

THE EFFECTS OF MONOMER STRUCTURE OF CYCLIC KETENE ACETALS ON THE BEHAVIOR OF CONTROLLED RADICAL RING-OPENING POLYMERIZATION*

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Abstract Polymerization of three cyclic ketene acetals: *i.e.*, 5,6-benzo-2-methylene-1,3-dioxepane (BMDO), 2-methylene-4-phenyl-1,3-dioxolane (MPDO) and 4,7-dimethyl-2-methylene-1,3-dioxepane (DMMDO) were carried out in the presence of ethyl α -bromobutyrate/CuBr/2,2'-bipyridine respectively. The structures of poly(BMDO), poly(MPDO) and poly(DMMDO) were characterized by ^1H and ^{13}C -NMR spectra. The effects of monomer structure on the behavior of atom transfer free radical ring-opening polymerization were investigated and the mechanism of controlled free radical ring-opening polymerization was discussed.

Keywords Controlled radical polymerization, Ring-opening polymerization, Atom transfer radical polymerization, Cyclic ketene acetal

INTRODUCTION

“Living”/controlled polymerization is among the best methods for the synthesis of polymers with controlled molecular weights and architectures. Due to its easy operation and because many commercial polymers have been prepared by free radical polymerization, “living” radical polymerization has become an intensive research field. Recently, significant progress has been made in this field including nitroxide-mediated stable free radical polymerization (SFRP)^[1, 2], atom transfer radical polymerization (ATRP)^[3-9] and reversible addition-fragmentation chain transfer (RAFT)^[10, 11].

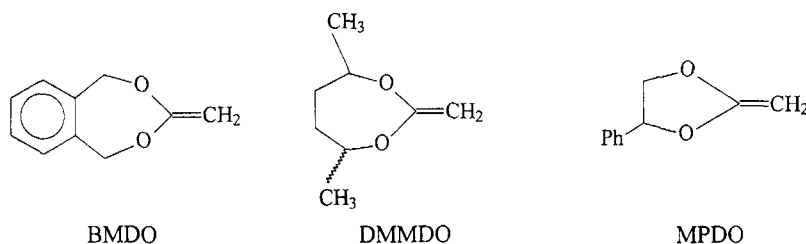
On the other hand, free radical ring-opening polymerization has also become an attractive research subject because it can produce polymers containing functional groups, such as ethers, esters, amides and carbonates in their backbone^[12-14], and polymers with low volume shrinkage during ring-opening polymerization can be achieved^[15-17]. Generally, the polymers thus obtained had low molecular weight and broad molecular weight distribution. Therefore, it would be very interesting to realize controlled/“living” radical ring-opening polymerization. It was reported by Wei^[18] that a cyclic ketene acetal, 2-methylene-1,3-dioxepane would undergo free radical polymerization with quantitative ring-opening by using SFRP method. In our previous papers^[19, 20], “living” free radical ring-opening polymerization of 2-methylene 4-phenyl-1,3-dioxolane (MPDO) and 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) respectively was investigated using the ATRP method. In order to study the effects of monomer structure on the behavior of free radical ring-opening polymerization, three typical cyclic ketene acetals, *i.e.*, BMDO, MPDO and 4,7-dimethyl-2-methylene-1,3-dioxepane (DMMDO) were selected (see Scheme 1) and their polymerization in the presence of ethyl α -bromobutyrate/CuBr/2,2'-bipyridine was conducted. Due to the differences in the properties of propagation radicals, different polymerization

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behaviors of the three monomers were observed.



Scheme 1 Structure of the three cyclic ketene acetals

EXPERIMENTAL

Materials

2,2'-Bipyridyl (bpy) was used as received. CuBr was purified in acetic acid, washed with methanol and dried under vacuum (100 °C/270 Pa) to afford a white powder. All solvents used were purified by standard procedures. Ethyl α -bromobutyrate (EBB) was prepared by the reaction of α -bromobutyric acid with ethanol in the presence of *p*-toluene sulfonic acid. Cyclic ketene acetals BMDO, MPDO and DMMDO were synthesized according to the method described in Refs [12] and [13].

