

Note

SYNTHESIS OF BLOCK COPOLYMER FROM 5,6-BENZO-2-METHYLENE-1,3-DIOXEPANE AND METHYL ACRYLATE VIA ATOM TRANSFER RADICAL POLYMERIZATION*

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Abstract Poly(methyl acrylate)-*b*-poly(5,6-benzo-2-methylene-1,3-dioxepane) (PMA-*b*-PBMDO) was synthesized by two-step atom transfer radical polymerization (ATRP). Firstly, ATRP of methyl acrylate (MA) was realized using ethyl α -bromobutyrate (EBrB) as initiator in the presence of CuBr/2,2'-bipyridine. After isolation, poly(methyl acrylate) with terminal bromine (PMA-Br) was synthesized. Secondly, the resulting PMA-Br was used as a macromolecular initiator in the ATRP of BMDO. The structure of block copolymer was characterized by ¹H-NMR spectroscopy. Molecular weight and molecular weight distribution were determined on a gel permeation chromatograph (GPC).

Keywords Atom transfer radical polymerization, Ring-opening polymerization, Block copolymer, Unsaturated cyclic acetal

INTRODUCTION

Free radical ring-opening polymerization has been an attractive subject because polymers containing functional groups, such as ethers, esters, amides and carbonates, in their backbone could be produced^[1–4], and low volume shrinkage of the polymerization system could be achieved during the polymerization^[5–7]. However, polymers with low molecular weights and broad molecular weight distributions were generally obtained. For solving this problem, great efforts to extend the controlled free radical polymerization have been made. Wei *et al.* reported^[8] that a cyclic ketene acetal, 2-methylene-1,3-dioxepane, underwent stable free radical polymerization (SFRP) to afford the polymers with quantitative ring-opening and $M_w/M_n \sim 1.5$. Using the same method, Jia *et al.* presented a first example of the controlled free radical double ring-opening polymerization of 8,9-benzo-2-methylene-1,4,6-trioxaspiro[4,4]nonane^[9]. Among the controlled free radical polymerization methods to appear in the literature, the ATRP method has been widely investigated, and could be successfully used in the synthesis of block copolymers^[10–19]. In our previous papers^[20, 21], we have clarified that the ATRP method could be extended respectively to the free radical ring-opening polymerizations of 2-methylene-4-phenyl-1,3-dioxolane (MPDO) and 5,6-benzo-2-methylene-1,3-dioxepane (BMDO), and BMDO underwent controlled free radical quantitative ring-opening polymerization. Although there have been some papers related to the copolymerization of unsaturated cyclic monomers and conventional vinyl monomers^[1, 4], the copolymers obtained were random, and their block copolymerization has not been reported so far.

In this article, we describe the synthesis and characterization of well-defined block copolymers from BMDO and conventional vinyl monomer, methyl acrylate (MA) via the ATRP method, and block copolymer of PMA and polyester, *i.e.* PMA-*b*-PBMDO was successfully prepared by two-step ATRP.

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EXPERIMENTAL

Materials

MA (Beijing Chemical Reagent Plant) was stirred over CaH_2 overnight and distilled under vacuum prior to use. 2,2'-Bipyridine (bpy) (Beijing Chemical Reagent Plant) was re-crystallized from *n*-hexane. CuBr (Shanghai Chemical Reagent Plant) was purified from acetic acid, washed with methanol and dried under vacuum (100°C/2.6 Pa) to afford a white powder. All other solvents were purified by standard procedures. Ethyl α -bromobutyrate (EBrB) was prepared by the reaction of α -bromobutyric acid and ethanol in the presence of *p*-toluene sulfonic acid. BMDO was synthesized according to the method described in Ref. [1], and its structure was verified by ^1H -NMR spectrum. ^1H -NMR (in CDCl_3) for BMDO: δ = 3.70 (s, 2H, $\text{CH}_2=\text{C}$), 5.06 (s, 4H, 2OCH_2) and 7.05–7.30 (m, 4H, aromatic H's).

