



Synthesis, characterization and bulk properties of well-defined poly(hexafluorobutyl methacrylate)-block-poly(glycidyl methacrylate) via consecutive ATRP



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ABSTRACT

A well-defined fluorine-containing copolymer with pendant epoxy groups, poly(2,2,3,4,4,4-hexafluorobutyl methacrylate)-block-glycidyl methacrylate (PHFBMA-*b*-PGMA), was prepared by sequential atom transfer radical polymerization (ATRP). The amphiphilic copolymer PHFBMA-*b*-PGMA(OH) with pendant hydroxyl groups was obtained after ring-opening reaction of the epoxy groups from PGMA. The macroinitiator agent PHFBMA-Br and its copolymers were proved to be successfully synthesized by characterization of FTIR, ¹H NMR and gel permeation chromatography (GPC). The chain growth experiment demonstrated that a linear first-order relationship was fitted under the conditions. In addition, the fluorinated copolymers with functional groups in the side chain could keep the contact angle and the advantages of fluoropolymers while improving the hydrophilic property. Meanwhile, TGA testing showed that the copolymers had better thermal stability than its homopolymer. TEM observation indicated that microspheres were embedded in the stable micelles when the final copolymer concentration of aqueous solution was 1 wt%.

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1. Introduction

Fluoropolymers with high electro-negativity and small fluorine atoms possess a number of unique features, such as high chemical and thermal resistance, oil and water repellence, low surface energy and low refractive index [1–3]. Additionally, fluorine monomers have good compatibility with other (methyl)acrylates and can be incorporated conveniently [4,5]. So many functional fluorinated polymers apply in various ways, such as surfactants, paints, biomaterials and lubricants, etc. [6–9].

To obtain multifunctional fluorinated polymers with well-defined structure and features, the most popular and efficient controlled/living radical polymerization (CLRP) techniques [10–14] are atom transfer radical polymerization (ATRP) with good controllability with monomers and well-defined property [15–18]. Many hydrophobic fluoropolymers are synthesized by ATRP method, such as poly(butyl methacrylate)-*b*-poly(perfluoroalkyl acrylate) (PBMA-*b*-PPFAA) [19], poly(styrene)-*b*-poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate) (PS-*b*-PHFBMA) [20], poly(methyl

acrylate)-*b*-poly(2,2,3,3,3-pentafluoropropyl acrylate) (PMA-*b*-PPFPA) [21], poly(2,3,4,5,6-pentafluorostyrene)-*b*-poly(styrene)-*b*-poly(2,3,4,5,6-pentafluorostyrene) (PFS-*b*-PS-*b*-PFS) [22], poly(hexafluorobutyl methacrylate)-*b*-poly(isobutyl methacrylate) (PHFMA-*b*-PIBMA) [23] and poly(ethylene oxide)-(o-nitrobenzyl)-poly[2-(perfluorooctyl)ethyl methacrylate]-*b*-poly(2-cinnamoyloxyethyl methacrylate) (PEO-ONB-PFOEMA-*b*-PCEMA) [24]. In addition, many amphiphilic fluorinated polymers also have been attracted significant research interest in many fields. For example, He et al. used hydroxyethyl methacrylate (HEMA) and trifluoroethyl methacrylate (TFEMA) as monomers to synthesize diblock copolymers by ATRP, and then compared the controllability of the polymerization process by using different ligands [25]; Luo et al. prepared well-defined diblock copolymers poly(dimethylsiloxane)-*b*-poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate) by ATRP and then investigated their self-assembly behavior with micro-phase-separation when containing enough PHFBMA segments [26]; Tan et al. synthesized well-defined fluorinated brush-like amphiphilic copolymers of methoxy poly(ethylene glycol)-*b*-poly[poly(ethylene glycol)methyl ether methacrylate]-*b*-poly(pentafluorostyrene) (PEO-*b*-PmPEGMA-*b*-PPFS) via ATRP method and studied the self-assembly behavior in aqueous solutions [27]; Guo et al. prepared novel amphiphilic fluorinated ABC-type

