

Controlled/"Living" Radical Ring-Opening Polymerization of 5,6-Benzo-2-Methylene-1,3-Dioxepane Based on Reversible Addition-Fragmentation Chain Transfer Mechanism

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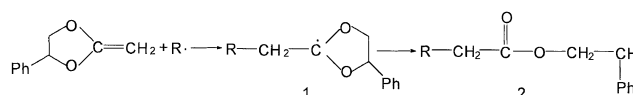
(Received September 17, 2001; Accepted December 28, 2001)

ABSTRACT: The radical ring-opening polymerization of 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) was performed in the presence of 1-(ethoxycarbonyl)prop-1-yl-dithiobenzoate (EPDTB) and dicumyl peroxide (DCP). The completely ring-opening polymerization of BMDO *via* reversible addition-fragmentation transfer mechanism was proved to be controlled by the following experimental evidences: the straight line of $\ln([M]_0/[M]_t)$ vs. polymerization time; linear increase of molecular weight with increasing conversion and relatively narrow molecular weight distribution. The mechanism of the polymerization was discussed. The complete ring-opened structure of the PBMDO was characterized by ¹H and ¹³C NMR spectroscopies as well as gel permeation chromatography (GPC).

KEY WORDS Controlled Polymerization / Radical Ring-Opening Polymerization / Reversible Addition-Fragmentation Chain Transfer (RAFT) / 5,6-Benzo-2-Methylene-1,3-Dioxepane /

Free radical ring-opening polymerization has been an attractive subject because it produces polymers with various functional groups (such as ethers, esters, amides, and carbonates) in their backbone.^{1–14} Addition of unsaturated heterocycles into polymerization system of commercial monomers will improve the properties of the polymers obtained. For example, when 2-methylene-4-*n*-decyl-1,3-dioxolane was copolymerized with vinyl chloride, the thermal stability and flexibility of the polymer obtained improved.¹⁵ However, free radical ring-opening polymerization of the unsaturated heterocycles yields polymers with low molecular weight and broad molecular weight distribution. For instance, the radical ring-opening polymerization of 2-methylene-4-phenyl-1,3-dioxolane proceeds *via* chain radicals 1 and 2 as shown in Scheme 1.^{16–18} The chain radicals 1 and 2 are stabilized respectively by two oxygens and phenyl group. The former radical is more active than the later one. The low molecular weight polymer with broad polydispersity index may be due to the transfer reaction during the polymerization.

Recently, significant progress has been made in the field of living free radical polymerization including nitroxide-mediate stable free radical polymerization (SFRP),^{19–23} atom transfer radical polymerization (ATRP),^{24–26} and reversible addition-fragmentation transfer (RAFT) process.^{27, 28} In these polymerizations, there is a fast equilibrium between propagating radi-



Scheme 1.

cals and dormant chains, which is prerequisite for the synthesis of controlled polymers.²⁹ When the methods apply in the polymerization of unsaturated heterocycles, the termination of propagating radicals must be affected. To produce polymers with controlled molecular weights and architectures, Wei *et al.*³⁰ 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. Jia *et al.*³¹ 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. In our research program on controlled free radical ring-opening polymerization of unsaturated cyclic acetals, cyclic ethers and spiro orthocarbonates, we studied controlled radical ring-opening polymerization of several unsaturated heterocycles and block copolymerization of these cyclic compounds with some commercial monomers. In the case of 2-methylene-4-phenyl-1,3-dioxolane (MPDO), the ATRP of MPDO yielded a polymer consisted of addition and ring-opening units with well-controlled molecular weight and narrow molecular weight distribution,³² which is different from its conventional free radical polymerization.² How-

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ever, 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) underwent complete ring-opening polymerization using ATRP initiator system, a polyester with well-controlled molecular weight and narrow polydispersity was produced.³³ We want to clarify whether RAFT process can be extended to free radical ring-opening polymerization of unsaturated cyclic acetals. Here, we report the controlled radical ring-opening polymerization of BMDO with 1-(ethoxycarbonyl)prop-1-yl-dithiobenzoate (EPDTB) and dicumyl peroxide (DCP) as transfer agent and initiator respectively.