Synthesis of PMA-Macroinitiator

The general procedure is as follows: A mixture of CuBr (0.063 g, 0.44 mmol), bpy (0.206 g, 1.32 mmol), MA (8.7 g, 0.101 mol) and EBrB (0.079 g, 0.44 mmol) was placed in a 30 mL sealed polymerization tube with magnetic stirring bar, and the tube was closed with a three-way stopcock. After three freeze-thaw cycles had been performed, the tube was sealed under vacuum, and finally placed in an oil bath kept at 100°C. After a prescribed time, the polymerization tube was cooled down to room temperature rapidly and then opened. The mixture was dissolved in THF and passed through a neutral alumina column to remove the copper complexes. The polymer obtained was precipitated from an excess of methanol, then filtered, and dried at 40°C in a vacuum oven for 48 h.

Synthesis of Block Copolymer PMA-*b*-PBMDO

With a similar procedure in the preparation of PMA-Br, block copolymer PMA-*b*-PBMDO was synthesized by solution ATRP in chlorobenzene at 120°C with PMA-Br as macroinitiator.

Characterization

^1H -NMR spectra of the polymers obtained were recorded on a 500 MHz Bruker NMR spectrometer using CDCl_3 as solvent and tetramethylsilane as internal standard. Molecular weight and molecular weight distribution were determined on a Waters 150 C gel permeation chromatograph (GPC) equipped with ultrastaygel columns (50, 100, 10^3 and 10^4 nm) using THF as eluent at a flow rate of 1 mL/min.. Polystyrene was used as the calibration standard

RESULTS AND DISCUSSION

Synthesis of PMA-Macroinitiator

The polymerization conditions and results are listed in Table 1. It could be observed that the molecular weight distribution becomes narrow with the increase of monomer conversion (see Table 1), which is a general phenomenon observed in ATRP. As reported in our previous paper^[14], the bulk ATRP of MA using EBrB as initiator in the presence of bpy and CuBr had living character. Good agreement of M_n (theoretical) with M_n (NMR) (see Table 1) demonstrates that the molecular weight of polymers produced can be controlled by varying the feed ratio and conversion. As we know that the terminal bromine group may be lost after atom chain transfer reactions occur many times. In order to ensure no formation of homopolymer in the block polymerization, it is necessary that no terminal bromine is lost during the polymerization, so each macroinitiator has one terminal bromine. Therefore, we chose the products obtained at conversion of 28% and 55% as macroinitiators. Figure 1(a) shows the ^1H -NMR spectrum of PMA-Br. Except for characteristic signals of PMA, the signals at δ = 0.91 and 4.14 correspond respectively to the methyl protons originating from initiator EBrB and methine proton next to terminal bromine. The integration ratio of the signal at δ = 0.91 to that at δ = 4.14 is 3 / 1, indicating that the terminal bromine was not lost during the polymerization.

Block Polymerization of BMDO using PMA-Br as Macroinitiator

ATRP of BMDO using EBrB as initiator was already verified as "living" free radical polymerization^[21]. In this article, BMDO was polymerized in the presence of CuBr/bpy/PMA-Br. The polymerization conditions and

results are summarized in Table 2. The conversion was measured by gravimetrically, and calculated according to Eq. (1).

$$\text{Conv (\%)} = (W_p - W_i)/W_m \times 100\% \quad (1)$$

where W_p , W_i and W_m are the weight of the copolymer produced, the initial weights of the macroinitiator and BMDO, respectively.

