

SYNTHESIS AND ANIONIC POLYMERIZATION OF 2-METHYL-2-METHOXY CARBONYL-5-METHYLENE-1,3-DIOXOLAN-4-ONE*

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ABSTRACT

A new cyclic monomer, 2-methyl-2-methoxycarbonyl-5-methylene 1, 3-dioxolan-4-one, was synthesized successfully. The monomer and intermediate were characterized by ^1H NMR, ^{13}C NMR, INEPT (Intensive Nuclei Enhanced by Polarization Transfer) technique, IR and elemental analysis. Anionic polymerization of the monomer was carried out in anhydrous THF at -70°C , and 9-fluorenyllithium was used as initiator. The polymer structure was determined by IR, NMR and elemental analysis. Molecular weight of the polymer was estimated by viscosity measurement in DMSO at 30°C .

INTRODUCTION

In a research program designed to investigate polymerization of cyclic monomers, a variety of spiro carbonates, unsaturated spiro ortho esters, vinyl ethers, cyclic ketene acetals and cyclic acrylates were synthesized and polymerized^[1,2]. All these monomers were suitable to cationic or free radical ring opening polymerization, because they contained C—O unit at a proper position of the molecule and that is necessary for ring opening process during polymerization. Since a carbon-oxygen double bond is more stable than a carbon-carbon double bond, the C—O bond at the proper position of molecule will be broken during polymerization to form more stable carbon-oxygen double bond. The ring opening polymerization of these monomers may render the resulting polymers some interesting properties^[3].

However there is no anionic ring opening polymerization of such kind of cyclic monomers reported yet. In order to investigate anionic polymerization of some cyclic monomers, a new monomer, 2-methyl-2-methoxy carbonyl-5-methylene-1, 3-dioxolan-4-one, was designed. This paper is going to describe the synthesis and polymerization of the monomer. The anionic polymerization was carried out in THF at -70°C under nitrogen with

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hindered 9-fluorenyllithium as initiator.

EXPERIMENTAL

Materials and Instruments

Methyl pyruvate, 1, 8-diazabicyclo [5, 4, 0] undec-7-ene (DBU), butyllithium (1.6 mol/L in hexane) and fluorene were purchased from Aldrich Co. and used without further purification. All solvents were dried before use. β -Bromolactic acid was synthesized according to the method of Baer and Robison^[4] and recrystallized from benzene to give a pure material, mp 88—89°C [lit. mp 88—89°C]. ¹H NMR and ¹³C NMR were obtained with Af-200 NMR spectrometer at 200 MHz and 50 MHz respectively. IR spectra were measured by Perkin Elmer 298 infrared spectrophotometer.

Synthesis of 2-methyl-2-methoxy carbonyl-5-bromomethyl-1,3-dioxolan-4-one (1)

To a 250ml flask were added 17.7g (0.105 mol) of β -bromolactic acid, 10.7g (0.105 mol) of methyl pyruvate, 0.6g of paratoluene sulfonic acid and 150ml of benzene. The mixture was heated to reflux under nitrogen. Water formed during the reaction was collected in a Dean Stark trap. After 24 hr, 1.8ml of water was collected and the benzene solution was neutralized with 5% sodium bicarbonate aqueous solution, followed by washing with brine twice and water once, and then drying over anhydrous sodium sulfate. After benzene was removed, 9.3g of the product was obtained by vacuum distillation; bp 83—84°C/13.33 Pa (yield is about 35%). IR (neat) 2950—3000, 1810 (lactone carbonyl), 1765 (ester carbonyl), 1450, 1395, 1305, 1200, 1140, 1090, 930—980, 840, 780, 760;

¹H NMR (CDCl₃) δ 1.68, 1.70, 1.75, 1.76 (d, d 3H, —CH₃), 3.56—3.60 (d, d 2H, Cl—CH₂—), 3.72—3.75 (t, 3H, —OCH₃), 4.71—4.76, 4.83—4.86 (m, 1H, Cl—CH₂—CH—); ¹³C NMR (CDCl₃) δ 20.83, 22.63 (—CH₃), 29.00, 29.32 (Br—CH₂—CH), 53.11 (—CO₂CH₃), 74.23, 74.39 (—CH₂—CH—), 104.55, 105.23 (—O—C—O—), 167 (—CO₂—, lactone carbonyl), 168.11, 168.90 (—CO₂—, ester carbonyl); INEPT: the peaks at δ 20.83, 22.63, 53.11, 74.23 and 74.39 were up; the peaks at δ 29.00 and 29.32 were down; other peaks were disappeared.

