurements. ^dcalculated by using formula: $M_{n,theo} = M_{w,monomer} \times [\text{Monomer}]/[\text{Initiator}] \times \text{Conv.} + M_{w,initiator}$ ^edetermined from GPC measurements.

Finally, propargyl moieties were introduced via the Steglich esterification between the hydroxyl side-functionalities of HEMA and propiolic acid. Alkyne-P(HEMA-*co*-MMA)-*block*-PPEGMA (**3b**, **3d**) was then click-coupled with model compound, namely, 2,3,4,5,6-pentafluorobenzyl azide to yield (**4**). Copolymerization of methyl methacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) was carried out via ATRP using ethyl α -bromoisobutyrate (EBIB), CuCl, and bipyridine as initiator, catalyst, and ligand, respectively, at room temperature in methanol. Conditions and results are summarized in Table 1. Molar ratio of MMA and HEMA was varied to get random copolymers with different HEMA contents. For instance, to obtain P(HEMA(20)-*co*-MMA(80)), in which the numbers in parenthesis refer to v/v percentages, reagents at the molar ratio of [HEMA]/[MMA]/[EBIB]/[CuCl]/[bpy]: 18/82/1/1/2.5 were added.

Chemical structures of the copolymers were identified using several techniques. The FT-IR spectra of four different compositions of copolymers P(HEMA-*co*-MMA) are given in Figure 3. The broad band at 3540 cm^{-1} due to the -OH stretching, increasing with the HEMA content in the copolymers, was an apparent characteristic peak of the series. The -CH stretching appeared around 2957 cm^{-1} . The characteristic -C=O stretching band in both HEMA and MMA units in the copolymer occurred at 1726 cm^{-1} [37, 38]. The strong -C-O-C- type ester stretching band appeared at 1151 cm^{-1} [38].

The ¹H-NMR spectra of P(HEMA-*co*-MMA) copolymers are given in Figure 4. The signal for methyl protons of -OCH₃ (a) in MMA units appeared at 3.55 ppm [38, 39]. The signals of α -CH₃ protons were seen at 0.88–1.36 ppm in both MMA and HEMA units, while for methylene protons they were in the range of 1.5–2.1 ppm. The signals at 3.78 ppm (b) and 4.05 ppm (c) correspond to -CH₂OH and -CH₂O protons, respectively [38].

Copolymer compositions from ¹H-NMR were calculated by integral area of the -OCH₃ and -OCH₂ protons using the following [38]:

$$\text{Molar percent of HEMA} = \frac{(1b/2)}{[(1b/2) + (1a/3)]} \times 100. \quad (1)$$

The copolymer compositions obtained from ¹H-NMR agreed well with the charged monomer ratio in feed as shown in Table 2.

FIGURE 3: FT-IR spectra of P(HEMA-*co*-MMA) copolymers.

Polymerization of poly(ethylene glycol) methyl ether acrylate was carried out via ATRP using P(HEMA(20)-*co*-MMA(80)) (**1b**) and P(HEMA(50)-*co*-MMA(50)) (**1d**) as macroinitiator and CuBr/PMDETA as catalyst system at room temperature in methanol/water. Conditions and results are summarized in Table 3.

For both P(HEMA-*co*-MMA)-*block*-PPEGMA (**2b**, **2d**) block copolymers, the ¹H-NMR spectrum exhibited signals originating from α -CH₃ protons and -CH₂ protons between 0.84–1.4 ppm and 1.8–2.1 ppm, respectively, in both MMA and HEMA units [38], as depicted in Figure 5. The appearance of signals at 2.3–2.5 ppm and 3.38 ppm was attributed to -CH₂ and CH₃O- protons arising from PEGMA units [39–41]. The methyl protons for -OCH₃ in MMA units were at 3.55 ppm, while -CH₂O protons in PEGMA units appeared at 3.65 ppm [24, 32, 34]. Methylene protons of -CH₂OH in HEMA and -CH₂ in PEGMA gave a sharp signal around 4.2 ppm [38–41].

Figure 6 shows the DSC curves of P(HEMA-*co*-MMA) copolymers (**1b** and **1d**), recorded between 0–180°C. A substantial decrease in the glass transition temperature with increasing HEMA content was observed, which agreed with the literature [38]. The T_g of P(HEMA(20)-*co*-MMA(80)) (**1b**) and P(HEMA(50)-*co*-MMA(50)) (**1d**) were detected

FIGURE 4: ^1H -NMR spectra of P(HEMA-*co*-MMA) copolymers (**1a–1d**).TABLE 2: Compositions of P(HEMA-*co*-MMA) obtained from ^1H -NMR data.