EXPERIMENTAL

Materials

The monomer BMDO was synthesized according to the method described in ref 1, ¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm), 7.05–7.3 (m, 4H, aromatic Hs), 5.06 (s, 4H, 2OCH₂), 3.70 (s, 2H, CH₂ = C).

Dicumyl peroxide (DCP analytical grade) was purchased from Shanghai Chemical Reagent Plant and used as received. All other reagents used were of analytical grade.

Synthesis of EPDTB

The transfer agent EPDTB was prepared as follows: Magnesium (2 g, 0.083 mol) and 80 mL dry THF were added into a 250 mL three-necked flask, and then, 15.7 g (0.1 mol) of bromobenzene was dropwise added into the reaction mixture in 0.5 h. The reaction was carried out at 40°C until magnetism was completely disappeared. Then, carbon disulfide (7.62 g, 0.1 mol) was dropped in about 20 min. After reaction proceeded for 4 h at 40°C 17.5 g (0.09 mol) ethyl α -bromobutyrate was added. The reaction temperature rose to 80°C, and reaction was carried out at this temperature for 80 h. After the addition of 100 mL ice water into the reaction mixture, the water phase was extracted with carbon disulfide (3 \times 50 mL). The organic extracts were combined and washed with water, and dried over anhydrous magnesium sulfate. After removing the solvent by rotating evaporator, the product obtained was purified through column chromatography, and hexane/diethyl ether (9–1 v/v) was used as eluents. After the solvent was removed under reduced pressure, EPDTB was obtained as red oil (9.31 g, yield 43.5%).

¹H NMR (500 MHz, CDCl₃), δ (TMS, ppm), 0.91(t 3H CHCH₂CH₃), 1.25(t 3H OCH₂CH₃), 1.56 (m 2H CHCH₂CH₃), 4.18(q 2H OCH₂CH₃), 4.76(t 1H CHCH₂CH₃), 7.25(dd 1H p-ArH), 7.35(dd 2H m-aromatic H), 7.95(d 2H o-ArH).

Polymerization

The general procedures is as follows: Into a 5 mL polymerization tube with magnetic stirring bar, 1 g (6.2 mmol) of BMDO, 27.5 mg (0.103 mmol) of EPDTB, 2.71 mg (0.01 mmol) of DCP, and 1 mL THF were added. The mixture was degassed by three freeze-vacuum-thaw cycles. The tube was sealed under high vacuum, and then placed in an oil bath preheated at 120°C while stirring. After a prescribed time, the tube was put into ice water, cooled to room temperature and then opened. The polymer was obtained by pouring the polymer solution in THF into hexane while stirring; and the precipitate was collected by filtration, and dried at 40°C in vacuum overnight.

Characterization of Polymers

¹H and ¹³C NMR spectra of the polymers obtained were recorded on a Bruker DMX-500 nuclear magnetic resonance spectrometer using CDCl₃ as solvent, and tetramethylsilane (TMS) as internal reference. Molecular weight and polydispersity indexes were determined on a Waters 150C gel permeation chromatograph (GPC) equipped with Ultrastayragel columns (500, 10³, 10⁴ Å) using monodisperse polystyrene as calibration standard. THF was used as an eluent at a flow rate of 1.0 mL min⁻¹.

RESULTS AND DISCUSSION

Free Radical Ring-Opening Polymerization

The free radical ring-opening polymerization of BMDO was carried out at 120°C using EPDTB as chain transfer agent and DCP as initiator. The conditions and results are listed in Table I. The yield was measured by gravimetric method, and calculated according to eq 1.

$$\text{Yield (\%)} = [W_p / (W_i + W_m)] \times 100\% \quad (1)$$

Where W_p is the weight of the isolated polymer and W_i and W_m are initial weights of initiator and monomer respectively.

