



Synthesis and characterization of fluorinated diblock copolymer of 2,2,2-trifluoroethyl methacrylate and methyl methacrylate based on RAFT polymerization



Guanghan Li^{a,b,c}, Anhou Xu^{a,b,c}, Bing Geng^{a,b,c}, Shuaishuai Yang^{a,b,c}, Guangxing Wu^{a,b,c}, Shuxiang Zhang^{a,b,c,*}

^a School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China

^b Shandong Key Laboratory of Fluorine Chemistry and Chemical Engineering Materials, Jinan 250022, China

^c Shandong Engineering Research Center for Fluorinated Material, Jinan 250022, China

ARTICLE INFO

Article history:

Received 27 December 2013

Received in revised form 17 June 2014

Accepted 30 June 2014

Available online 6 July 2014

Keywords:

Fluorinated acrylate

Diblock copolymer

Reversible addition–fragmentation chain transfer (RAFT)

2,2,2-Trifluoroethyl methacrylate (TFEMA)

Controlled copolymer

ABSTRACT

A fluorinated diblock copolymer of methyl methacrylate (MMA) and 2,2,2-trifluoroethyl methacrylate (TFEMA) was prepared by reversible addition–fragmentation chain transfer (RAFT) polymerization in the presence of cumyl dithiobenzoate (CDB) as the chain transfer agent (CTA). ¹H NMR spectroscopy, Fourier transform infrared spectroscopy, gel permeation chromatography and differential scanning calorimetry were used to characterize the block copolymers obtained. Contact angle measurement indicated that the diblock copolymer has considerable hydrophobicity ($\theta_{\text{water}} = 104.3^\circ$) and lipophobicity ($\theta_{\text{oil}} = 80.0^\circ$). The results are almost the same as those for PTFEMA and superior to those for a random copolymer of MMA and TFEMA. It was also found that P(MMA-*b*-TFEMA) has high thermostability. The self-assembly behaviour of the copolymer in selective solvents was evaluated by SEM, and stable micelles with a diameter of 400–600 nm were observed when the copolymer content was approximately 0.2 wt.%. Comparison studies with P(MMA-*b*-TFEMA), PTFEMA and PMMA revealed that the copolymer with a controllable distribution of fluorine atoms possesses a good performance.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Fluorinated polymers and copolymers have received significant attention over the past several decades due to their high thermal stability, superb chemical resistance, excellent mechanical properties at extreme temperatures, superior weatherability, superb oil and water repellence, low flammability and low refractive index [1,2]. Fluorinated monomers have been used in diblock copolymers, where they are expected to feature the merit of good miscibility with each monomer and possess the desirable property of residing at the interface of the two phases.

The fluorinated acrylate polymers cannot only exhibit the characteristics of acrylate polymers but also possess the excellent properties of fluoropolymer to a certain extent. However, the main applications of such polymers are still limited because the traditional free radical polymerization is liable to chain termination and chain transfer. Thus, the product's molecular structure

cannot be well controlled, preventing the distribution of fluorinated monomers from being adjusted. The properties of the resulting polymers with a wide molecular weight distribution are poor [3].

Living polymerization has recently emerged as one of the more effective synthetic routes to well-defined polymers. Over the past decade, great progress has been made in controlled/living free radical polymerization, such as nitroxide-mediated free radical polymerization (NMP) [4], atom transfer radical polymerization (ATRP) [5] and reversible addition–fragmentation chain transfer (RAFT) [1,3,6–9]. Simple, easily realized polymerization conditions and a straightforward polymerization process are huge advantages of RAFT polymerization. Compared to the conventional radical polymerization, RAFT polymerization generally only introduces a small amount of CTA [10–12]. In theory, RAFT polymerization can achieve the conditions of the ordinary radical polymerization without changing the polymerization system. This provides an excellent opportunity for the development of the controlled radical (co)polymerization of fluoromonomers [3] and its industrialization. In addition, the RAFT process is suitable for most monomers, including carboxylic acid, carboxylic acid salt, hydroxyl, amino and

* Corresponding author at: School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, China. Tel.: +86 531 89736365; fax: +86 531 89736365.

E-mail addresses: chm_zhangsx@ujn.edu.cn, fhx_zhangsx@163.com (S. Zhang).

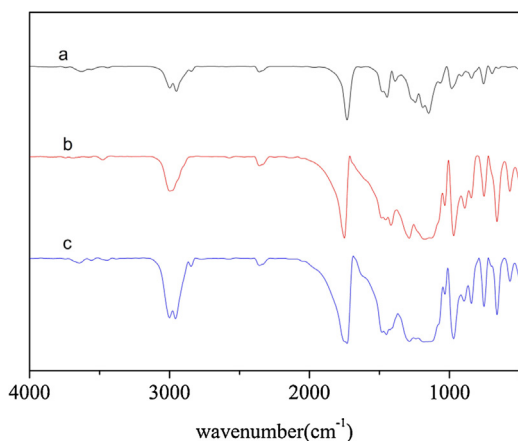


Fig. 1. FT-IR spectra of PMMA (a), PTFEMA (b) and P(MMA-b-TFEMA) (c).

other monomers with functional groups or fluorinated groups [1]. The polymerization of methyl acrylic acid ester monomers has always been accompanied by disproportionation and hydrogen transfer reaction, which readily leads to a wide molecular weight distribution, whereas this side reaction is so rare that it can almost be ignored in the RAFT method.

