

SYNTHESIS AND POLYMERIZATION OF 2-OXO-3-METHYLENE- 5,6-DIPHENYL-1,4-DIOXAN*

FENG Pinzhen(冯品珍)and LU Jiantao(鲁剑涛)

(Chemistry Department, Graduate School, Academia Sinica, Beijing, 100039)

ABSTRACT

A new cyclic monomer, 2-oxo-3-methylene-5, 6-diphenyl-1, 4-dioxan, was synthesized. The structure of the intermediates and the monomer were determined by IR, ^1H NMR, ^{13}C NMR and elemental analysis. This new monomer is different from other cyclic monomers in this series, it is a solid (mp 108—109°C) and not very reactive, but still can undergo free radical ring-opening polymerization. The free radical polymerization was carried out at 130°C. The structure of the resulting polymer was discussed and characterized by IR, ^1H NMR, ^{13}C NMR and elemental analysis. The molecular weight of the polymer was estimated by viscosity determination.

INTRODUCTION

In recent years a research program was undertaken for the purpose of synthesizing new functional monomers^[1]. It was found that cyclic acrylates such as 2-phenyl-5-methylene-1, 3-dioxolan-4-one^[2], 2-oxo-3-methylene-5-phenyl-1, 4-dioxan^[3] were very reactive functional monomers, they can undergo free radical ring opening polymerization. The ring opening polymerization of these cyclic acrylates make it possible to introduce ketone ester group into the backbone of various addition polymer by a free radical mechanism. However a great care should be taken in handling the monomers because of their high reactivity.

In this paper a new cyclic acrylate, 2-oxo-3-methylene-5, 6-diphenyl-1, 4-dioxan, was designed, synthesized and polymerized. This new monomer is rather stable but still can undergo free radical ring opening polymerization. Because of the presence of two phenyl group, unsymmetric elements present in the intermediates and monomer molecule were reduced. And this made it easier than the situation where only one phenyl group was present^[3] to be separated, purified and characterized.

EXPERIMENTAL

Chloroacetaldehyde dimethyl acetal, trimethylsilylcyanide, 1,8-diazabicyclo(5, 4, 0)undec-7-ene (DBU) and hydrobenzoin were purchased and used without further purification. All 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 on Perkin Elmer 298 infrared spectrophotometer.

2-Chloromethyl-4,5-diphenyl-1,3-dioxolane (1)

To a 500ml flask were added 50g (0.23 mol) of hydrobenzoin, 29g (0.23 mol) of chloroacetaldehyde dimethylacetal, 1.0g of paratoluene sulfonic acid (PTSA) and 200ml of toluene. The mixture was heated to 110–120°C. Methanol formed during the reaction was distilled out as azeotropic mixture with toluene. After the reaction was complete, 100ml of benzene was added into the reaction mixture, and then the solution was washed with aqueous sodium bicarbonate once and brine twice, followed by drying on anhydrous sodium sulfate. After the removal of solvent, white solid was obtained, which was recrystallized from hexane-benzene, 56g (88.6%) of crystal were obtained. mp 86–87°C; IR (KBr) 2880–3010, 1600, 1150, 1010–1030, 700, 670, 630; ^1H NMR (CDCl_3) δ 3.9(d, 2H); 5.41–5.54(m, 3H); 7.0(m, 5H); ^{13}C NMR (CDCl_3) δ 43.5 ($\text{Cl}-\text{CH}_2$); 82.66 ($\text{O}-\text{CHPh}$); 102.18 ($\text{O}-\text{CH}-\text{O}$); 126.8, 127.0, 127.31, 127.52, 127.57, 128.14, 136.53 (aromatic carbons); Anal. Calcd. for $\text{C}_{16}\text{H}_{15}\text{O}_2\text{Cl}$: C%, 69.95; H%, 5.50; Cl%, 12.9. Found: C%, 69.81; H%, 5.45; Cl% 13.10.

1-Chloromethyl-(1', 2'-diphenyl-2'-trimethylsilyloxy) ethoxy acetonitrile(2)

To a solution of 69.2g (0.252mol) of 2-chloromethyl-4,5-diphenyl-1,3-dioxolane in 250ml of ether were added 30g (0.30mol) of trimethylsilylcyanide and 3.3g of zinc iodide under nitrogen. The mixture was stirred at room temperature. The progress of the reaction was monitored by ^1H NMR spectroscopy. The disappearance of the trimethylsilyl cyanide at chemical shift of 0.3 ppm and the appearance of new peak of the trimethylsiloxy group at $\delta=0.1$ ppm showed the end of the reaction. This reaction lasted for two days, then the ether solution was washed with 10% of aqueous sodium thiosulfate in order to remove iodine formed during the reaction, followed by washing with brine twice and drying on anhydrous sodium sulfate. When most of ether was removed by evaporation, white solid precipitated out,

which was collected by filtration, 64.2g (68%) of white solid were obtained, mp 79—80°C; IR (KBr) 2880—3060, 1350, 1110, 1000, 890, 840, 760, 700, 610; ^1H NMR (CDCl_3) δ -0.22(s, 9H); 3.3(m, 2H); 4.1(T, 1H); 4.4(d, 1H); 4.6(d, 1H); 7.2—7.3(m, 10H); ^{13}C NMR (CDCl_3) δ -0.46 (Si—CH₃); 42.4 (Cl—CH₂); 68.7, 77.8 (O—CHPh—CHPh—O); 88.12 (Cl—CH₂—CH); 115.97 (—CN); 126.92, 127.10, 127.78, 127.85, 127.91, 128.00, 128.43, 137.38, 141.25 (aromatic carbons); Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{NSiCl}$: C%, 64.23; H%, 6.47; N%, 3.75; Cl%, 9.48. Found: C%, 64.29; H%, 6.42; N%, 3.63; Cl%, 9.20.

