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Synthesis of fluorine-containing block copolymers via ATRP 2. Synthesis and characterization of semifluorinated di- and triblock copolymers☆

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Abstract

A series of semifluorinated fluorocarbon/hydrocarbon di- and triblock copolymers were prepared by atom transfer radical polymerization (ATRP). The mono- and difunctional macroinitiators, which were obtained from bulk ATRP of styrene, butyl acrylate and methyl acrylate, initiated solution ATRP of 2-[(perfluorononenyl)oxy]ethyl methacrylate and ethylene glycol mono-methacrylate mono-perfluorooctanoate, respectively. The formation of the block copolymer was confirmed with size exclusion chromatography and ^{1}H NMR spectrum. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Atom transfer radical polymerization; Semifluorinated block copolymer

1. Introduction

Control over polymeric material properties implies controlling the molecular structure of the constituent macromolecules. Living polymerization techniques allow the preparation of polymers with narrow molecular weight distribution and the synthesis of block copolymers by the sequential addition of different monomers [1–4]. Anionic, cationic and group transfer polymerization are widely applied methods. However, these techniques have been limited by the need for high-purity monomers and solvents, reactive initiators and anhydrous conditions. In contrast, free radical polymerization process is easy to operate and can be readily performed in bulk or in solution. More recently, atom transfer radical polymerization (ATRP) [5,6] has been developed as a new route to well-controlled polymers.

Amphiphilic block copolymers are of considerable interest for various applications. They may be utilized as emulsifiers, dispersion stabilizers, and compatibilizers. In particular, block copolymers composed of fluorocarbon–hydrocarbon segments exhibit their own unique properties such as excellent chemical and thermal stability, low surface energy, and low refractive index and dielectric constant, which cannot be achieved by the corresponding non-fluorinated materials [7,8].

Previously, we reported the synthesis of PSt–PVDF–PSt triblock copolymers using ATRP technique [9]. In this article, we describe how well-defined semifluorinated di- and triblock copolymers may be prepared by the ATRP route.

2. Experimental

2.1. Materials

Styrene (St), methyl acrylate (MA) and butyl acrylate (BA) were washed with 5% NaOH and ion-free water, dried over $CaCl_2$ overnight, and then vacuum distilled from finely powdered CaH_2 before use. 1-Bromoethyl benzene (1-BrEB) (Acros, 97%) was used as received. CuBr (AR, Shanghai No. 1 Chemical Reagent Factory) was purified according to the procedure of Keller and Wycoff [10]. Benzotrifluoride (BTF) (Fluka, 99%) was used as received. α,α'-Bispyridine (bpy) (AR, Shanghai No. 1 Chemical Reagent Factory) was recrystallized from *n*-hexane. α,α'-Dibromo-*p*-xylene (DBX) was prepared as reported [11]. β-Hydroxyethyl methacrylate (HEMA) (Fluka, 95%) was used as received. Hexafluoropropylene trimer and perfluorooctanoic acid were kindly supplied from Shanghai Institute of Organo-fluorine Materials. 2-[(Perfluorononenyl)oxy]ethyl methacrylate (FNEMA) and

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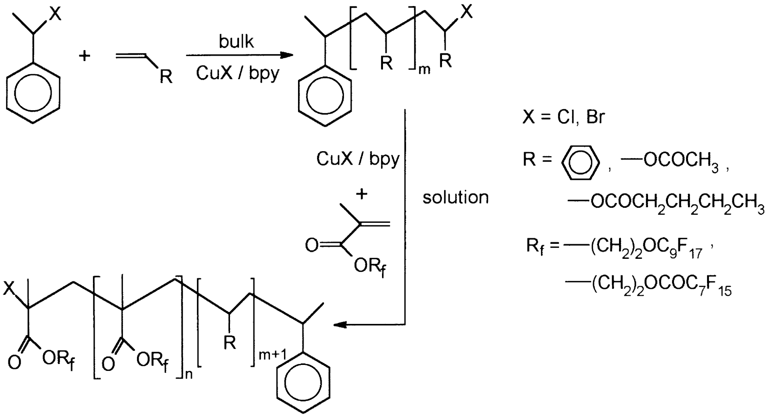


Scheme 1. Synthesis of fluorocarbon/hydrocarbon diblock copolymers by ATRP.

ethylene glycol mono-methacrylate mono-perfluorooctanoate (EGMAFO) were synthesized by the reaction of hexafluoropropylene trimer and perfluorooctanoic acid with β-hydroxyethyl methacrylate, separately [12,13].

