

SYNTHESIS AND FREE RADICAL POLYMERIZATION OF 2-OXO-3-METHYLENE-5-PHENYL-1,4-DIOXAN

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ABSTRACT

The novel cyclic monomer, 2-oxo-3-methylene-5-phenyl-1,4-dioxan, was synthesized by a set of reactions. Several intermediates were prepared and characterized in order to determine the monomer structure. The presence of chiral centers in the intermediates and resulting monomer makes it complicated to separate, purify and characterize them. It is a very reactive monomer which will polymerize even at room temperature if exposed to moisture and air. This monomer can undergo essentially quantitative free radical ring opening polymerization. The driving force for ring opening is the formation of new carbonyl group and benzylic radical. The monomer and polymer structure were established by IR, ^1H NMR, ^{13}C NMR and elemental analysis or high resolution mass spectrum. The molecular weight of the resulting polymer was estimated by viscosity determination.

INTRODUCTION

Since a carbon-oxygen double bond is more stable than a carbon-carbon double bond, cyclic monomer containing C—O unit at a proper position of a molecule will facilitate free radical polymerization with ring opening. Cyclic ketene acetal is the kind of this monomer which can undergo free radical ring opening polymerization^[1]. However, there is one problem for copolymerization of cyclic ketene acetal with some common monomer, for example, in the copolymerization of 2-methylene-1,3-dioxepane with styrene $r_1=0.021$, $r_2=22.6$ at 120 °C^[2,3]. In an effort to produce cyclic monomers with higher reactivity in copolymerization and high degree of ring opening ability, a series of cyclic acrylates have been designed and synthesized^[4]. One interesting monomer among them is 2-oxo-3-methylene-5-phenyl-1,4-dioxan, which is very reactive, and shows the general characteristics of cyclic acrylates. In addition to its high reactivity, it is more difficult to be separated, purified and characterized, the reason why it is so complicated is the presence of unsymmetric elements in intermediate and resulting monomer molecules. This new monomer can undergo nearly quantitative free radical ring opening polymerization. The ring opening polymerization of the monomer provides a way to introduce a ketone ester group unit into the backbone of the addition polymer, and may render the polymer both biodegradable and photodegradable.

EXPERIMENTAL

Chloroacetaldehyde dimethylacetal, trimethylsilylcyanide, 1,8-diazabicyclo(5,4,0)undec-7-ene (DBU) and 1-phenyl glycol were purchased and used

without further purification. The solvents were dried before use. ^1H NMR, ^{13}C 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. 2-chloromethyl-4-phenyl-1,3-dioxolane (**1**) was synthesized according Bailey's method, $^{[5]}$ bp 95 — 97 °C /133.3Pa.

1-Chloromethyl(1'-phenyl-2'-trimethylsilyloxy)ethoxy acetonitrile (**2**)

To a mixture 52.7g (0.265mol) of 2-chloromethyl-4-phenyl-1,3-dioxolane and 26.3g (0.265mol) of trimethylsilylcyanide, 1.5g of zinc iodide was added under nitrogen. The mixture was stirred at room temperature for 2 days. After reaction was complete, and the product was distilled out under vacuum, 42g (53%) of viscous liquid was obtained, bp 115 — 120 °C /133.3Pa. IR (neat) 2860 — 3070, 1250, 1060 — 1130, 840, 760, 700; ^1H NMR (CDCl_3): δ 0.1 (T, 9H), 3.55 — 3.86 (m, 4H), 4.2 — 4.92 (m, 2H), 7.2 — 7.5 (m, 5H); ^{13}C NMR (CDCl_3): δ -0.68, -0.53, 0.02 (Si — CH_3), 42.64, 42.87, 42.97 (Cl — CH_2), 66.61, 67.29, 67.53, 69.00, 69.88, 70.08, 73.55, 74.31, 76.37, 76.72, 83.55, 84.24 (Cl — CH_2 — CH, — CH_2 — CH — ph), 115.89, 116.30 (— CN), 126.19, 126.76, 127.28, 127.83, 127.93, 128.27, 128.36, 128.56, 128.62, 128.76, 128.94, 136.98, 140.39, 140.82 (aromatic carbons); Anal. Calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{NClSi}$: C%, 56.46; H%, 6.77; N%, 4.70; Cl%, 11.90. Found: C%, 56.69; H%, 6.91; N%, 4.71; Cl%, 12.25.