Comonomers in feed (volume ratio) ^a	Comonomers in feed % HEMA/% MMA (mol %) ^b	Comonomers in polymer % HEMA/% MMA (mol %) ^c
HEMA(5)-MMA(95)	4.4/95.6	4.7/95.3
HEMA(20)-MMA(80)	18.1/81.9	18.5/81.5
HEMA(30)-MMA(70)	27.4/72.6	25.0/75.0
HEMA(50)-MMA(50)	46.9/53.1	49.1/50.9

^aby volume, ^bby moles, and ^ccalculated from ^1H -NMR.TABLE 3: Conditions^a and results for the synthesis of P(HEMA-*co*-MMA)-*block*-PPEGMA.

Entry	Macroinitiator	P(HEMA- <i>co</i> -MMA)- <i>block</i> -PPEGMA	^b $M_{n,\text{GPC}}$	^c $M_{n,\text{theo}}$	^d M_w/M_n
1	(1b)	(2b)	112620	108080	1.58
2	(1d)	(2d)	58040	60440	1.39

^a[MeOH]/water = 2:1 v/v, [M]/[I]/[CuBr]/[PMDETA]: 400/1/1/2; temperature: r.t. ^bdetermined from GPC measurements. ^ccalculated by using formula: $M_{n,\text{theo}} = M_{w,\text{monomer}} \times [\text{Monomer}]/[\text{Initiator}] \times \text{Conv.} + M_{w,\text{initiator}}$ ^d M_n : the number average molecular weight; M_w : the weight average molecular weight.

around 100°C and 57°C [38], respectively. PHEMA and PMMA homopolymers as well as their copolymers are amorphous and do not show any melting temperature, as expected. Figure 7 shows DSC analysis of P(HEMA-*co*-MMA)-*block*-PPEGMA (**2b** and **2d**), evaluated during the heating process from −48 to 180°C. P(HEMA-*co*-MMA)-*block*-PPEGMA shows a T_m due to the presence of crystalline domains originating from PPEGMA blocks. The presence of T_m at around 0°C supports the block copolymer formation. It is also noteworthy that T_m values for (**2b**) and (**2d**) are almost the same although different feed ratios of precursor

P(HEMA-*co*-MMA) were employed in the block copolymer formation, which might have resulted in an evident shifting of T_m since variation of HEMA and MMA content can possibly affect the crystallinity in the microstructure. However, a careful inspection reveals that the final copolymer content (in mol) of **2b** (HEMA/MMA/PEGMA ~ 1/4/22) and **2d** (HEMA/MMA/PEGMA ~ 4/4/22) is very close and the fact that T_m values are nearly the same is just as expected.

The thermal stabilities of P(HEMA-*co*-MMA) copolymers (**1b** and **1d**) and P(HEMA-*co*-MMA)-*block*-PPEGMA (**2b** and **2d**) block copolymers were analyzed as well, as

TABLE 4: Temperatures of various decompositions and char yield in N₂ at 750°C.

Sample	Temperature of 5% weight loss (°C)	Temperature of 10% weight loss (°C)	Temperature of the rapid weight loss $T_{\max}$ (°C)	Char yield at 750 (°C) in N ₂ (wt%)
P(HEMA(20)- <i>co</i> -MMA(80))	213	292	367	0
P(HEMA(50)- <i>co</i> -MMA(50))	184	251	371	0
P(HEMA(20)- <i>co</i> -MMA(80))- <i>block</i> -PPEGMA	185	277	327	0
P(HEMA(50)- <i>co</i> -MMA(50))- <i>block</i> -PPEGMA	298	334	350	0

FIGURE 5: The ¹H-NMR spectrum of P(HEMA-*co*-MMA)-*block*-PPEGMA (**2b**, **2d**). FIGURE 7: The DSC of P(HEMA-*co*-MMA)-*block*-PPEGMA (**2b**, **2d**). FIGURE 6: The DSC curves of P(HEMA(20)-*co*-MMA(80)) (**1b**) and P(HEMA(50)-*co*-MMA(50)) (**1d**) copolymers.

shown in Figure 8. The TGA curves of P(HEMA-*co*-MMA) copolymers with varying composition of HEMA indicated a thermal stability up to 340–350°C [38]. On the other hand, in the analysis of P(HEMA-*co*-MMA)-*block*-PPEGMA block copolymers, the decomposition temperatures are shifted to relatively lower values with the incorporation of PEGMA units.

The temperature of 5% weight loss, the temperature of 10% weight loss, the temperature of the rapid weight loss ($T_{\max}$) before 750°C, and the char yield at 750°C in nitrogen are summarized in Table 4.

FIGURE 8: TGA curves of P(HEMA-*co*-MMA) (**1b**, **1d**) and P(HEMA-*co*-MMA)-*block*-PPEGMA (**2b**, **2d**).

Propargyl side-functional block copolymers, alkyne-P(HEMA-*co*-MMA)-*block*-PPEGMA (**3b** and **3d**), were prepared by the Steglich esterification between hydroxyl groups of HEMA and propiolic acid in the presence of DCC and

FIGURE 9: The FT-IR spectra of P(HEMA-*co*-MMA)-*block*-PPEGMA (**2b**, **2d**) and alkyne-P(HEMA-*co*-MMA)-*block*-PPEGMA (**3b**, **3d**).