2.2. Polymerization procedure

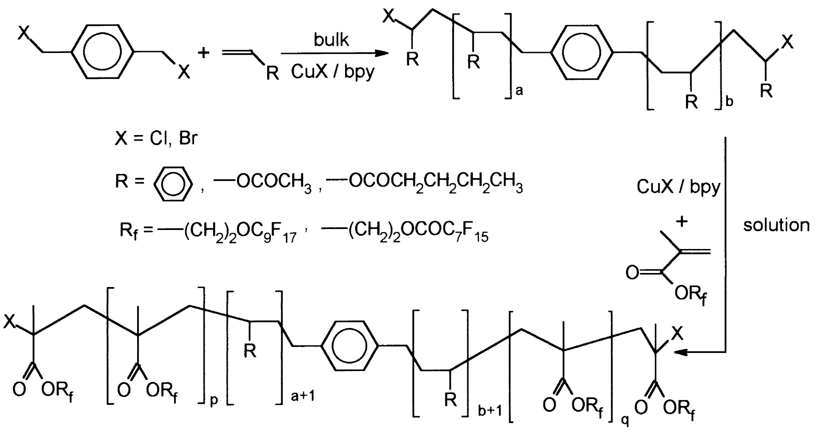
Catalyst, initiator and ligand were added to a 50 ml one-neck round bottom flask equipped with a stopcock and a magnetic stirring bar. The reaction flask was tightly sealed with a rubber septum, degassed under vacuum, and charged with nitrogen (three times). The monomers and solvents were purged with nitrogen just before use, and then introduced by syringe. The reaction mixture was immersed in an oil bath heated at the desired temperature. The polymers were isolated by precipitation with methanol. Samples for GPC measurement were purified by passing through a column of alumina.

2.3. Characterization

Monomer conversion was determined gravimetrically. Molecular weight and molecular weight distribution were measured on a Waters 150C gel permeation chromatography equipped with Ultrastyragel columns of 100 Å, 10 000 Å porosities using tetrahydrofuran as eluent. Narrow molecular weight distribution polystyrene standards were used for calibration. Copolymer structures were analyzed using a Bruker 500 MHz ^{1}H NMR spectrometer. $CDCl_3$ was used as solvent.

3. Results and discussion

Transition metal catalyzed ATRP seems to be one of the most robust systems in the reported “living”/controlled radical polymerization, and can be used for larger number of monomers. ATRP also gives a good control over chain topologies, compositions and functionalities and uses many initiators and macroinitiators with halogen atoms activated by aryl, allyl, sulfone or carbonyl groups. ATRP can be applied to block copolymer synthesis in two ways. The first is the simple addition of a second monomer to the reaction medium after nearly complete consumption of the first monomer. The second method involves the isolation and purification of the first polymer, then using it as a macroinitiator. Although the first method is easy to operate, the second block is not pure. In this article, the fluorinated



Scheme 2. Synthesis of fluorocarbon/hydrocarbon triblock copolymers by ATRP.

Table 1
Synthesis of mono- and di-functional bromine endcapped macroinitiators by ATRP[a]

Sample	Reaction temperature (°C)	Reaction time (h)	$M_{n,SEC}$	M_w/M_n
PSt–Br	110	5	7816	1.29
PBA–Br	110	6	14 013	1.53
PMA–Br	80	6	11 039	1.48
Br–PSt–Br	110	5	6242	1.37
Br–PBA–Br	110	6	9742	1.48
Br–PMA–Br	80	6	12 925	1.33

[a] Bulk polymerization: $[St]_0 = 8.70$ M; $[BA]_0 = 6.98$ M; $[MA]_0 = 11.1$ M; $[1\text{-BrEB}]_0 = 0.11$ M; $[DBX]_0 = 0.13$ M; R–Br or Br–R–Br/CuBr/bpy = 1:1:3 (mole ratio).

block copolymers were prepared according to the second approach. The first hydrocarbon block was obtained from bulk ATRP of styrene, methyl acrylate and butyl acrylate, separately. After isolation, purification and characterization, it was used as a macroinitiator to initiate ATRP of fluorinated methacrylates, thus the second fluorocarbon block was formed (Schemes 1 and 2).