Table 1. PMA-Br macroinitiator prepared by ATRP method^a

No.	Macro-initiator	Time (h)	Conv (%)	$M_{n, \text{theor.}}^b$ ($\times 10^{-3}$)	$M_{n, \text{NMR}}^c$ ($\times 10^{-3}$)	$M_{n, \text{GPC}}$ ($\times 10^{-3}$)	M_w/M_n
1	(PMA-Br) ₁	4	19	3.93	3.89	4.51	1.36
2	(PMA-Br) ₂	7	28	5.84	6.23	6.95	1.23
3	(PMA-Br) ₃	12	55	11.1	12.0	13.4	1.15
4	(PMA-Br) ₄	18	75	15.3	16.9	18.5	1.14

^a Feed molar ratio: [MA]:[EBrB]:[CuBr]:[bpy] = 230:1:1:6 (molar ratio), MA = 15 g, $T = 100^\circ\text{C}$

^b Theoretical number average molecular weight $M_{n, \text{theor.}} = [(M)_0/[EBrB]_0] \times \text{Conv} \times M_m + M_{\text{EBB}}$, where $[M]_0$ and $[EBrB]_0$ are initial molar concentrations of MA and EBrB; M_m and M_{EBB} are molecular weights of MA and EBrB

^c $M_{n, \text{NMR}}$ is calculated based on NMR data

Table 2. Molecular weight Data for AB diblock copolymers^a

No.	Macroinitiator ^b	Conv (%)	$M_{n, \text{theor.}}^c$ ($\times 10^{-3}$)	$M_{n, \text{NMR}}^d$ ($\times 10^{-3}$)	$M_{n, \text{GPC}}$ ($\times 10^{-3}$)	M_w/M_n
5	(PMA-Br) ₂	30	9.19	9.36	8.70	1.36
6	(PMA-Br) ₂	47	11.0	11.3	12.2	1.17
7	(PMA-Br) ₂	61	12.4	13.2	12.5	1.16
8	(PMA-Br) ₃	31	15.1	16.0	16.6	1.27
9	(PMA-Br) ₃	58	17.8	18.8	19.3	1.18
10	(PMA-Br) ₃	66	20.0	20.4	22.2	1.17

^a Polymerization conditions: $T = 120^\circ\text{C}$, BMDO = 1 g, chlorobenzene = 2 mL

[BMDO]:[macroinitiator]:[CuBr]:[bpy] = 60:1:1:3 (molar ratio)

^b The macroinitiator is the same as that listed in Table 1

^c $M_{n, \text{theor.}} = \{([M]_0 - [M]_t)/[I]\} \times 162 + M_i$, where 162 and M_i are the molecular weights of BMDO and the macroinitiator ($M_{n, \text{theor.}}$ listed in Table 1), respectively

^d Calculated according to Eq. (2)

Figure 1(b) shows a typical 500 Hz $^1\text{H-NMR}$ spectrum of block copolymer PMA-*b*-PBMDO. The signals originating from PMA and PBMDO blocks could be clearly observed. The signal at $\delta = 5.06$ due to the identical methylene protons in the BMDO ring was split into two peaks at $\delta = 5.10$ and 2.94 corresponding to the different methylene groups in the polyester. The former is the proton d between the ester oxygen and the benzene ring while the latter is the proton b in *ortho* position to the proton d. The identical methylene protons at 5.06 in the BMDO ring could not be observed in Fig. 1(b). All these facts verify that BMDO underwent completely free radical ring-opening polymerization. Based on the integral values of the peaks at $\delta = 3.62$ ($I_{3.6}$) and $\delta = 5.10$ ($I_{5.1}$), $M_{n, \text{NMR}}$ of PMA-*b*-PBMDO could be calculated according to Eq. (2).

$$M_{n, \text{NMR}} = (M_{n, \text{NMR}})_{\text{PMA}} + [(3 \times I_{5.1} \times M_{\text{BMDO}})/(2 \times I_{3.6} \times M_{\text{MA}})] \times (M_{n, \text{NMR}})_{\text{PMA}} \quad (2)$$

where M_{BMDO} , M_{MA} and $(M_{n, \text{NMR}})_{\text{PMA}}$ are the number average molecular weights of monomer BMDO, MA and PMA block. The results calculated are also listed in Table 2.

It can be observed from Table 2 that $M_{n, \text{theor.}}$ of PMA-*b*-PBMDO agrees quite well with $M_{n, \text{NMR}}$, but is slightly different from the results obtained from GPC ($M_{n, \text{GPC}}$) measurement. This may be due to the difference in solvent property between block copolymer and standard polystyrene.