Anal. Calcd for C₇H₉O₅Br: C%, 33.23; H%, 3.58; Br%, 31.58.

Found: C%, 33.00; H%, 3.69; Br%, 31.67.

Synthesis of 2-methyl-2-methoxy carbonyl-5-methylene-1,3-dioxolan-4-one (2)

To a solution of 4.6g (0.018 mol) of 2-methyl-2-methoxy carbonyl-5-

bromomethyl-1,3-dioxolan-4-one in 30ml of diethylether, 2.7g (0.018 mol) of DBU in 40ml diethylether was added dropwise at 0°C with stirring under nitrogen. After the reaction was complete, DBU salt was filtered out, then ether was removed by evaporation, 3.3g of yellow crude product was obtained, which was purified by vacuum distillation. After that 2.8g (90.4%) colourless liquid was obtained; bp 35°C/13.33 Pa; IR(neat) 2960—3000, 1815 (lactone carbonyl), 1760 (ester carbonyl), 1670 (double bond), 1430—1450, 1390, 1290, 1320, 1200, 1140, 1040, 930—990, 850—880, 780, 760; ^1H NMR (CDCl_3) δ 1.762, 1.764 (d, 3H, $-\text{CH}_3$), 3.744, 3.748 (d, 3H, $-\text{OCH}_3$), 4.87, 4.88 (d, 1H), 5.143, 5.157 (d, 1H), two alkene protons; ^{13}C NMR (CDCl_3) δ 21.21 ($-\text{CH}_3$), 53.30 ($-\text{CO}_2\text{CH}_3$), 92.95 ($-\text{CH}_2-\text{C}-$), 104.02 ($-\text{O}-\text{C}-\text{O}-$) 143.08 ($\text{CH}_2=\text{C}$), 161.20 ($-\text{CO}_2-$), 165.72 ($-\text{CO}_2-$); INEPT: the peaks at δ 21.00 and 53.08 were up; the peaks at δ 92.74 was down; other peaks were disappeared; Anal. Calcd. for $\text{C}_7\text{H}_8\text{O}_5$; C%, 48.84; H%, 4.68. Found: C%, 48.92; H%, 4.78.

Polymerization of 2-methyl-2-methoxy carbonyl-5-methylene-1,3-dioxolan-4-one

1. Preparation of anionic initiator—a solution of 9-fluorenyllithium in THF

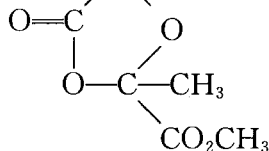
In a 50ml three-necked flask equipped with magnetic stirrer, inlet and outlet tubes for nitrogen, one neck of the flask is covered by a rubber serum cap. A solution of 1.6g (0.01mol) of fluorene in 17.5ml of anhydrous THF was added. Then the flask was flashed with dry nitrogen. After that, 7.5ml (0.012 mol) of butyllithium solution (1.6 mol/L in hexane) was transferred by dry syringe inserted through the rubber cap and the mixture was stirred under N_2 for an hour. When the metallation of the fluorene was complete, it was an orange-red coloured solution which was kept in refrigerator.