3.1. Synthesis and characterization of macroinitiators

Mono- and di-functional bromine endcapped macroinitiators were prepared by bulk ATRP of styrene, butyl acrylate and methyl acrylate in the presence of 1-bromoethyl benzene or α,α′-dibromo-*p*-xylene/cuprous bromide/α,α′-bispyridine (1/1/3) at 110°C and 80°C, respectively. The experimental molecular weights and molecular weight distribution of the macroinitiators are listed in Table 1.

3.2. Synthesis and characterization of the block copolymers containing FNEMA segments

The block polymerization were performed using bromine terminated polystyrene (PSt), polybutylacrylate (PBA) and polymethylacrylate (PMA) as macroinitiators, separately. Size exclusion chromatography (SEC) showed that the molecular weight of copolymer increased after the polymerization. The monomodel shape of the SEC trace of the obtained polymer suggests the formation of block copolymer without homopolymerization (Fig. 1). As shown in Table 2, the polydispersities of the resulting block copolymers were lower than those of the starting macroinitiators except bromine endcapped polystyrene. There might be two main reasons resulting in broadening the molecular weight distributions of St–FNEMA block copolymers: (1) The C–Br bond originated from styrene unit is not as weak as that from the acrylate unit; (2) FNEMA is a non-solvent for polystyrene. Thus, the factors of structure and solubility led to a slow initiation process. Moreover, it has to be noted that the $M_{n,SEC}$ (determined by GPC with polystyrene standards) were expected to be lower than the $M_{n,th}$ (calculated from the equation: $M_{n,th} = ([M]_0/[I]_0 \times MW_0 \times \text{conv.} + M_I)$. Presumably, the strong aggregation in tetrahydrofuran solvent of fluorinated blocks leads to smaller hydrodynamic volumes relative to the base block copolymers.

The ^{1}H NMR spectrum of PFNEMA–PSt–PFNEMA triblock copolymer is depicted in Fig. 2. The signals at 4.13 ppm correspond to the two methylenes of the ester group of FNEMA, and the peaks at 6.6 and 7.1 ppm can be assigned to the aromatic protons in the styrene units. On the basis of the ratio of the area of the two peaks and the molar mass of Br–PSt–Br, the chemical composition of

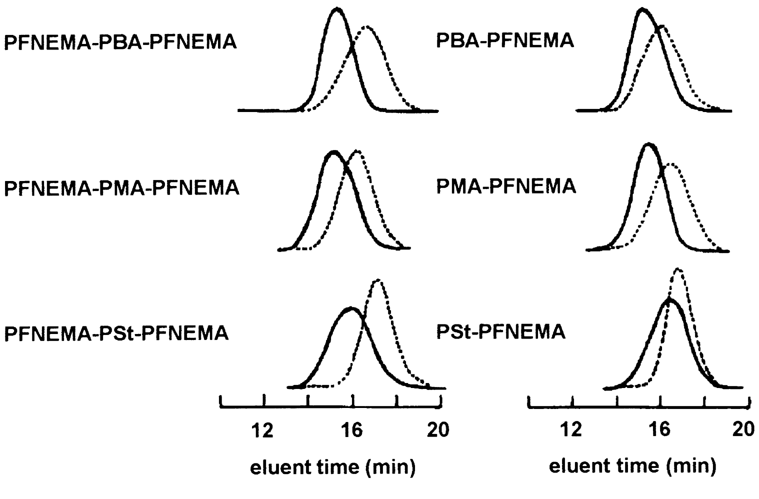


Fig. 1. GPC traces of macroinitiators (--) and the produced block copolymers (—) described in Table 2.

Table 2
Results of block copolymerization of FNEMA with polystyrene, poly(butyl acrylate) and poly(methyl acrylate)[a]

Sample	Reaction time (h)	Conversion[b](%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n	Yield[c] (%)
PSt-b-PFNEMA	20	60.8	19 111	12 326	1.45	72.4
PBA-b-PFNEMA	24	49.7	30 566	28 660	1.34	64.6
PMA-b-PFNEMA	24	55.9	31 745	27 148	1.29	66.1
PFNEMA-b-PSt-b-PFNEMA	20	59.8	23 996	13 438	1.49	66.8
PFNEMA-b-PBA-b-PFNEMA	24	59	37 076	25 519	1.27	66.1
PFNEMA-b-PMA-b-PFNEMA	20	54.1	46 178	28 336	1.31	62.1

[a] Solution polymerization: $[FNEMA]_0 = 0.57$ M; $[PSt–Br]_0 = 1.7 \times 10^{-2}$ M; $[PBA–Br]_0 = 9.5 \times 10^{-3}$ M; $[PMA–Br]_0 = 8.57 \times 10^{-3}$ M; $[Br–PSt–Br]_0 = 1.1 \times 10^{-2}$ M; $[Br–PBA–Br]_0 = 6.84 \times 10^{-3}$ M; $[Br–PMA–Br]_0 = 5.16 \times 10^{-3}$ M; MI/CuBr/bpy = 1:5:14; Reaction temperature, 100°C.