Figure 2 shows the GPC curves of PMA-Br and PMA-*b*-PBMDO. Both curves have single symmetric peaks, and in Fig. 2(b), the GPC curve of macroinitiator is almost absent, but a new peak appears at higher molecular weight position, which is the evidence that all macroinitiator participated in the initiation of BMDO.

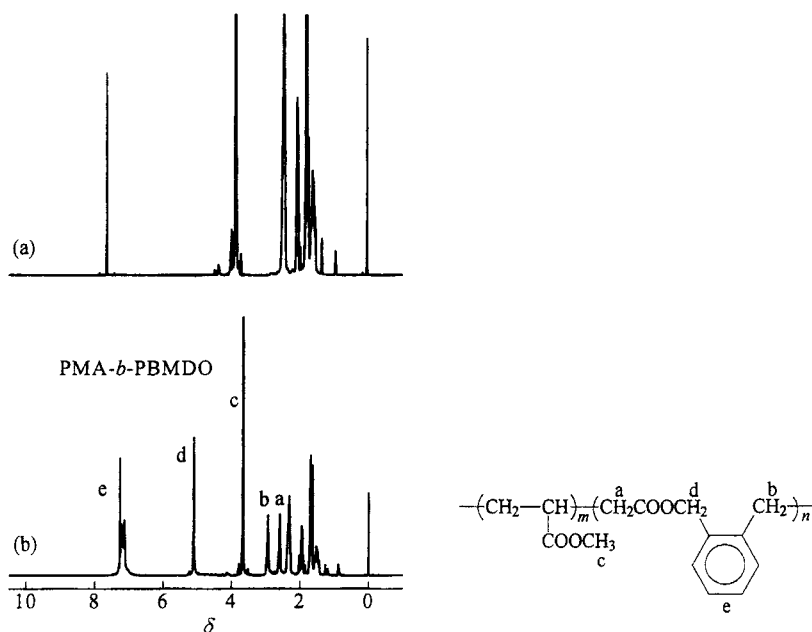


Fig. 1 ^1H -NMR spectra of (a) PMA-Br (sample 2 in Table 1) and (b) PMA-*b*-PBMDO (sample 6 in Table 2)

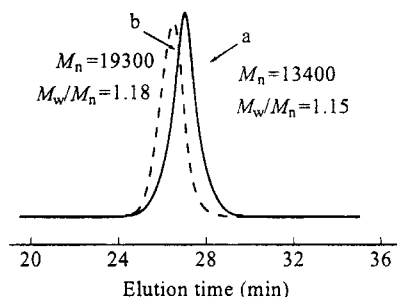


Fig. 2 GPC curves of (a) (PMA-Br)₃ (sample 3 in Table 1); (b) PMA-*b*-PBMDO prepared by ATRP of BMDO using (PMA-Br)₃ as initiator (sample 9 in Table 2)

The data listed in Table 2 and shown in Fig. 2 demonstrate that the molecular weight distribution of the block copolymers is quite narrow. This may be explained in terms of the following points. (1) The molecular weight distribution of macroinitiators obtained was very narrow, and (2) chlorobenzene is a good solvent for PMA-Br which was used in the block polymerization of BMDO, and would not affect the initiation activity of PMA-Br. (3) In our previous research^[21], we verified that BMDO underwent “living” free radical ring-opening polymerization.

CONCLUSIONS

Block copolymers of poly(methyl acrylate) and polyester with narrow polydispersity were successfully prepared by two-step ATRP. In the preparation of PMA-Br, loss of terminal bromine could be negligible before monomer conversion of 55%. PMA-Br is an effective initiator for the block polymerization of BMDO in chlorobenzene with CuBr/bpy as catalyst and ligand, and the molecular weight of PBMDO segment could be controlled by varying the feed molar ratio of monomer consumed to macroinitiator.

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