2-Oxo-3-chloromethyl-5-phenyl-1,4-dioxan (**3**)

To a 125ml flask containing 6.7g (0.022mol) of 1-chloromethyl-1'-phenyl-2'-trimethylsilyloxy)ethoxy acetonitrile was added 5.6ml of hydrochloric acid (37%). The mixture was stirred at room temperature for 12hrs. Then 70ml of benzene was added and heated to reflux. 4.3ml of water formed during the reaction was collected in a Dean-Stark trap over a period of 16hrs. After the reaction was complete, the benzene solution was washed with 5% of aqueous sodium bicarbonate once and with brine twice, and then dried on anhydrous sodium sulfate. After the product was distilled out under vacuum, 3.5g (69%) of viscous liquid was obtained, bp 160 — 165 °C at 133.3Pa. Among them 0.5g (14%) of white crystal was obtained from the viscous liquid by adding small amount of ether, mp 101 — 103 °C. IR (KBr): 2820 — 3080, 1730, 1200 — 1220, 1110, 1020, 940, 820, 760, 700, 660; ^1H NMR (CDCl_3): δ 3.67 (m, 4H), 4.65 (T, 1H), 5.65 (d, d, 1H), 7.29 — 7.40 (m, 5H); ^{13}C NMR (CDCl_3): δ 44.48 (Cl — CH_2), 68.39 (— O — CH_2), 75.86 (— O — CHPh), 80.92 (— O — CH — O —), 126.05, 128.82, 129.22, 134.14 (aromatic carbons), 166.25 (CO_2). Anal. Calcd. for $\text{C}_{11}\text{H}_{11}\text{O}_3\text{Cl}$: C%, 58.29; H%, 4.89; Cl%, 15.64. Found: C%, 58.10; H%, 4.89; Cl%, 15.61.

2-Oxo-3-methylene-5-phenyl-1,4-dioxan (**4**)

To a solution of 1g (0.004 mol) of 2-oxo-3-chloromethyl-5-phenyl-1,4-dioxan in 10ml of ether was added dropwise a solution of 0.67g (0.004mol) of DBU in 10ml of ether at 0 °C under nitrogen with stirring. The mixture was stirred at 0 °C for 2 hrs. After that DBU salt formed during elimination reaction was removed by filtration and ether was evaporated, 0.6g (84%) of product was obtained, which is pure enough to be polymerized. IR (CHCl_3): 2860 — 3015,

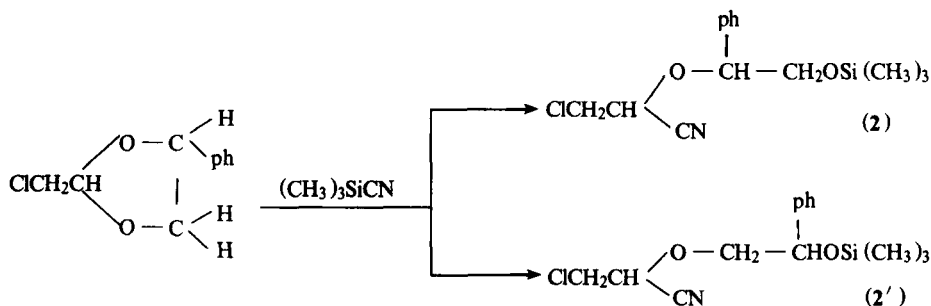
1735, 1625, 1290 — 1315, 1110 — 1150, 860 — 950, 730, 700; ^1H NMR (CDCl_3): δ 3.87 — 4.19 (m, 2H), 5.0 (d, 1H), 5.51 — 5.57 (d, d, 1H), 5.6 (d, 1H), 7.2 — 7.3 (s, 5H); ^{13}C NMR (CDCl_3): δ 68.14 ($\text{CO}_2 - \text{CH}_2$), 78.93 ($-\text{O}-\text{CHPh}-$), 103.41 ($\text{CH}_2=$), 126.0, 128.2, 128.6, 129.0, 133.76 aromatic carbons), 149.29 ($\text{CH}_2 = \text{C}$), 159.56 (CO_2); HRMS (m/e): Calcd. for $\text{C}_{11}\text{H}_{10}\text{O}_3$: 190.06299; Found: 190.06343.