[b] Conversion of monomer, calculated from the weight ratio of converted monomer to added monomer.

[c] Yield of block copolymer equals the weight of obtained copolymer divided by the total weight of added monomer and macroinitiator.

block copolymer was calculated: [St]:[FNEMA] = 65.2:34.8, which was in good agreement with the theoretical value ([St]/[FNEMA] = 65.4/34.6), corrected for the amount of unconverted FNEMA.

3.3. Synthesis and characterization of the block copolymers containing EGMAFO segments

The block copolymerization procedure was the same as described earlier. The SEC traces of macroinitiators and block copolymers are plotted in Fig. 3. An interesting phenomenon was observed that there was a high molecular weight (MW) tail in the molecular weight distribution, what is more, a high MW shoulder appeared in the SEC trace of the block copolymer containing styrene segments. This might indicate irreversible termination, e.g. by recombination of radicals. The process would lead to doubling of the MW, i.e. to a significant high MW shoulder in the SEC traces, and to decreasing the number of chains in the polymerization system. As shown in Table 3, the polydispersities of all block copolymers were broader than those of the macroinitiators. This further confirmed that permanent deactivation (e.g. termination, activity loss by any kind of reactions) of the propagating species occurs during the polymerization period. Similar results were obtained from atom transfer radical homopolymerization of EGMAFO [14]. The precise molecular weights of the copolymers could not be determined directly from SEC data, owing to the difference in hydrodynamic volumes between block copolymers and linear polystyrene standards.

The ^{1}H NMR spectrum of PMA-b-PEGMAFO is shown as Fig. 4. The methoxy group in MA unit gives a signal at 3.66 ppm. The methylene groups next to the ester moiety in EGMAFO unit result in the signals around 4.23 and 4.56 ppm. The composition of block copolymer ([MA]:[EGMAFO] = 75:25, found by ^{1}H NMR) corresponded very well to the calculated value ([MA]:[EGMAFO] = 75.4:24.6).

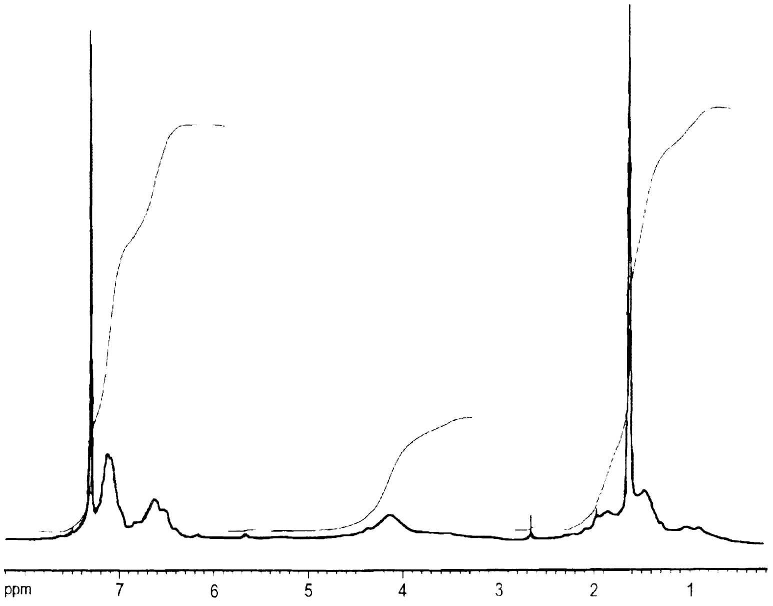


Fig. 2. 500 MHz ^{1}H NMR spectrum of PFNEMA-b-PSt-b-PFNEMA prepared by ATRP.