2. Polymerization

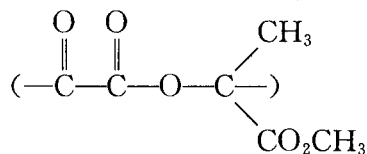
In a 50ml three-necked flask equipped with magnetic stirrer, a thermometer, inlet and outlet tubes for nitrogen, one neck of the flask is covered by a rubber serum cap was placed into 2.5g (0.015 mol) of 2-methyl-2-methoxy carbonyl-5-methylene-1,3-dioxolan-4-one, then cooled to -70°C in dry ice-acetone. 1 ml of 9-fluorenyllithium solution, prepared above, was added by a syringe inserted through the rubber cap. The polymerization was continued for 6 hr. to give a viscous solution. 2.0g

(80%) of polymer was obtained by filtration after precipitated in ether. IR (KBr) 2960—3000, 1805 (lactone carbonyl), 1750 (ester carbonyl), 1630, 1450, 1380, 1230, 1180, 1140, 980, 940, 850, 770; ^1H NMR (DMSO- d_6) δ 2.37—2.51 (bro., 3H, CH_3), 3.37 (bro., 2H, mixture of $-\text{CH}_2-$ $\begin{array}{c} \text{C} \\ \parallel \\ \text{O} \end{array}$ and

$-\text{CH}_2(-\text{C}-)$, 4.35 (bro., 3H, $-\text{OCH}_3$); ^{13}C NMR (DMSO- d_6)

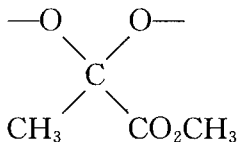


δ 26.5 ($-\text{CH}_3$), 51.8 ($-\text{CH}_2-$), 61.9 ($-\text{CO}_2\text{CH}_3$), 89.7



this is a quaternary carbon in the polymer chain

formed during ring opening process, the (b) pathway in Scheme II, 117.8



this is a quaternary carbon in the ring of the polymer

formed through (a) pathway of Scheme II, 174 ($-\text{CO}_2$), 179 ($-\text{CO}_2$), 196 ($\text{C}=\text{O}$).

Anal. Calcd. For $(\text{C}_7\text{H}_8\text{O}_5)_n$: C%, 48.84; H%, 4.68.

Found: C%, 49.01; H%, 4.97.