Polymerization

The general procedure is as follows: A mixture of 0.206 mmol of ethyl α -bromobutyrate (EBB), 0.206 mmol of CuBr, 0.618 mmol of bpy and 12.3 mmol of monomer BMDO was placed in a 5 mL glass tube. The tube was degassed by three freeze-vacuum-thaw cycles and sealed under vacuum, then placed in an oil-bath preheated at 120 °C. After a prescribed time, the sealed tube was cooled with ice-water, and then opened. The reaction mixture was dissolved in CH₂Cl₂ (10 mL) and eluted through a neutral alumina column to remove the metal salts. The crude polymer was precipitated by pouring the solution obtained into *n*-hexane with stirring, then the precipitate was collected by filtration and dried at 40 °C in a vacuum oven for 48 h.

Characterization

The structures of the polymers were characterized by ¹H and ¹³C-NMR spectra, recorded with a 500 MHz Bruker NMR spectrometer using CDCl₃ as solvent and tetramethylsilane as standard. Molecular weight and molecular weight distribution were determined on a Waters 150 C gel permeation chromatograph (GPC) equipped with ultrastaygel columns (50 nm, 100 nm, 10³ nm and 10⁴ nm). Polystyrene was used as internal standard and THF was used as eluent at a flow rate of 1 mL/min.

RESULTS AND DISCUSSION

ATRP of BMDO MPDO and DMMDO

Free radical ring-opening polymerization of BMDO, MPDO, and DMMDO using conventional initiators, such as di-*tert*-butyl peroxide (DTBP) and benzoyl peroxide (BPO), has already been investigated, and structural analysis verified that they underwent quantitative ring-opening polymerization to afford polyester^[12, 13]. When these three monomers were polymerized in the presence of CuBr, bpy, and EBB, their polymerization behaviors were different, and also different from that of the conventional free radical polymerization. The polymerization conditions and part of the results are listed in Table 1. The conversion was measured 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 polymer produced, the initial weights of initiator and monomer, respectively.

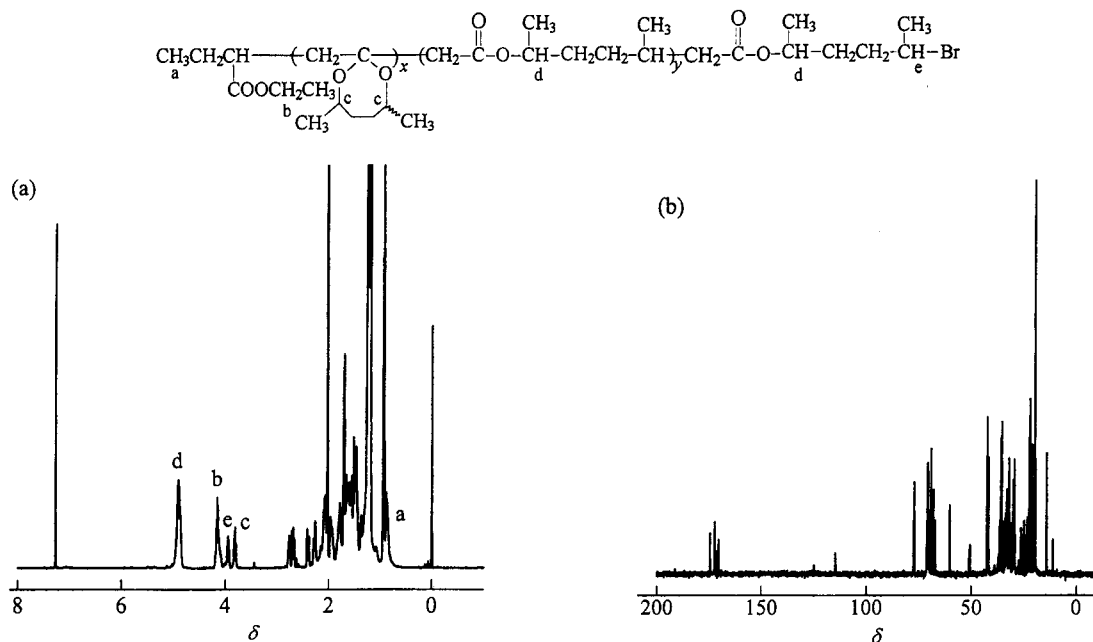
Table 1 Conditions and results of free radical ring-opening polymerization^a

