"Living" Free Radical Ring-Opening Polymerization of 5,6-Benzo-2-methylene-1,3-dioxepane Using the Atom Transfer Radical Polymerization Method

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ABSTRACT: To clarify whether atom transfer radical polymerization can be extended to free radical ring-opening polymerization, the polymerization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) was carried out in the presence of ethyl α-bromobutyrate/CuBr/2,2′-bipyridine. The structure of poly(BMDO) was characterized by ^{1}H and ^{13}C NMR spectroscopy as well as gel permeation chromatography. The living polymerization of BMDO was identified by the following facts: a straight line of $\ln([M]_0/[M])$ versus polymerization time, linear increase of molecular weight with increasing conversion, and narrowing polydispersity. The mechanism of living free radical ring-opening polymerization was discussed.

Introduction

Recently, significant progress has been made in the field of living free radical polymerization including nitroxide-mediated stable free radical polymerization,[1,2] atom transfer radical polymerization (ATRP),[3−7] and reversible addition−fragmentation chain transfer.[8,9] Among them, ATRP has been extensively studied, and most vinyl monomers, such as styrene and (meth)-acrylates, proceed in a living fashion. New advances have been aimed toward new metals[10−13] and new ligands.[14,15] Of all the transition metals, copper appears to be the most common because of its versatility.

On the other hand, free radical ring-opening polymerization has been an attractive subject because it produces polymers containing functional groups, such as ethers, esters, amides, and carbonates, in their backbone,[16−20] and low volume shrinkage during ring-opening polymerization can be achieved.[21−23] However, the polymers obtained generally have low molecular weight and broad molecular weight distribution. To produce polymers with controlled molecular weights and architectures, Wei et al.[24] reported the study on nitroxide-mediated stable free radical polymerization of 2-methylene-1,3-dioxepane, which underwent quantitative ring-opening polymerization to afford a polyester with polydispersity less than 1.5. Similarly, Jia et al.[25] presented the first example of a controlled free radical double ring-opening polymerization of 8,9-benzo-2-methylene-1,4,6-trioxaspiro[4,4]nonane. We want to clarify whether ATRP can be extended to free radical ring-opening polymerization of unsaturated cyclic ethers, cyclic acetals, and spiro orthocarbonates. Among these monomers, 2-methylene-1,3-dioxolanes are the most extensively investigated monocyclic monomers.[18,19] In our previous paper, living free radical ring-opening polymerization of 2-methylene-4-phenyl-1,3-dioxolane (MDPO) using ATRP was investigated.[26] Different from its conventional free radical polymerization,[16] the polymers we obtained consisted of addition and ring-opened units with well-controlled molecular weights and narrow molecular weight distributions.[26] As a comparison, 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) was synthesized for studying its ATRP with ethyl α-bromobutyrate (EBB) as initiator and CuBr/2,2-bipyridine (bpy) as catalyst/ligand.

Experimental Section

Materials. 2,2′-Bipyridine (The First Shanghai Chemical Reagent Plant) was of analytical grade and used as received. CuBr (Shanghai Chemical Reagent Plant) was purified in acetic acid, washed with methanol, and dried under vacuum (100 °C/2 mmHg) to afford white powder. All other solvents used were purified by standard procedures. EBB was prepared by the reaction of α-bromobutyric acid and ethanol in the presence of *p*-toluenesulfonic acid. BMDO was synthesized according to the method described in ref 17, and its structure was verified by NMR analysis. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 3.70 (s, 2H, $CH_2{=}C$), 5.06 (s, 4H, $2OCH_2$), 7.05−7.30 (m, 4H, aromatic Hs).

Polymerization. The general procedure is as follows. Into a 5 mL sealed polymerization tube with magnetic stirring bar were added 40.1 mg (0.206 mmol) of EBB, 29.5 mg (0.206 mmol) of CuBr, 96.4 mg (0.618 mmol) of bpy, and 2.0 g (12.3 mmol) of BMDO. The tube was closed with three-way stopcocks. The system was degassed by a freeze−vacuum−thaw cycle three times. The tube was sealed under vacuum and then placed in an oil bath preheated at 120 °C while stirring. After 48 h, the polymerization tube was put into ice water and then opened. The solution of the reaction mixture dissolved in CH_2Cl_2 (10 mL) was passed through a short neutral alumina column to remove the metal salts. The polymer was precipitated by pouring the filtered solution into hexane under stirring. The precipitate was collected by filtration and dried at 40 °C in a vacuum oven. Poly(BMDO) was obtained in 73% with $M_{n,NMR} = 7600$ and $M_w/M_n = 1.23$. ^{1}H NMR (500 MHz, $CDCl_3$), δ (TMS, ppm): 7.12−7.22 (4H, aromatic Hs), 5.10 (2H, $PhCH_2O$), 2.91−2.96 (2H, CH_2CO), 2.56−2.61 (2H, $PhCH_2$).