As we know, BMDO underwent complete ring-opening polymerization using conventional free radical initiator.¹ To clarify whether RAFT process of BMDO proceeds *via* complete ring-opening polymerization, ¹H and ¹³C NMR spectra of the polymer obtained are shown in Figures 1 and 2. The signal at δ 5.06 due to the identical methylene protons in the BMDO ring is split into two peaks at 5.10 and 2.91–2.96 (see Figure 1) corresponding to the two different methylene groups in the polyester. The former is the proton i between the ester oxygen and the benzene ring, while the latter is the proton f at the ortho position of the proton i. The signal at 2.56–2.60 ppm corresponds the proton d of methylene

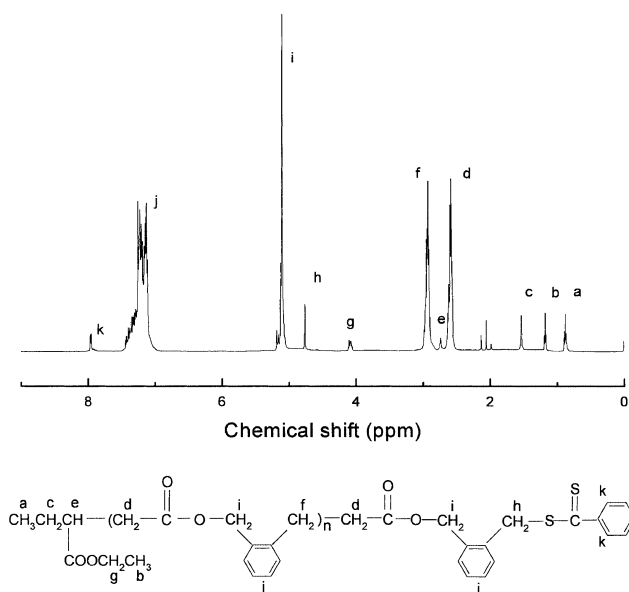


Figure 1. ^1H NMR spectra of PBMDO (No.2 in Table I).

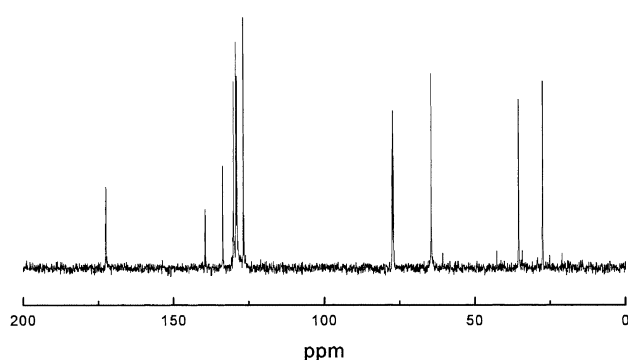


Figure 2. ^{13}C NMR spectra of PBMDO (No.2 in Table I).

group next to carboxylate group, which results from the ring-opening of 1,3-dioxepane ring. The integration ratio of i: f: d = 1:1:1 indicates that the polymer obtained is consisted of only ring-opened unit, so polyester was produced. Another evidences of complete ring-opening polymerization of BMDO lies in the facts that no acetal carbon signal at 95–120 ppm and ester carbon signal at 172.8 ppm appear in Figure 2.

Except the characteristic signals from PBMDO, several small peaks from transfer agent of EPDTB can be found in Figure 1. The signals at δ 0.91 and 1.25 belong to the protons a and b of two methyl groups in ethyl butyrate. The signals at δ 1.57 and 4.18 are ascribed to methylene protons c adjacent methine group and g next to ester oxygen. The signal at δ 4.76 of methine proton next to sulfur in EPDTB is shifted to δ 2.74 ppm (e) in Figure 1, and a new signal at δ 4.80 corresponded to methylene protons next to sulfur, indicating that ethyl butyrate and dithio benzoate are separately situated at the both end of the polymer chain.