DMAP at room temperature [35]. The GPC analysis provided evidence for the success of reaction. As expected, there was a slight increase in the M_n values.

For P(HEMA(20)-MMA(80))-*b*-PPEGMA (**2b**), M_n changed from 112620 to 113350 (PDI = 1.53), while, for P(HEMA(50)-MMA(50))-*b*-PPEGMA (**2d**), there was a change from 58040 to 59514 (PDI = 1.39), which showed the incorporation of propargyl units.

Further proof was supplied by FT IR analysis as depicted in Figure 9. As compared to the spectrum of P(HEMA-*co*-MMA)-*block*-PPEGMA, two new bands (**2b**, **2d**) appeared at around 2350 and 3320 cm^{-1} in the spectrum of alkyne-P(HEMA-*co*-MMA)-*block*-PPEGMA (**3b**, **3d**), which were assigned to the stretching vibration of the alkyne group [35].

Finally, to assess the applicability of alkyne-P(HEMA-*co*-MMA)-*block*-PPEGMA in postfunctionalization, **3b** and **3d** having different molecular weights were click coupled with 2,3,4,5,6-pentafluorobenzyl azide. For this purpose, first, 2,3,4,5,6-pentafluorobenzyl azide was prepared upon reaction between their halo-compounds and NaN_3 in DMF at room temperature. The halogen atoms were substituted with azide groups via nucleophilic substitution. The FT-IR spectra are illustrated in Figure 10. The appearance of sharp $-\text{N}_3$ stretching bands between 2110 cm^{-1} and 2090 cm^{-1} for 2,3,4,5,6-pentafluorobenzyl azide supported that azidation was successful [32–36, 42, 43].

In the second step, Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) was carried out between propargyl side functionalities on the backbone and 2,3,4,5,6-pentafluorobenzyl azide. The ^1H -NMR spectra of the click products are illustrated in Figure 11. The appearance of the new signals at 7.64 (f) and 5.59 (e) ppm, regarding the methine proton and the methylene protons adjacent to the triazole ring, respectively, were observed [32, 34–36, 42, 43].

Further evidence for the incorporation of 2,3,4,5,6-pentafluorobenzene was provided by ^{19}F -NMR analysis as presented in Figure 12. The signals which appeared in the spectrum of 2,3,4,5,6-pentafluorobenzyl azide also existed in that of click product. The signals detected at -142 ppm, -151 ppm, and -161 ppm originated from the aromatic fluorines: 2F at *o*-position, 1F at *p*-position, and 2F at *m*-position, respectively [44].

FIGURE 10: The FT-IR spectra of 2,3,4,5,6-pentafluorobenzyl chloride and azido-2,3,4,5-pentafluorobenzene.

FIGURE 11: The ^1H -NMR spectra of the click product (**4**).

4. Conclusions

The strategy of combining ATRP with Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) in the preparation of a novel clickable amphiphilic block copolymer was demonstrated. First, P(HEMA-*co*-MMA) copolymers were prepared via ATRP. Molar ratio of MMA and HEMA was varied

FIGURE 12: (a) The ^{19}F -NMR spectra of click product; (b) the ^{19}F -NMR spectra of 2,3,4,5,6-pentafluorobenzyl azide.

to get random copolymers with different HEMA contents. The copolymer compositions were obtained from ^1H -NMR and agreed well with the charged monomer ratio in feed. Polymerization of poly(ethylene glycol) methyl ether acrylate was carried out via ATRP using P(HEMA(20)-*co*-MMA(80)) (**1b**) and P(HEMA(50)-*co*-MMA(50)) (**1d**) as macroinitiator to get block copolymers. GPC analysis of the obtained block copolymers was measured as $M_n = 112620$ (PDI = 1.58) and $M_n = 58040$ (PDI = 1.39), respectively. Both ^1H -NMR and FT-IR spectra showed peaks associated with MMA, HEMA, and PEGMA repeating units. Thermal properties of the copolymers and the block copolymers were also studied by TGA and DSC. For the copolymers, a thermal stability of up to 340–350°C was detected. In the next step, alkyne-P(HEMA-*co*-MMA)-*block*-PPEGMA (**3b**, **3d**) was prepared by the Steglich esterification between hydroxyl groups of HEMA and propionic acid in the presence of DCC and DMAP at room temperature. Finally, Cu(I) catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) was employed as a tool for postfunctionalization. The click coupling between propargyl side functionalities on the backbone and 2,3,4,5,6-pentafluorobenzyl azide were evidenced by ^1H -NMR and ^{19}F -NMR. This synthetic route might be useful in tuning the lengths of the hydrophilic and hydrophobic segments in amphiphilic polymers as well as the average number of functionalities situated in the side chain.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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