A similar procedure was used for the polymerization using di-*tert*-butyl peroxide (DTBP) as initiator.

Characterization. ^{1}H and ^{13}C NMR spectra of the polymers were obtained on a Bruker-500 NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. The molecular weights and polydispersity indexes were estimated on a Waters 150C gel permeation chromatograph (GPC) equipped with Ultrastyragel columns (500, 10^3,

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Table 1. Free Radical Ring-Opening Polymerization of BMDO[a]

no.	initiator[b]	temp (°C)	time (h)	yield (%)	$M_{n,th}{}^{c}/10^{-3}$	$M_{n,NMR}/10^{-3}$	$M_{n,GPC}{}^{d}/10^{-3}$	$M_w/M_n{}^{d}$
1	DTBP	120	48	39			2.2	4.90
2	EBB	80	48	8	1.0	1.2	0.9	1.48
3	EBB	100	48	38	3.9	4.3	4.0	1.32
4	EBB	120	8	18	1.9	2.0	1.4	1.41
5	EBB	120	16	35	3.6	3.8	3.2	1.38
6	EBB	120	24	46	4.7	4.9	4.5	1.32
7	EBB	120	32	60	6.0	6.3	6.8	1.28
8	EBB	120	40	68	6.8	7.1	6.7	1.26
9	EBB	120	48	73	7.3	7.6	7.5	1.23
10	EBB	140	18	70	7.0	7.1	6.6	1.20

[a] BMDO: 2 g, $[BMDO]_0/[EBB]_0/[CuBr]_0/[bpy]_0 = 60/1/1/3$ (molar ratio). [b] DTBP: di-*tert*-butyl peroxide; EBB: ethyl α-bromobutyrate. [c] Calculated according to eq 4. [d] Estimated by GPC (polystyrene calibration).

10^4, and 10^5 Å), using monodisperse polystyrenes as calibration standards. THF was used as eluent at a flow rate of 1 mL/min.

Results and Discussion

The ATRP of BMDO was carried out under various conditions as shown in Table 1. The yield was measured by weight method and calculated according to eq 1:

$$\text{yield (\%)} = [W_p/(W_I + W_m)] \times 100\% \qquad (1)$$

where W_P is the weight of the isolated polymer and W_I and W_m are respectively the initial weights of the initiator and monomer.

The ^{1}H and ^{13}C NMR spectra of poly(BMDO) are shown in Figure 1. The signal at δ 5.06 due to the identical methylene protons in the BMDO ring was split into two peaks at δ 5.10 and 2.94 corresponding to the two different methylene groups in the polyester. The former is the proton *e* between the ester oxygen and the benzene ring while the latter is the proton *f* at the ortho position of the proton *e*. Figure 1b shows a signal at δ 172.8 corresponding to the ester carbon and no signal around δ 100−115 associated with acetal carbon. These facts verify that BMDO has undergone complete ring-opening polymerization, which is consistent with the polymerization results using conventional initiators such as DTBP or BPO.[17] Figure 1a shows that, in addition to the signals at δ 5.10, 2.91−2.96, 2.56−2.61, and 7.12−7.22 from the ring-opening polymerization product of BMDO, there are several resonance peaks originating from EBB. Signals at δ 0.88 and 1.26 correspond respectively to the methyl protons *a* at the end of the polymer chain and the methyl protons *b* of the ester group and the methylene protons *b* next to the methine group of EBB. The signals at δ 4.10 and 4.75 are respectively ascribed to the methylene protons next to the ester oxygen (*c*) and adjacent to bromine at the end of the polymer chain (*g*). All the spectral data support the molecular structure of poly(BMDO) shown in Scheme 1 (polymer **5**).