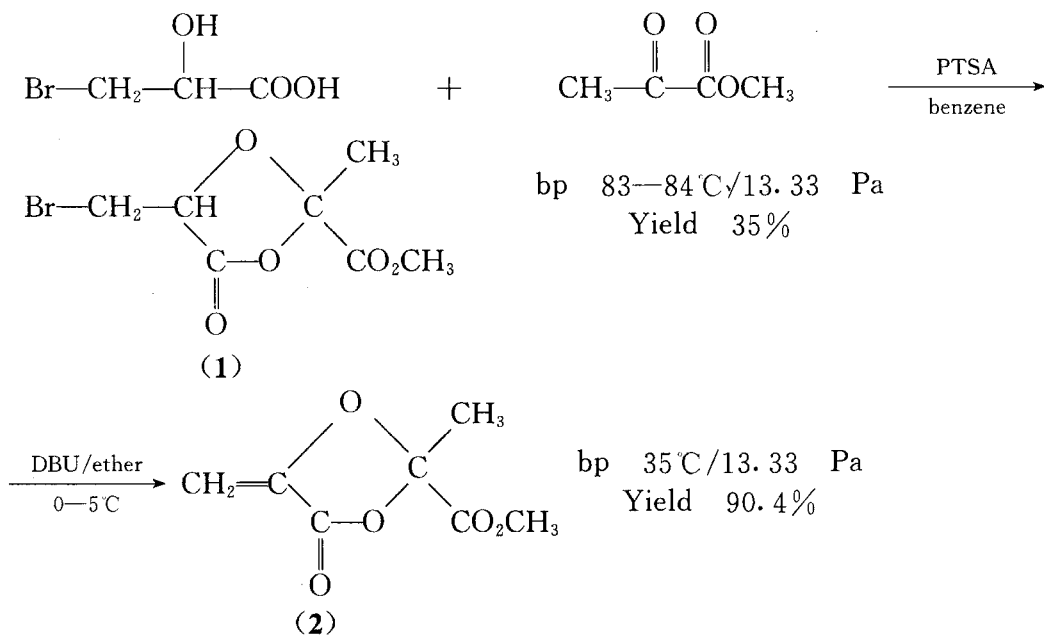
RESULTS AND DISCUSSION

The new monomer, 2-methyl-2-methoxy carbonyl-5-bromomethyl-1,3-dioxolan-4-one, was synthesized successfully by the reaction between β -bromolactic acid and methyl pyruvate, followed by dehydrobromination with DBU in ether at 0—5°C (see scheme I). Because the ketone carbonyl group of methyl pyruvate conjugated with ester group, the reactivity of this ketone carbonyl was lower than that of normal ketone carbonyl (i. e. non-conjugated ketone carbonyl group). Long reaction time was necessary to make the reaction completed. However during the long heating period there may be some side reactions occurred. This was the reason why the yield of the compound (1) was so low, even the reaction lasted for 24 hr. Although

the use of excess amount of β -bromolactic acid would increase the yield, since β -bromolactic acid is not a commercial available compound, so the equal molar ratio of the two starting materials was still used.

The structures of the compound (1) and (2) were determined by IR, ^1H NMR, ^{13}C NMR and elemental analysis, and further confirmed by INEPT technique which can distinguish CH_3 , CH , CH_2 and quaternary carbon.