Sample	Monomer	<i>t</i> (h)	Conv (%)	<i>M_n</i> _{th}	<i>M_n</i> _{NMR}	<i>M_n</i> _{GPC}	<i>M_w</i> / <i>M_n</i>	A ^b (%)	R ^c (%)
1	BMDO	16	35	3600	3800	3200	1.38	-	100
2	BMDO	24	46	4700	4900	4500	1.32	-	100
3	BMDO	32	60	6000	6300	6800	1.28	-	100
4	BMDO	48	73	7300	7600	7500	1.23	-	100
5	MPDO	32	72	7350	7300	8100	1.21	46	54
6	DMMDO	72	7	791	788	-	-	10	90

^a Conditions: for BMDO: 2 g; [BMDO]₀: [EBB]₀: [CuBr]₀: [bpy]₀ = 60:1:1:3 (molar ratio); for the other two monomers, the same molar ratios were used. *T* = 120 °C

^b The mole percentage of addition unit

^c The mole percentage of ring-opening units

**Fig. 1** The ^1H -NMR (a) and ^{13}C -NMR (b) spectra of PDMMDO

In the case of DMMDO, after polymerization in bulk at 120 °C for 72 h, no precipitation occurred when the polymer solution was poured into *n*-hexane with stirring, only around 7 wt% oligomer was obtained after the low boiling-point compounds in polymer solution were evaporated. Both MPDO and BMDO underwent “living”/controlled free radical ring-opening polymerization^[19, 20]. Although the polymerization of BMDO and MPDO could produce the corresponding polymers with various yields depending on the polymerization conditions, but MPDO showed a faster polymerization rate (72% of conversion) than BMDO (60%) at 120 °C for 32 h. BMDO underwent quantitative ring-opening polymerization, while MPDO included addition and ring-opening reactions. All these differences reflect the effects of monomer structures on polymerization behavior.

Structures of Poly(BMDO), Poly(MPDO) and Poly(DMMDO)

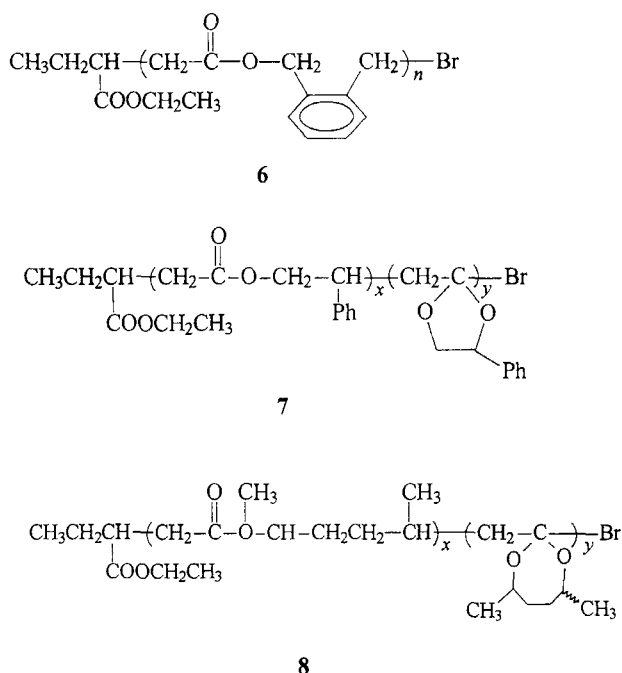
From the proton and ^{13}C -NMR spectra of poly(BMDO) and poly(MPDO), it was found that the structure of poly(BMDO) and poly(MPDO) can be described as the structure 6 and 7 (Scheme 2)^[19, 20].