Polymerization of 2-oxo-3-methylene-5-phenyl-1,4-dioxan (4)

To a solution of 1.0g of 2-oxo-3-methylene-5-phenyl-1,4-dioxan in 10ml of *t*-butylbenzene was added 0.02g of *t*-butylperoxide. The solution was heated to 120 °C for 20hrs under nitrogen with stirring. After removing solvent and vacuum evaporation under 40 °C for 8hrs, 0.7g of polymer was obtained. IR (KBr): 3050, 2900 — 3000, 1730 — 1740, 1210, 1150, 950, 870, 760, 700. ^1H NMR (CDCl_3): δ 2 — 3.5 (bro, 2.9H), 4.0 (bro, 2H), 5.75 (bro, 0.1H), 7.2 (bro, 5H); ^{13}C NMR (CDCl_3): δ 40 ($\text{CH}_2 - \text{CHPh} - \text{CH}_2$), 45 ($\text{CH}_2 - \text{C} = \text{O}$), 65 ($\text{CO}_2 - \text{CH}_2$), 125, 130, 135 (aromatic carbons), 172 (CO_2), 194 ($\text{C} = \text{O}$).

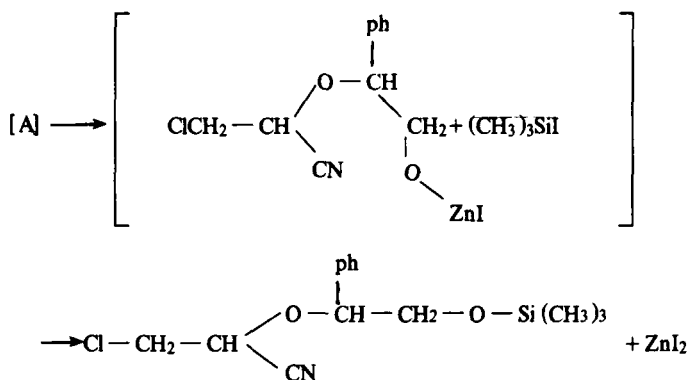
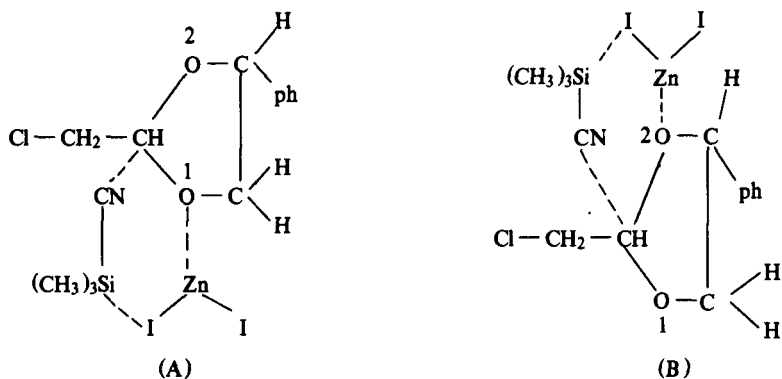
RESULTS AND DISCUSSION

The new monomer was synthesized by the reaction of trimethyl silylcyanide and cycloketal, followed by hydrolysis, ring closure and dehydrochlorination. The cycloketal, 2-chloromethyl-4-phenyl-1,3-dioxolane, was prepared according to Bailey's method^[5]. This cycloketal contains unsymmetrical elements. There are two stereoisomers (*cis* and *trans*). ^1H NMR and ^{13}C NMR spectra confirmed the presence of two isomers. For the reaction between the cyclic ketal and trimethylsilylcyanide, there are two ways for the attack of trimethylsilylcyanide to the cycloketal as shown in scheme I.