There have been several reports on the RAFT polymerization of fluorinated acrylate. Koiry [13] reported the RAFT polymerization of 2,2,3,3,4,4,4-heptafluorobutyl acrylate, and Guo [14] described the RAFT polymerization of 2,2,3,4,4,4-hexafluorobutyl methacrylate and 2,2,2-trifluoroethyl methacrylate. The copolymerization of fluorinated acrylate based on RAFT has also been reported [15–18]. However, the literature on the RAFT polymerization of 2,2,2-trifluoroethyl methacrylate (TFEMA) with other acrylates, especially methyl methacrylate (MMA), is very limited [19–22]. All of the existing reports on the controlled/living free-radical polymerization of the copolymer of TFEMA and MMA are based exclusively on ATRP [22]. In this study, we describe a preliminary study in which we applied RAFT polymerization to synthesize controlled block polymers. Here, we use MMA, which has similar properties to TFEMA, to prepare the macromolecular chain transfer agent and then apply it to control the polymerization of TFEMA, which was used as a fluoromonomer, to produce a fluorine-nonfluorine block polymer. In this way, we can retain the excellent properties of the fluorine-containing acrylate polymer and broaden

its application range. The structure and performance of product were investigated as well.

2. Results and discussion

2.1. Characterization of PMMA, PTFEMA and P(MMA-b-TFEMA)

CDB was selected as the RAFT agent, as it had been confirmed to be effective in the polymerization of methacrylate monomers. The formation of a narrow-polydispersity AB block copolymer requires that the first-formed polymeric thiocarbonylthio compound have a high transfer constant in the subsequent polymerization so that the B block can be consumed. Thus, the methyl methacrylate block was prepared first when we prepared the block copolymer.

The FT-IR spectra of the PMMA (a), the PTFEMA (b) and P(MMA-b-TFEMA) (c) are shown in Fig. 1. Here, we emphasized the analysis of the copolymer. The characteristic stretching peaks of C–H and C=O groups were clearly observed at $2850\text{--}3000\text{ cm}^{-1}$ and 1732 cm^{-1} , respectively. The peaks at 1450 and 1400 cm^{-1} were the two characteristic bands of C–H in $-\text{CH}_3$ in the copolymer. In addition, the bands at 666 cm^{-1} and 754 cm^{-1} were attributed to the band vibration of C–F in $-\text{CF}_3$ and the $-\text{CH}$ of the phenyl group of the end group [23].

Fig. 2(a) shows the ^1H NMR spectrum of the PMMA homopolymer. The signals at $7\text{--}7.5\text{ ppm}$ are characteristic of the two aromatic protons ortho to the dithio group, indicating that the RAFT agent moiety remains at the end of the polymer. These signals can be found in the ^1H NMR spectrum of the two-block copolymer P(MMA-b-TFEMA) (b). The signal at $\delta = 3.67\text{ ppm}$ is characteristic of $-\text{O}-\text{CH}_3$ of PMMA, and that at $\delta = 4.65\text{ ppm}$ corresponds to $-\text{O}-\text{CH}_2-\text{CF}_3$ of P(MMA-b-TFEMA). The other signals are characteristic of the H of the groups; for example, $\delta = 0.8\text{--}1.3\text{ ppm}$ corresponds to $-\text{CH}_3$, and $\delta = 1.7\text{--}2.1\text{ ppm}$ corresponds to $-\text{CH}_2-$ [23].

The two-step polymerization has been confirmed by GPC. Fig. 3 and Table 1 show the molecular weights and molecular weight distributions (MWDs) of polymers. As shown in Fig. 2, PMMA-CTA was synthesized with a narrow MWD of 1.09. After reacting with TFEMA, a significant shift toward higher molecular weight could be observed in the GPC chromatograms, while the MWD remains narrow at approximately 1.27. The molecular weight and the MWD of the homopolymer and copolymer have been given in Table 1. The molecular weight of the polymer is almost the same as the theoretical value.

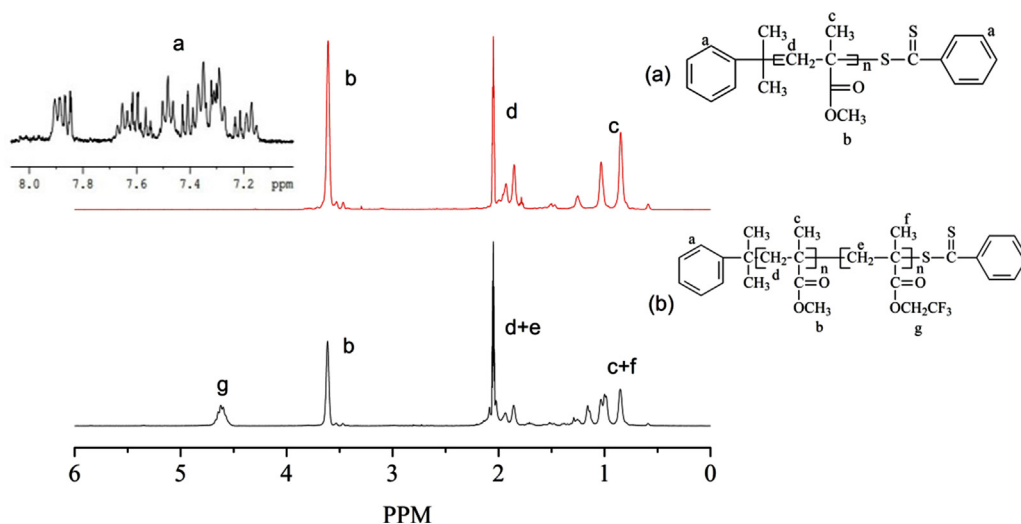


Fig. 2. ^1H NMR spectrum of PMMA (a) and P(MMA-b-TFEMA) (b).

Download English Version:

<https://daneshyari.com/en/article/1313989>

Download Persian Version:

<https://daneshyari.com/article/1313989>

[Daneshyari.com](https://daneshyari.com)