The structure of oligo (DMMDO) was evidenced by its ^1H and ^{13}C -NMR spectra (Fig. 1). By analyzing Fig. 1, it is easier to draw the conclusion that the oligomer of DMMDO consisted of addition and ring-opening units from the following facts: (1) Signals at $\delta = 4.90$ (d) and $\delta = 3.81$ (c) which were ascribed to the two methine groups respectively next to ester oxygen and attached to oxygen of cyclic acetal. The former is the result of ring-

opening of 1,3-dioxepane and the latter results from the addition reaction of DMMDO with its tertiary radical. (2) Carbonyl and acetal carbons signals at around $\delta = 171$ –174, and $\delta = 114$ in Fig. 1(b) also confirm the presence of ring-opening and addition units in oligo (DMMDO). In Fig. 1(a), several signals at $\delta = 0.89$ (a), $\delta = 1.20$ and $\delta = 4.14$ (b) originated from EBB suggest that the oligomer of DMMDO was produced from the ATRP process. Based on the integral values of the peaks at $\delta = 4.14$ ($I_{4.1}$), 4.90 ($I_{4.9}$) and 3.81 ($I_{3.8}$), and assuming that each macromolecule contains one molecule of EBB, the number average molecular weight ($M_{n, \text{NMR}}$) of oligo (DMMDO) can be calculated:

$$M_{n, \text{NMR}} = 2 \times [I_{4.9} + (I_{3.8}/2)]/I_{4.1} \times 142 + 194.9 \approx 788$$

The mole percentage of addition unit could be calculated based on $I_{4.9}$ and $I_{3.8}$. The results are listed in Table 1.