Based on the above facts and general RAFT mech-

anism, we proposed the free radical ring-opening polymerization mechanism of BMDO as shown in Scheme 2. Primary radical can initiate the polymerization of BMDO, or reacts with EPDTB to produce a new radical, butyrate radical, which initiates monomer to polymerize. Thus, we should observe a small amount of $\text{Ph}(\text{CH}_3)_2\text{CO}$ groups stood at the end of polymer chain. Based on the ^1H NMR spectrum of DCP, the two methyl protons of $\text{Ph}(\text{CH}_3)_3\text{CO}$ group appear at δ 1.60, which is overlapped with methylene protons signal of butyrate group. This can be confirmed by the integration ratio (1:1.2) of the signal at 7.95 ppm to that at 1.56 ppm, because the ratio of ortho aromatic protons to methylene protons of butyrate should be 2:2.

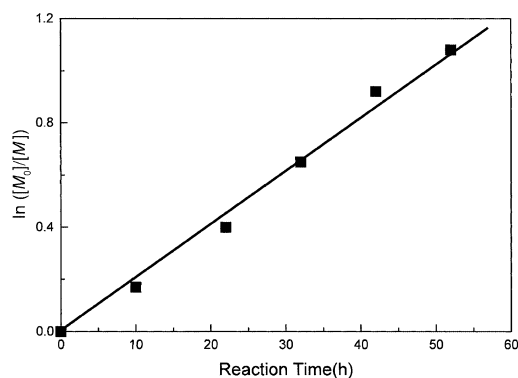
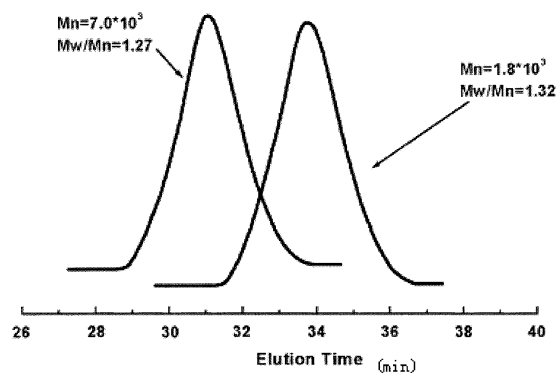
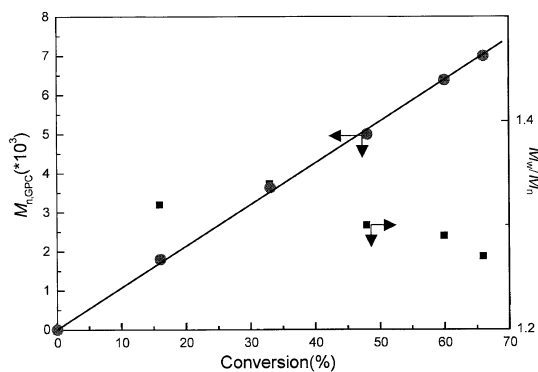
As we know, in RAFT process, the controlled behavior of the polymerization is maintained through the reversible addition fragmentation sequence between propagating chain radicals and dormant species with $-\text{SC}(\text{S})-\text{Ph}$ moiety. Comparison with conventional free radical ring-opening polymerization of BMDO initiated by DTBP at 120°C for 48 h, polymerization in presence of EPDTB produced polyester in high yield, and with higher molecular weight as well as narrow polydispersity index (see Table I). The conventional radical polymerization of BMDO involves the propagation reaction *via* the reaction of chain radical with vinyl group of BMDO. It should be considered that the chain transfer reaction of chain radicals with methylene group of BMDO forms benzyl radical stabilized by benzene ring and oxygen. From filtration, we can obtain low molecular weight oligomers which may be an evidence of chain transfer reactions. As a result, after precipitation, the polyester with low yield and broad polydispersity was obtained. The fast reversible addition-fragmentation reaction between propagating radicals and dormant polymer chain will reduce the concentration of propagating radicals, also lowered the possibility of chain transfer reaction. Since transfer reaction constant of chain radical with dithiobenzoate is larger than that with BMDO. This is the reason for the better-controlled natures of the polymerization, which will be discussed later.