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triblock copolymers of poly[(ethylene oxide) monomethyl ether]-*b*-poly(styrene)-*b*-poly(perfluorohexylethyl acrylate) (mPEG-*b*-PS-*b*-PPFHEA) by ATRP [28]. Other amphiphilic copolymers synthesized by ATRP method include (Zonyl FSO-100)-*b*-poly[(ethylene glycol) methyl ether methacrylate] (FSO-*b*-PmPEGMA) [29], poly(1,1-dihydroperfluorooctyl methacrylate)-*b*-poly(2-dimethylaminoethyl methacrylate) (PFOMA-*b*-PDMAEMA) [30], poly(methyl methacrylate)-*b*-poly[(ethylene glycol)methyl ether methacrylate]-*b*-poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecyl methacrylate) (PMMA-*b*-PmPEGMA-*b*-PFM) [31], poly(acrylic acid)-*b*-poly[4-(4'-*p*-tolylxy perfluorocyclobutoxy)benzyl methacrylate] (PAA-*b*-PTPFCBBMA) [32], and so on. However, it is difficult to dissolve many fluoropolymers with excellent hydrophobicity and other advantages in common solvents, which greatly limits their application.

Some work have been reported about fluorinated copolymers with active groups by ATRP method. Davis et al. synthesized poly(pentafluorostyrene)-*b*-poly(glycidyl methacrylate) (PPFS-*b*-PGMA) using PGMA as the macro-RAFT agent and then hydrolyzed the epoxy groups to obtain amphiphilic copolymer [33]. Yu group prepared poly(2,2,2-trifluoroethyl acrylate)-*b*-poly(glycidyl methacrylate) (PTFEA-*b*-PGMA) diblock copolymer via sequential reversible addition-fragmentation chain transfer (RAFT) polymerization and then incorporated it into epoxy to form nano-structure thermosets [34]. However, few reports investigate the properties of fluorinated copolymers with many active groups on the side chain, especially obtaining active hydroxyl groups by ring-opening of epoxy groups to increase the hydrophilicity or to supply active sites. Fluorinated homopolymers with low initiating efficiency and poor compatibility with other hydrophilic polymer greatly limit their further research. So it is essential to investigate the mechanism of copolymerization by using fluoropolymer as initiator agent, and to prepare many functional polymers by post-modification of the active sites to broaden their application.

In this study, hexafluorobutyl methacrylate (HFBMA) was chosen as the fluorine-containing monomer. The other functional monomer was glycidyl methacrylate (GMA) with reactive pendant oxirane rings. Homopolymer poly(hexafluorobutyl methacrylate) was firstly synthesized by ATRP and then was used as macroinitiator to prepare copolymer poly(hexafluorobutyl methacrylate)-*b*-poly(glycidyl methacrylate), which was followed by ring-opening reaction. The aim of this work is to investigate the polymerization kinetic of the fluorinated homopolymer and the surface property of the as-prepared fluorinated copolymers. The surface property and the thermal stability of the polymers were investigated as well. The copolymers with epoxy groups and hydroxyl groups would provide many active sites to prepare many novel materials, and this work is currently in progress.

2. Results and discussion

The copolymer was prepared by consecutive ATRP method after monomer HFBMA was transformed into the macroinitiator agent PHFBMA-Br, and then hydrolyzed the epoxy groups on PGMA conducted in the present of the acid. The scheme for the synthesis of well-defined copolymers is shown in Scheme 1. And the polymerization result and structural parameter are summarized in Table 1.