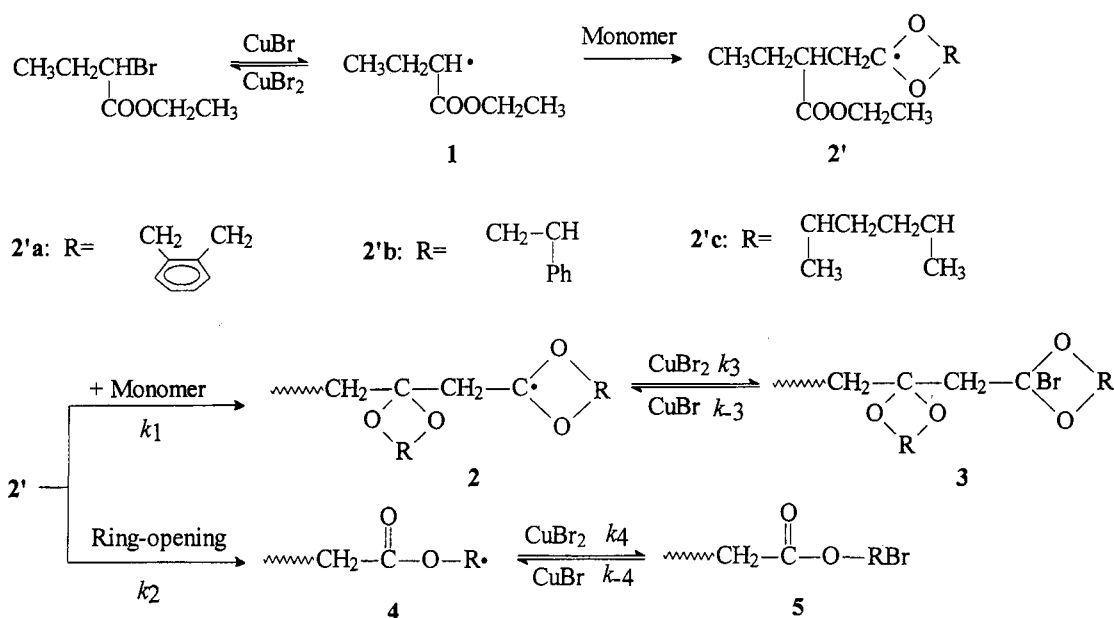


Scheme 2 Structure of polymers

Polymerization Mechanism

Based on the structure of the polymers, the ATRP mechanism was proposed for BMDO, MPDO and DMMDO as shown in Scheme 3. The monomer is attacked by primary radical **1** formed from reaction of EBB with CuBr to afford the intermediate radical **2'** which reacts further with the monomer to form radical **2**, or opens its ring to form radical **4**. The reversible reactions of these two radicals with CuBr₂ are shown in Scheme 3. Although all the radicals, **2a**, **2b** and **2c**, are stabilized by two oxygen atoms, the driving forces opening their rings are different. For **2a** and **2c**, the release of their seven-membered ring strain is a strong driving force to open their rings. However, **2a** should have a much stronger driving force than **2c** because a more stable radical **4a** stabilized by benzene ring is formed. The radical **4c** is an active secondary radical. Considering the equilibria between **4a** and **5a**, **4c** and **5c**, benzyl bromide is a well-known initiator of ATRP, the reversible reaction of poly(BMDO) bromide **5a** with CuBr to form radical **4a** should take place easily as compared with the equilibrium between **5c** and **4c**. The redox reaction of oligo (DMMDO) bromide with CuBr is difficult. This can be verified by the analysis of end groups. The ratio of integral values of the signal at $\delta = 3.92$ (e) corresponding to methine proton next to bromine at the end of the oligomer and the signal at $\delta = 4.14$ corresponding to methylene protons of the ester group in EBB was around 0.4. This fact indicates that ethyl butyrate is located at one end of the oligomer; 80% of the units at the other end were ring-opened units of DMMDO. Due to the formation of active **4c** and

stable bromide **5c** during the propagation, only oligomer with structure **8** (Scheme 2) was formed from the polymerization of DMMDO in the presence of CuBr/bpy/EBB.



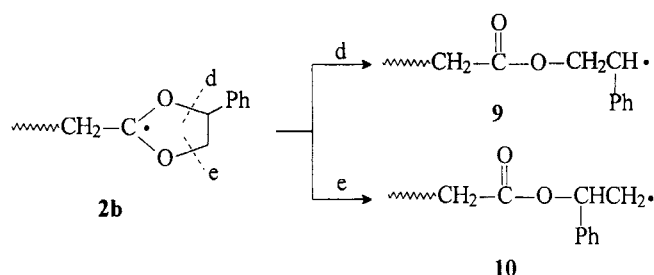
Scheme 3

BMDO underwent quantitative ring-opening polymerization to afford polyester with structure **6** (Scheme 2).

For ATRP of MPDO, the five-membered ring is stable; the driving force for ring-opening of radical **2** must be the stabilizing effect of the phenyl group in the radical **4b**. Unlike the quantitative ring-opening in the conventional free radical polymerization of MPDO^[12], ATRP of MPDO comprises addition and ring-opening reactions to produce poly(MPDO) having addition and ring-opening units as shown in structure **7** (Scheme 2). This result is probably due to the increase of ratio of competition rate constants k_1/k_2 . k_1 and k_2 are the rate constants of the addition and ring-opening reactions respectively. The polymerization rate of MPDO in ATRP process (conversion = 72% at 120 °C for 32 h) is faster than the conventional free radical ring-opening polymerization of MPDO (conversion = 32% at 120 °C for 35 h) as shown in Table 1. Probably, the process that CuBr abstracts bromine from dormant halide involves the participation of monomer and will increase the propagation reaction. This acceleration occurs only in the addition reaction of **2b** with MPDO monomer for the competition reactions involving ring-opening and addition reactions. Therefore, the ratio of k_1/k_2 in the ATRP process was larger than that in conventional free radical ring-opening polymerization.