Generally, free radical ring-opening polymerization requires higher reaction temperature. The polymerization of BMDO in the presence of EPDTB at 90°C produced polyester in very low yield (see No.6 in Table I). When the polymerization was performed in bulk, the polyester with broader molecular weight distribution ($M_w/M_n = 1.53\text{--}1.76$) were obtained. Linear relationship between molecular weight and conversion, and first order kinetic of polymerization were not observed. The possible reason may be explained as follows: after the polymerization was performed in bulk

Table I. Conditions and experiment results of radical ring-opening polymerization of BMDO based on the RAFT method^a

No.	Initiator ^b	Transfer agent ^c	Solvent	Time h	Temp. °C	Yield %	$M_{n,GPC}^d/10^{-3}$	M_w/M_n^d
1	DCP	EPDTB	THF	10	120	16	1.8	1.32
2	DCP	EPDTB	THF	22	120	33	3.6	1.34
3	DCP	EPDTB	THF	32	120	48	5.0	1.30
4	DCP	EPDTB	THF	42	120	60	6.4	1.29
5	DCP	EPDTB	THF	52	120	66	7.0	1.27
6	DCP	EPDTB	THF	32	90	—	—	—
7	DCP	EPDTB	—	24	120	45	4.4	1.53
8	DCP	EPDTB	—	45	120	50	5.3	1.57
9	DCP	EPDTB	—	60	120	53	5.8	1.76
10	DTBP	—	—	48	120	39	2.2	4.90

^aPolymerization conditions: BMDO: 1 g (6.2 mmol), EPDTB: 27.5 mg (0.103 mmol), DCP: 2.71 mg (0.01 mmol), THF: 1 mL. ^bDTBP: di-*tert*-butyl peroxide, DCP: dicumyl peroxide. ^cEPDTB: 1-(ethoxycarbonyl)prop-1-yl-dithiobenzoate. ^dEstimated by GPC (polystyrene calibration).

**Figure 3.** Relationship between $\ln([M_0]/[M])$ and polymerization time for solution polymerization of BMDO in THF at 120°C.**Figure 5.** GPC curves of PBMDO of polymerization in THF solution at 120°C (No.1 and No.5 in Table I).**Figure 4.** Dependence of $M_{n,GPC}$ and M_w/M_n of conversion in the polymerization of BMDO in THF solution at 120°C.

polystyrene standard was used in the calibration of molecular weight of PBMDO, $M_{n,GPC}$ does not affect the linear relation. Thus, the molecular weight of the polyester can be simply controlled by polymerization time. Further evidences for the controlled radical polymerization are the low polydispersity indexes (1.27–1.34) and the symmetric GPC curves as shown in Figure 5.

CONCLUSION

In the presence of EPDTB and DCP, BMDO underwent completely free radical ring-opening polymerization to produce polyester. The controlled radical polymerization of BMDO was supported by the following evidences: constant concentration of propagating chain radicals, linear relationship between molecular weight and conversion, lower polydispersity indexes ($M_w/M_n = 1.27$ – 1.34) and control of molecular weight by molar ratio of monomer to EPDTB or by polymerization time at molar ratio of EPDTB/DCP > 10. Comparison with conventional radical polymerization of BMDO, this radical polymerization had high yield, and produced polyester with narrow molecular weight distribution, and well-controlled molecular weight.

Acknowledgment. This work is supported by the National Natural Science Foundation of China. (Grant 29774027).

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