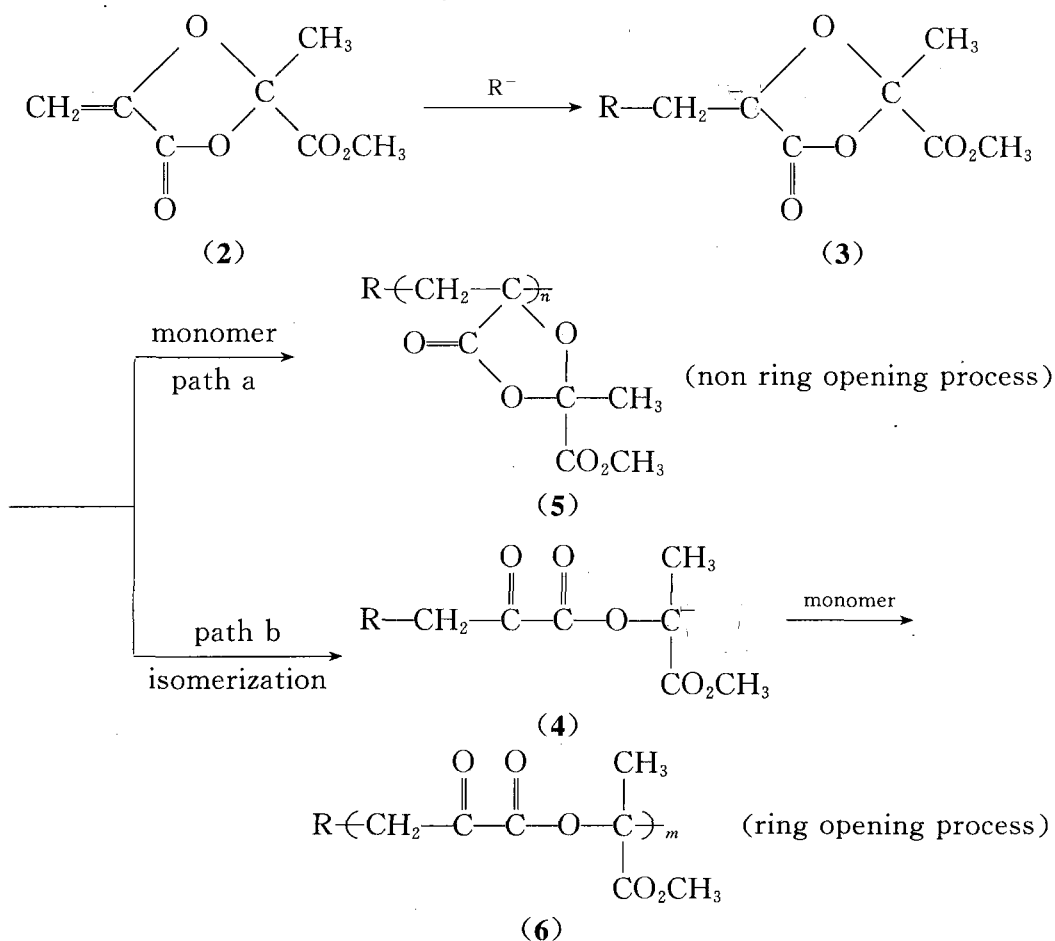
Scheme I Synthesis of Monomer



Anionic polymerization of the monomer was carried out at -70°C in anhydrous THF with anionic initiator. In order to avoid nucleophilic attack of anionic species to the two carbonyl groups present in the monomer, hindered 9-fluorenyllithium was used as anionic initiator, which was prepared by the metallation of fluorene with butyllithium. Because the 9-fluorenyllithium is very sensitive to oxygen and moisture, the polymerization must be carried out under strictly dry and oxygen-free nitrogen.

The polymer was characterized by IR, ^1H NMR, ^{13}C NMR and elemental analysis. From the spectra of IR and NMR it was found that there were two kinds of structure units in the polymer, one coming from ring opening process and the other coming from normal polymerization, (experimental section described the details). The possible polymerization process of the monomer was shown in Scheme II. As shown in the Scheme II, there were two pathways (a) and (b) during the polymerization.

Scheme II Polymerization of the monomer



First, the monomer (2) was initiated by anionic R⁻ to give a new anion (3). The polymer structure depends on the fate of the new anion (3). If the anion (3) is stable enough, it will propagate to give polymer structure (5) without ring opening; if the anion (3) isomerized to anion (4) by ring opening process, polymer structure (6) will be obtained. From the structures of (3) and (4), it is found that both of them are stabilized by ester group because of delocalization of their negative charge. Although there is some inductive effect of oxygen on the carbanion in the anion (3) and not in the anion (4), the formation of carbonyl group in anion (4) by ring opening process is favored thermodynamically, since the carbonyl group is more stable than the carbon-carbon double bond. In addition, the anion (4) is of less hindrance than anion (3) for further reaction, the reaction of anion (4) is favored dynamically too. So the stability of (3) and (4) should have an

effect on the relative amount of the two different structure units, but the ring opening process is favored thermodynamically and dynamically. Since the propagation of the anion (3) to monomer (path a of Scheme II) is a second order reaction, while the isomerization of the anion (3) to (4) (path b of Scheme II) is a first order reaction, the ring opening process is favored by solution polymerization.

As demonstrated by IR and NMR, the resulting polymer contained both structure units of (5) and (6), which may be distributed statistically. Although it is rather difficult to determine the ratio of the two units, the ^1H NMR spectrum of the polymer has showed that the structure unit (6) is the major one, for chemical shift $\delta = 3.37$ represents the methylene protons α to carbonyl group. ^1H NMR spectrum of the polymer was shown in Fig. 1.

The polymer is of poor solubility in CHCl_3 , but good solubility in DMSO. The molecular weight of the polymer was estimated by viscosity measurement at 30°C in DMSO. The intrinsic viscosity of the polymer $[\eta] = 0.24 \text{ dl/g}$.

Keywords:

Anionic polymerization, Ring opening polymerization, Cyclic monomer

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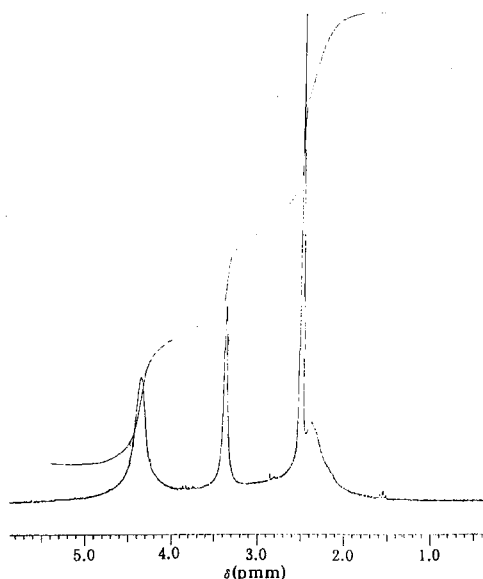


Fig. 1 ^1H NMR spectrum of the polymer in DMSO-D_6