Scheme I

Two different intermediates, (2) and (2'), will be produced through different ways. However the experimental result showed that only one compound was formed during the reaction. The NMR spectra further confirmed that only compound (2) was formed during the reaction. This may be reasoned from reaction mechanism that oxygen 1 is more bare than oxygen 2 and favors the formation of transition state (A) which produced the desired compound (2) (see Scheme II). The formation of transition (B) is not favored because of steric hindrance. The compound (2) contains two chiral centers, and there are four stereoisomers. The ^1H NMR spectrum showed that there are four sets of chemical shift for one proton. Hydrolysis and ring closure of compound (2) under acidic condition

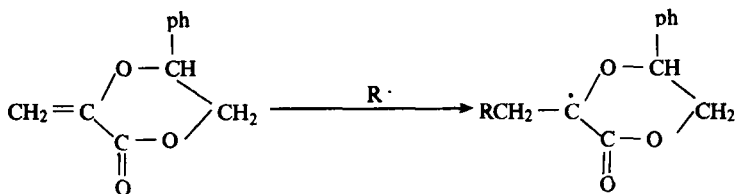


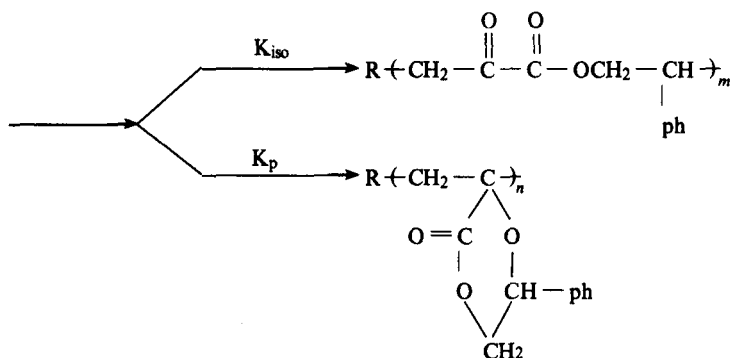
Scheme II

produces compound (3) which is viscous liquid, bp: 160 — 165 °C /133.3Pa. The spectra of ^1H NMR and ^{13}C NMR demonstrated the compound (3) consisting of four isomers. One of them was isolated by crystallization from ether, mp: 101 — 103 °C. The following reactions are based on the crystal compound (3). After dehydrochlorination of the compound (3), the desired monomer was obtained. Both ^1H NMR and ^{13}C NMR spectra of the monomer are much more simple than that of compound (3), because only one chiral center is left after elimination.

Similar to other cyclic acrylates the monomer is very reactive and sensitive to moisture and air. Under carefully controlled condition, polymerization was carried out at 120 °C, *t*-butyl peroxide as initiator and *t*-butylbenzene as solvent. The polymer structure was characterized by ^1H NMR and ^{13}C NMR. There are two possible processes for polymerization (see Scheme III).

According to the ^1H NMR spectrum of the polymer, it was found that the extent of ring opening during polymerization was nearly 100% since the chemical





Scheme III

shift at 5.75 almost disappeared and this chemical shift responds to methine proton with phenyl substituted group. The phenyl group favors ring opening process because of the formation of stabilized benzyl radical, so the driving force for ring opening is the formation of the new carbon-oxygen bond and benzylic radical. The polymerization result confirmed that the regioisomer formed in the reaction between 2-chloromethyl-4-phenyl-1,3-dioxolone and trimethylsilylcyanide was compound (2). Otherwise the essentially quantitative ring opening would not be obtained. Compared to other cyclic acrylates, this monomer is easier to undergo ring opening polymerization because of the phenyl substituted group. The ring opening polymerization of the monomer provides a way to introduce a ketone ester group into the backbone of the addition polymer and this may render the polymer both biodegradable and photodegradable.

The molecular weight of the polymer was estimated by viscosity measurement at 30 °C in dioxane. The intrinsic viscosity $[\eta] = 25 \text{ ml/g}$. The molecular weight of the polymer can be calculated as an approximation by the use of the constant of polyacrylic acid, $K = 7.6 \times 10^{-2} \text{ ml/g}$ and $\alpha = 0.5$ at 30 °C in dioxane: $MW = 3.3 \times 10^4$.

Keywords :

Free radical ; Ring opening polymerization ; Cyclic acrylate

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