2.1. ATRP polymerization of PHFBMA-Br and PHFBMA-*b*-PGMA

The macroinitiator PHFBMA-Br was prepared in cyclohexanone at 75 °C with CuBr/Bpy as catalyst and ethyl 2-bromoisobutyrate as initiator. The ¹H NMR spectrum of PHFBMA is shown in Fig. 1a. The characteristic peaks of PHFBMA can be observed at

0.9–1.2 ppm and 1.8–2.0 ppm, corresponding to the methyl (CH₃) and methylene (CH₂) groups in the polymer backbone. The peaks of 4.3–4.4 ppm and 4.8–5.0 ppm are corresponding to –OCH₂– and –CHF–, while the peaks of 5.67 ppm and 6.20 ppm (vinyl group in the monomer) are not presented in the spectrum. Fig. 2a shows the FTIR spectrum of homopolymer PHFBMA from ATRP. The characteristic band at 1750 cm⁻¹ corresponds to ester carbonyl (C=O) bonds, the peaks at 1290 cm⁻¹ (ν_s(CF₂) + r(CF₂)) and 1190 cm⁻¹ (ν_s(CF₂) + δ(CF₂)) are ascribed to the characteristic absorbance of –CF₂ and two medium bands at 685 cm⁻¹ and 723 cm⁻¹ are assigned to a combination of rocking and wagging vibrations of C–F [19]. Two characteristic bands at 3000–3100 cm⁻¹ and 1650 cm⁻¹ (stretching vibration of C=C bond) disappear. The NMR result and FTIR spectroscopy confirmed that the homopolymer was successfully prepared. Meanwhile, the typical GPC trace of homopolymer is shown in Fig. 3a, revealing a unimodal and symmetric elution peak. Comparing to the results of the molecular weight in Table 1, the number average molecular weight (20, 300 g mol⁻¹) of PHFBMA-Br tested by GPC is higher than that (18, 900 g mol⁻¹) calculated by ¹H NMR. This could be attributed to the difference of the hydrodynamic volume of PHFBMA to that of PS used for the calibrating the GPC columns.

The controlled polymerization of block copolymer was confirmed by comparing the ¹H NMR spectra of PHFBMA-*b*-PGMA (Fig. 1b) and PHFBMA (Fig. 1a). Additional peaks are observed at 3.21 ppm, 2.82 ppm and 2.62 ppm, corresponding to the methine protons and methylene protons on the epoxy ring. The peak of 3.78 ppm is attributed to the methylene protons near the ester groups, while the peak 4.30 ppm is a mixed peak of the methene protons copolymer of GMA and HFBMA. Meanwhile, FTIR spectrum of diblock PHFBMA-*b*-PGMA in Fig. 2b is clearly observed the characteristic band of epoxy group at 907 cm⁻¹, 844 cm⁻¹ and 755 cm⁻¹. The apparent number-average molecular weight and molecular weight distribution of diblock polymer are presented in Table 1, and the GPC trace is shown in Fig. 3b. It is obvious that the curve of block polymer is symmetric and nearly unimodal and the position of peak shifts toward high molecular weight compared with its precursor. The chain extension was further demonstrated well-controlled ATRP of copolymer.

2.2. Polymerization kinetic of PHFBMA-*b*-PGMA

The polymerization kinetic of chain growth experiment was investigated from ¹H NMR and GPC to better understand the controlled character of the polymerization macroinitiator PHFBMA. The monomer conversion was obtained by contrasting the sum of the peak intensity for the double bond protons (5.86 and 6.18 ppm) and that of the epoxy protons at 3.27 ppm of GMA. The molecular weight and PDI of all samples by intermittent sampling method were also applied for GPC testing.

On the basis of the results of ¹H NMR and GPC, the relationship of monomer conversion and ln([M]₀/[M]_t) with copolymerization time was conducted at [GMA]₀/[I]₀/[Cu(I)Cl]₀/[PMDTA]₀ = 80:1:1:2.3. It can be seen from the semilogarithmic kinetic plots for copolymerization of PHFBMA-*b*-PGMA in Fig. 4 that the monomer conversion increases with time increasing and reaches a relatively high value (>90%) after 20 h. As shown in Fig. 4, ln([M]₀/[M]_t) is proportional to the copolymerization time, which indicated that the copolymerization reaction could be expressed by the first-order reaction kinetic model under the conditions. This demonstrated that the copolymerization rate was proportional to monomer conversion and also indicated that the concentration of growing radicals remained constant during the copolymerization as well as no detectable termination occurred in the polymerization [16,35]. Therefore, the macroinitiator agent PHFBMA-Br has enough initiator capability to promote the copolymerization

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