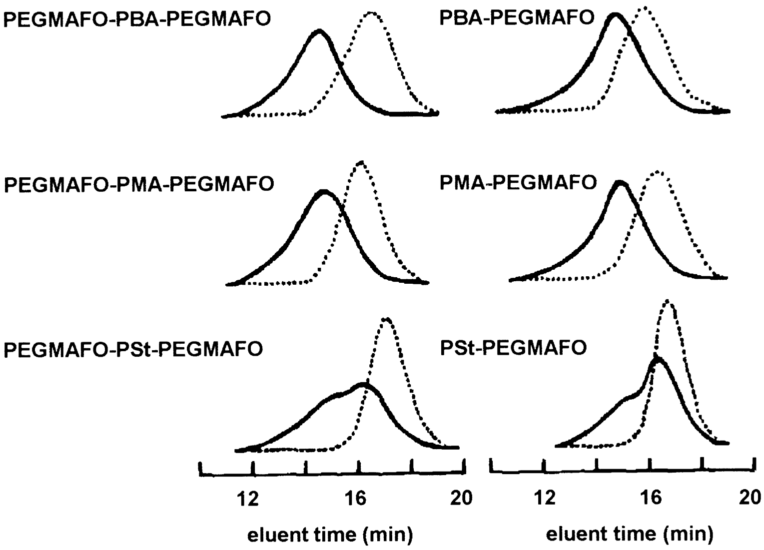


Fig. 3. GPC traces of macroinitiators (--) and the produced block copolymers (—) described in Table 3.

Table 3
Results of block copolymerization of EGMAFO with polystyrene, poly(butyl acrylate) and poly(methyl acrylate)[a]

Sample	Reaction time (h)	Conversion (%)	$M_{n,th}$	$M_{n,SEC}$	M_w/M_n	Yield (%)
PSt-b-PEGMAFO	30	60.8	19 001	13 605	2.0	72.1
PBA-b-PEGMAFO	24	47.9	29 912	39 336	2.3	63.3
PMA-b-PEGMAFO	24	68	36 125	40 806	2.0	75.4
PEGMAFO-b-PSt-b-PEGMAFO	24	66	25 774	16 161	2.41	71.9
PEGMAFO-b-PBA-b-PEGMAFO	24	59.3	37 118	36 745	2.0	66.4
PEGMAFO-b-PMA-b-PEGMAFO	20	64.4	52 383	45 125	1.70	70.6

[a] Solution polymerization: $[EGMAFO]_0 = 0.6$ M; for other conditions, see Table 2.

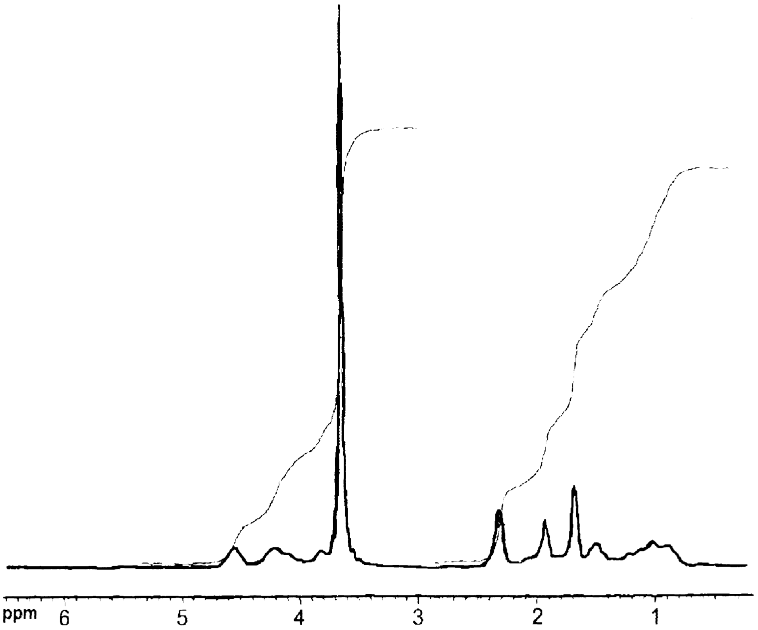


Fig. 4. 500 MHz ^{1}H NMR spectrum of PMA-b-PEGMAFO prepared by ATRP.

4. Conclusion

Several semifluorinated fluorocarbon/hydrocarbon di- and triblock copolymers were prepared by atom transfer radical polymerization. The formation of the block copolymer was supported by analysis of SEC and ^{1}H NMR. These block copolymers have great potential to be used as emulsifiers, surfactants, oil- and water-repellent agents. The study on the surface physical and chemical properties of the block copolymers is in progress in our laboratory.

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