Assuming that each macromolecule contains one molecule of EBB and based on the integration values of the peaks at δ 0.88 ($I_{0.9}$) and 7.12−7.22 ppm ($I_{7.2}$), the number-average molecular weight ($M_{n,NMR}$) was calculated according to eq 2:

$$M_{n,NMR} = (3I_{7.2}/(4I_{0.9}) \times 162 + 194.9 \qquad (2)$$

where 162 and 194.9 are the molecular weights of BMDO and EBB, respectively. The calculated results are listed in Table 1.

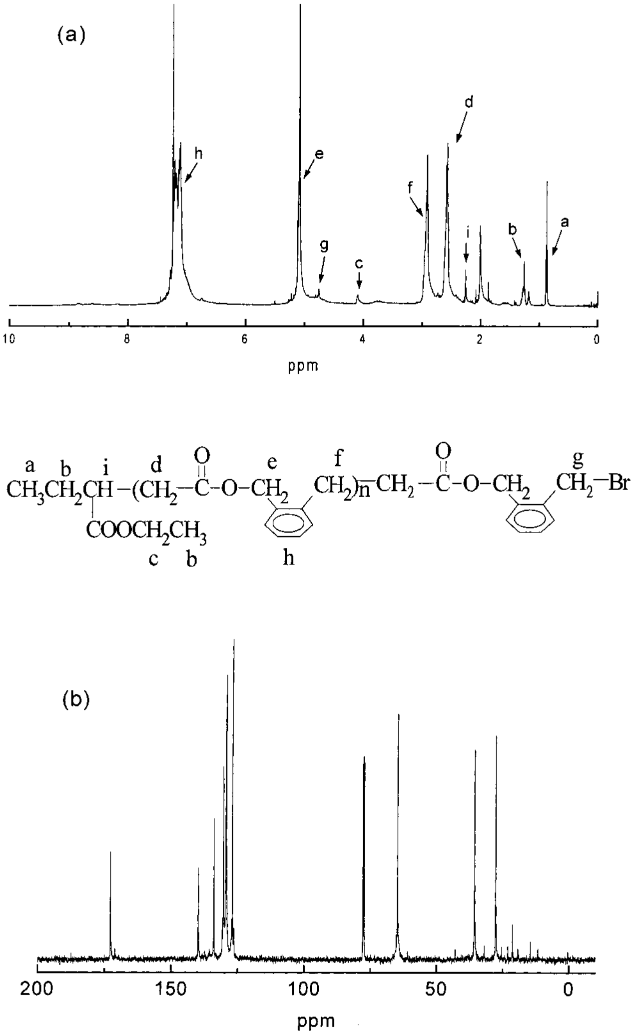
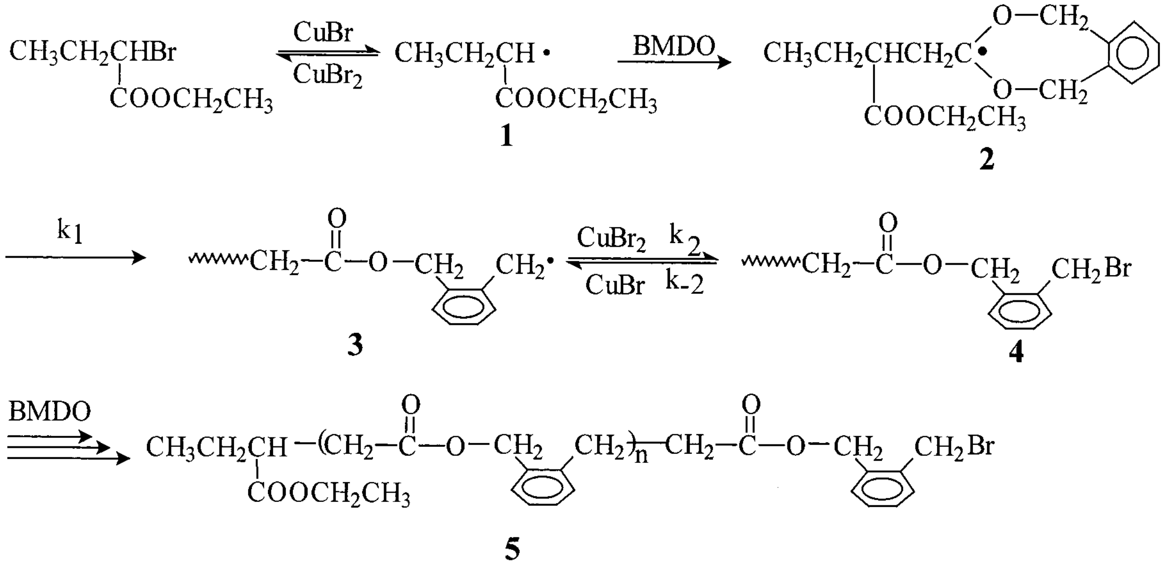


