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Controlled one-step synthesis of a diblock copolymer

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Abstract

Well-defined block copolymers were obtained from 4-hydroxy-butyl-2-bromoisobutyrate dual initiator, combining *tert*-butylmethacrylate ATRP and ε-caprolactone ROP in a one-step process. Using $AlEt_3$ as coinitiator in a ROP catalytic process, the variation of the $AlEt_3$/initiator ratio permits to modulate the ROP rate and so to control the final block copolymer composition. Nevertheless, slight interferences between the two polymerizations were observed.

Keywords: Dual initiator; Atom transfer radical polymerization; Coordinated anionic polymerization; One-step polymerization; Block copolymers

1. Introduction

The synthesis of block copolymers from monomers which polymerize by different mechanisms still remains difficult and constraining. For this purpose, the dual initiator route seems to be promising. A dual initiator (also called double-headed or heterobifunctional) bears two functional groups able to initiate independently and selectively two different polymerizations. Two approaches can be used:

- The sequential (two-step) process in which at least one initiating group can initiate a polymerization without interferences with the second initiating group, leading so to an intermediate macroinitiator.
- The one-step process, much more constraining, in which the two initiating groups must initiate selectively and simultaneously two independent polymerizations. It implies (i) no interactions between the initiating groups, the eventual catalysts or coinitiators and the monomers (ii) the two polymerization rates must be similar in the same experimental conditions (solvent, temperature).

Several articles have reported the use of a dual initiator in the two-step process for the synthesis of well-defined diblock copolymers, using combinations such as ATRP-NMP [1,2], ROP-ATRP [3–5], NMP-ROP [6–8], cationic-NMP [9], cationic-ATRP [10], cationic-anionic [11], ROP-photoinduced CTC [12]. We have also used this strategy to prepare triarm (or miktoarm) star block copolymers from a heterobifunctional macroinitiator [13–15].

Only few works have been done on the synthesis of block copolymers in a one-step process. Sogah et al. [9] (cationic and NMP), Hedrick et al. [5] (ROP and

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ATRP) and most recently Heise et al. [3] (enzymatic ROP and ATRP) have proved the feasibility of such syntheses. In these one-step process, as the two polymerization rates are very different, the final composition of the copolymer can only be modulated by the initial feed.

In this paper we report the one-step controlled synthesis of a block copolymer by using a dual initiator able to initiate the polymerizations of ε-caprolactone (CL) (through a hydroxyl function, in the presence of triethylaluminium in a catalytic process) and *tert*-butylmethacrylate (tBuMA) (through a tertiary bromide function, in the presence of CuBr/bipy$_2$). As the ROP rate in this catalytic process can be easily modified by varying the ratio AlEt$_3$/initiator, the final copolymers compositions can be so, for the first time, controlled. Slight interferences between the two catalyst systems were nevertheless observed.

2. Experimental part

2.1. Characterizations

Size exclusion chromatography was carried out using a Waters 2690 liquid chromatograph equipped with three columns, Waters Styragel 5 μm, 10^4, 500 and 100 Å (columns, injection and refractometer temperature, 35 °C; injection volume, 100 μl; solvent, THF at 1 ml/min), a refractive index detector (Waters 410) coupled with a UV/vis photodiode array detector (Waters 996). It was calibrated with PS standards. ^{1}H NMR spectra were recorded on a 400 MHz spectrometer (Brucker AC 400) using CDCl$_3$ as a solvent.

2.2. Materials

2-bromo-2-methylpropionyl bromide (98%, Aldrich 25,227-1), 2,2′-bipyridyl (>98%, Fluka 14453), 1,4-butanediol (99%, Acros 10763 0010), triethylaluminum (TEA, 0.9 M in hexane, purum, Fluka 90320), triethylamine (99.5%, Aldrich 47,128-3) were used as received. *Tert*-butylmethacrylate (tBuMA, 98%, Aldrich 46,335-3) and ε-caprolactone (CL, 99%, Aldrich 16,736-3) were dried over CaH$_2$ and distilled under vacuum just before use. Tetrahydrofuran (THF, 99.5%, SDS 0700248) and toluene (>99.5%, Fluka 89861) were distilled over CuCl/NaOH and over sodium, and stored over sodium and benzophenone. They were distilled and degassed by bubbling nitrogen for 15 min just before use. Copper (I) bromide (98%, Aldrich 21,286-5) was purified according to a published procedure [16].

2.3. Synthesis of 4-hydroxy-butyl-2-bromoisobutyrate (1)

To a round bottom flask were added 1,4-butanediol (13 ml; 150 mmol), triethylamine (13.5 ml; 105 mmol), and 100 ml of dry THF. To the reaction mixture, stirred at room temperature under nitrogen, was added dropwise 2-bromoisobutyryl bromide (4.5 ml; 37.5 mmol) over a period of 15 min. The reaction mixture was stirred at room temperature for 48 h. The salt was removed by filtration and after THF stripping, the crude product was purified by preparative TLC (99:1 ethyl acetate/methanol) to give **1** as a pale yellow oil (24 %).

^{1}HNMR (CDCl$_3$ at 25 °C, δ, ppm): 4.25 (s, 2H, –CH$_2$O–), 3.72 (s, 2H, –CH$_2$OH), 1.9 (s, 6H, 2–CH$_3$), 1.8 (s, 2H, –CH$_2$–CH$_2$O–), 1.7 (s, 2H, –CH$_2$–CH$_2$OH), 1.55 (s, 1H, –OH).

2.4. Synthesis of PCL-b-PtBuMA in a one-step process

To a Schlenk tube were added **1** (0.523 g; 2.19 mmol), triethylaluminium (0.17 ml; 0.146 mmol) and 125 ml of dry toluene. The reaction mixture was stirred at 60 °C for 2 h. Copper (I) bromide (314 mg; 2.19 mmol) and 2,2′-bipyridyl (682 mg; 4.38 mmol) were added to the mixture. Then CL (12 ml; 0.105 mol) and tBuMA (17 ml; 0.105 mol) were added, and the reaction was allowed to proceed for 24 h. Finally, the reaction mixture was concentrated, and the copolymer precipitated into cold methanol, filtered, and dried to provide a white powder.

Copolymer: M_n (SEC) = 14,000—pdi = 1.2—conversion = 100% for CL and 80% for tBuMA.

3. Results and discussion

3.1. Synthesis of the dual initiator

The dual initiator (4-hydroxy-butyl-2-bromoisobutyrate) was synthesized by esterification of an excess of 1,4-butanediol with 2-bromo-2-methylpropionyl bromide in the presence of triethyl amine. This dual initiator has recently been obtained by other authors, using a different synthetic approach [10]. It contains a primary alcohol used as the initiating site for the living ROP of CL in the presence of TEA (by formation in situ of aluminum alkoxides which are the actual active center), as well as a tertiary bromide function for the ATRP of *tert*-butylmethacrylate.

3.2. One-step polymerization

We have attempted to realize the copolymerization in a one-step process. We have focused our work on the simultaneous polymerizations of CL and tBuMA which proceed in similar reaction conditions (toluene, at 60 °C) (Scheme 1) [17].

As we have run the ROP using a catalytic process (alcohol is introduced in excess and acts as a transfer agent which allows reversible reactions between alcohol