In comparison with BMDO and DMMDO, the ring in MPDO is asymmetrical. Radical **2b** can open its ring at sites d and/or e to form unit **9** and/or **10** (Scheme 4). The presence of a signal at $\delta = 4.3$ and the absence of a signal between $\delta = 5.1$ and 6.0 corresponding to methine proton attached to an ester oxygen formed by ring-opening at site e clearly indicate that the ring has regioselectively opened at site d. This finding is the same as that investigated by Bailey *et al.*^[12]

Comparing the contents of ring-opening unit (R) in the polymers listed in Table 1, we can conclude that the ring-opening abilities of the three monomers have the following order: BMDO > DMMDO > MPDO. This is related to the driving force already discussed. Although the ATRP of DMMDO produces only oligomer, the content of ring-opening unit in poly(DMMDO) is higher than that in poly(MPDO), which demonstrates that the release of ring strain requires a much stronger driving force of ring-opening than the stability of the radical formed by ring-opening.



Scheme 4

CONCLUSIONS

Three unsaturated cyclic acetals, BMDO, MPDO and DMMDO, were selected to study their ATRP in the presence of EBB/CuBr/bpy. The release of ring strain is the more important driving force of ring-opening than the stability of the radical produced from ring-opening of acetal carbon radical **2**. The ring-opening ability of the three monomers has the following order: BMDO>DMMDO>MPDO. Because the reaction of dormant halide **5c** with CuBr to form radical **4c** was difficult, the termination of radical propagation occurred, and only oligomer with low yield was obtained. Poly(MPDO) comprises the addition and ring-opening unit, and BMDO underwent quantitative free radical ring-opening polymerization.

REFERENCES

- Georges, M.K., Vergin, R.P.N., Kazmaier, P.M. and Hamer, G.K., *Macromolecules*, 1993, 26: 2987
- Keoshkerian, B., Georges, M.K., Quinlan, M., Veregin, R.P.N. and Goodbrod, B., *Macromolecules*, 1998, 31: 7559
- Wang, J.S. and Matyjaszewski, K., *Macromolecules*, 1995, 28: 7901
- Sawamoto, M. and Kamigaito, M., *Trends Polym. Sci.*, 1996, 4: 371
- Pan, C.Y., Lou, X.D., Wang, Y.L. and Wu, C.P., *Acta Polym. Sin.*, 1998, (3): 311
- Chen, X.P. and Qiu, K.Y., *Chinese J. Polym. Sci.*, 2000, 18(2): 149
- Chen, X.P. and Qiu, K.Y., *Macromolecules*, 1999, 32: 8301
- Chen, G.Q., Wu, Z.Q., Wu, J.R., Li, Z.C. and Li, F.M. *Macromolecules*, 2000, 33: 232
- Guo, J.H., Luo, X.A., Wu, P.P. and Han, Z.W., *Acta Polym. Sin.*, 1999, (6): 725
- Chiefari, J., Chong, Y. K., Ercole, F., Kristina, J., Jeffery, J., Le, T.P.T., Mayadunne, R.T. A., Meijs, G.F., Moad, G., Rizzardo, E. and Thang, S.H., *Macromolecules*, 1998, 31: 5559
- Chong, Y.K., Le, T.P.T., Moad, G., Rizzardo, E. and Thang, S.H., *Macromolecules*, 1998, 32: 2071
- Bailey, W.J., Wu, S.R. and Ni, Z., *Makromol. Chem.*, 1982, 183: 1913
- Bailey, W.J., Ni, Z. and Wu, S.R., *Macromolecules*, 1982, 15: 711
- Pan, C.Y., Wang, Y. and Bailey, W.J., *J. Polym. Sci., Part A: Polym. Chem.*, 1988, 26: 2737
- He, P.S., Zhou, Z.Q., Pan, C.Y. and Wu, R.J., *J. Mater. Sci.*, 1989, 24: 1528
- Yuan, J.Y. and Pan, C.Y., *Chinese J. Func. Polym.*, 1999, 12: 109
- Yuan, J.Y., Pan, C.Y. and Bai, R.K., *Polym. Int.*, 2000, 49: 74
- Wei, Y., Connors, E.J., Jia, X. and Wang, C., *J. Polym. Sci., Part A: Polym. Chem.*, 1998, 36: 761
- Pan, C.Y. and Lou, X.D., *Macromol. Chem. Phys.*, 2000, (11): 1115
- Yuan, J.Y., Pan, C.Y. and Tang, B.Z., *Macromolecules*, 2001, 34: 211