Figure 1. ^{1}H (a) and ^{13}C (b) NMR spectra of PBMDO (sample from Table 1, no. 5).

On the basis of the molecular structure of the polyester obtained, the ATRP mechanism of BMDO is proposed as shown in Scheme 1. The primary radical **1** formed from the reaction of EBB with CuBr attacks the monomer to afford intermediate radical **2**. The radical **2** may undergo addition reaction with monomer and/or open its ring to form radical **3**. The former reaction would lead to addition polymer and the latter to ring-opening polymerization product. Experimentally we only obtained ring-opening polymer, revealing that only ring opening of **2** has occurred. BMDO thus has undergone quantitatively ring-opening polymerization. The strain release of the seven-membered ring of radical **2** and the formation of a more stable benzyl radical may be the driving forces to open the ring.

Scheme 1



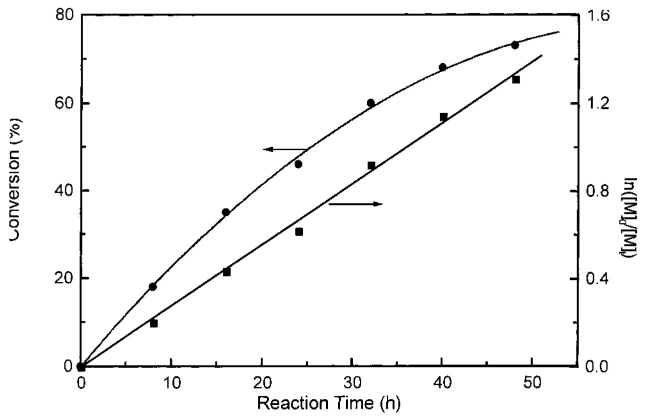


Figure 2. Relationship between ln([M]$_0$/[M]) and polymerization time for the bulk polymerization of BMDO at 120 °C; [BMDO]$_0$/[EBB]$_0$/[CuBr]$_0$/[bpy]$_0$ = 60/1/1/3 (molar ratio).

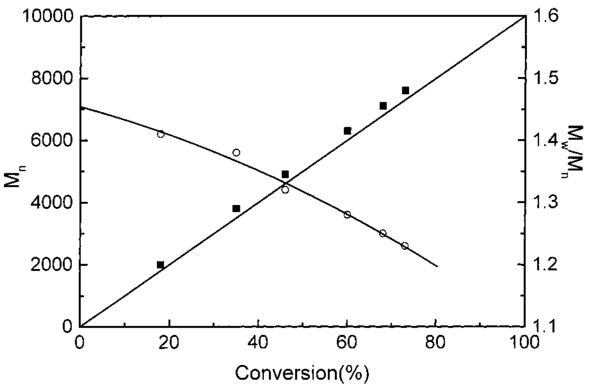


Figure 3. Dependence of M_n (■) and M_w/M_n (○) on conversion in the polymerization of BMDO at 120 °C; [BMDO]$_0$/[EBB]$_0$/[CuBr]$_0$/[bpy]$_0$ = 60/1/1/3 (molar ratio).

Compared to the polymerization using a conventional initiator at 120 °C for 48 h, it is clear that with the ATRP method the polymerization rate is faster and the polyester obtained has a higher molecular weight and a narrower polydispersity index (cf. Table 1). The lower concentrations of free radicals **2** and **3** reduce the possibility of termination and favor the complete ring-opening reaction of **2**. The fast equilibrium of radical **3** with dormant **4** is the reason for the better living characters of the polymerization, which will be discussed later.

To check whether the ATRP of BMDO is a "living" polymerization, the reactions in different tubes were stopped at given time intervals, and their conversions were measured. A plot of ln([M]$_0$/[M]) versus time *t* is shown in Figure 2. The straight line supports the constant concentration of the active species during the polymerization until conversion reaches to 70%, and termination of the radicals can be neglected.

Another evidence for the living polymerization is the absence of chain transfer shown by the linear molecular weight–conversion profile (Figure 3). This means that the molecular weight of the polyester can be simply controlled by polymerization time. Assuming that (i) EBB acts an efficient initiator, (ii) no termination reaction occurs, and (iii) each macromolecule contains only one unit of EBB, the theoretical number-average molecular weight ($M_{n,th}$) can then be calculated from eq 3:

$$M_{n,th} = ([M]_0/[I]_0 \times \text{conversion}) \times 162 + 194.9 \quad (3)$$

where [M]$_0$ and [I]$_0$ are respectively the initial molar concentrations of BMDO and EBB; 162 and 194.9 are respectively the molecular weights of BMDO and EBB. The calculated results are also listed in Table 1. The agreement between $M_{n,NMR}$ and $M_{n,th}$ offers another way for controlling the molecular weight of the polymer, that is, by varying the molar ratio of monomer to initiator.

Further evidence for the living polymerization is the narrow molecular weight distributions of the polymers (Figures 3 and 4). Single symmetric GPC curves of poly(BMDO) in Figure 3 show that the molecular weight distribution decreases with an increase in conversion, which is generally observed in ATRP of conventional monomers.[7]

An interesting phenomenon is that all $M_{n,NMR}$ are located above the straight line of $M_{n,th}$ versus conversion (cf. Figure 3). Probably, a small amount of initiator species was terminated during the initiation. Therefore, it is necessary to study the initiator efficiency (*f*) of EBB/CuBr/bpy. Assuming that no termination and no chain transfer reaction compete with propagation and all EBB

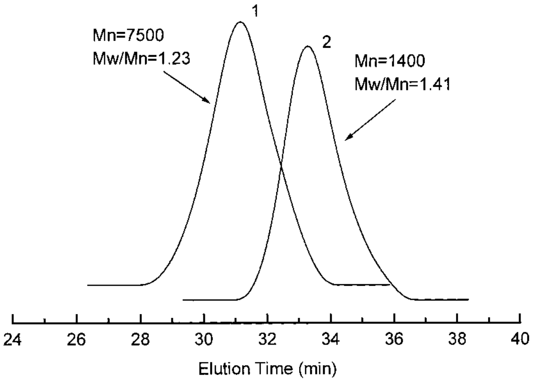


Figure 4. GPC curves of PBMDO prepared by polymerization at 120 °C; $[BMDO]_0/[EBB]_0/[CuBr]_0/[bpy]_0 = 60/1/1/3$ (molar ratio).

Table 2. Initiator Efficiency of EBB under Different Conditions[a]

no.	temp (°C)	time (h)	wt of polymer W_p (g)	$M_{n,NMR} \times 10^{-3}$	$W_p/M_{n,NMR}$ (mmol)	f (%)
1	80	48	0.210	1.2	0.175	85
2	100	48	0.779	4.3	0.185	90
3	120	48	1.502	7.6	0.198	96
4	140	18	1.393	7.1	0.202	98

[a] $[BMDO]_0/[EBB]_0/[CuBr]_0/[bpy]_0 = 60/1/1/3$ (molar ratio), $[EBB]_0 = 0.206$ mmol.

initiates the monomer to be polymerized, the initial moles of the initiator (I_0) will be the same as the moles of polymer produced. Therefore, f can be calculated according to eq 4:

$$f\,(\%) = [W_p/(I_0 M_{n,NMR})] \times 100\% \qquad (4)$$

The results are listed in Table 2: f increases with an increase in polymerization temperature. Higher temperature favors the initiation of BMDO by primary radical **1**.

In summary, BMDO underwent completely living free radical ring-opening polymerization to afford the polyester **5**. The living free radical polymerization of BMDO was supported by the following evidence: constant concentration of propagating species up to 70% conversion, narrow molecular weight distribution (down to 1.20), and molecular weight controlled by polymerization time and monomer/initiator ratio. The efficiency of the initiator increased with increasing temperature.

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