2-Oxo-3-chloromethyl-5,6-diphenyl-1,4-dioxan (3)

To a 250ml flask contained 7.5g (0.02mol) of 1-chloromethyl (1', 2'-diphenyl-2'-trimethylsilyloxy) ethoxy acetonitrile was added 5ml of hydrochloric acid (37%) and reflux for one hour. Then 100ml of benzene was added to the flask and reflux for 12 hours. 3.6ml of water formed during the reaction was collected in a Dean-Stark trap. After the reaction was complete, the benzene solution was washed with 5% aqueous sodium bicarbonate once and brine twice, followed by drying over anhydrous sodium sulfate. 5g of viscous crude product was obtained after removing solvent. The mixture was separated on silical gel column (elute solvents: 10% ether-90% hexane). 2.7g (56%) of white crystal was obtained, mp 92—93°C; IR (CHCl_3) 2880—3100, 1740, 1180—1220, 1120, 700; ^1H NMR (CDCl_3) δ 3.88—3.96(d, d, 1H); 4.1—4.2(d, d, 1H); 4.97(T, d, 1H); 5.68—5.85(d, d, 2H); 6.96—7.24(m, 10H); ^{13}C NMR (CDCl_3) δ 45.29, (Cl—CH₂); 74.18, 75.42 (CO₂—CH—CH—O—); 84.11 (Cl—CH₂—CH); 126.69, 127.22, 128.10, 128.33, 128.46, 133.68, 134.23 (aromatic carbons); 166.53 (CO₂); Anal. Calcd. for $\text{C}_{17}\text{H}_{15}\text{O}_3\text{Cl}$: C%, 67.44; H%, 4.99; Cl% 11.72. Found: C%, 67.62; H%, 4.98; Cl%, 11.45.

2-Oxo-3-methylene-5,6-diphenyl-1,4-dioxan (4)

To a solution of 4.0g (0.0132 mol) of 2-oxo-3-chloromethyl-5,6-diphenyl-1,4-dioxan in 20ml of ether was added dropwise the solution of 2.0g (0.0132 mol) of DBU in 15ml of ether under nitrogen at 0°C with stirring. The mixture was stirred at 0—5°C for 2 hours. After the reaction was complete, the ether solution was washed with water twice and dried on anhydrous sodium sulfate. Then ether was removed by evaporation and 3.0g (85%) of colorless crystal was obtained, mp 108—109°C; IR (KBr) 2840—3015, 1715, 1625, 1270—1300, 1140, 690—710; ^1H NMR (CDCl_3) δ 5.2 (d,

1H); 5.7(d, 1H); 5.8(d, 1H); 6.9—7.3(m, 10H); ^{13}C NMR(CDCl_3) δ 76.35, 83.06 ($\text{CO}_2\text{—CH—CH—O—}$); 104.31 ($\text{CH}_2=\text{C}$); 126.57, 127.31, 128.01, 128.04, 128.14, 128.56, 128.69, 133.02, 133.83 (aromatic carbons); 147.28 ($\text{CH}_2=\text{C}$); 159.76 (CO_2); Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_3$: C%, 76.68; H%, 5.30. Found: C%, 76.85%; H%, 5.22.

Polymerization of 2-oxo-3-methylene-5,6-diphenyl-1,4-dioxan (4)

To a solution of 1.0g of 2-oxo-3-methylene-5,6-diphenyl-1,4-dioxan in 10ml of *t*-butylbenzene was added 0.02g of *t*-butylperoxide. The solution was heated to 130°C for 12 hours under nitrogen. After that, polymer was precipitated in 100ml ether, 0.8g (80%) of polymer was obtained. IR (KBr) 2900—3080, 1795, 1735, 1130—1225, 700.

RESULTS AND DISCUSSION

As mentioned in the previous paper^[2], cyclic acrylates are very reactive monomers, thus a great care has to be taken for handling them. This restricted their applications in industry. In order to develop a new cyclic acrylate, which is not very reactive but still can undergo free radical ring opening polymerization, a new monomer, 2-oxo-3-methylene-5,6-diphenyl-1,4-dioxan (4), was designed and it was successfully synthesized according to scheme I.

The structures of the intermediates compounds (1), (2), (3) and monomer compound (4) were characterized by IR, NMR and further confirmed by elemental analysis as described in the experimental section.

Polymerization of the monomer was carried out at 130°C for 12 hours, with *t*-butylbenzene as solvent and *t*-butylperoxide as initiator. The structure of the resulting polymer was determined by IR, NMR and elemental analysis. Molecular weight of the polymer was estimated by viscosity measurement at 30°C in dioxane. The intrinsic viscosity $[\eta] = 20\text{ml/g}$.

What is surprised is the IR spectrum of the polymer. There is a new absorption peak at 1795 cm^{-1} in addition to the ketone ester peak at 1735 cm^{-1} . This new peak is not expected. And the presence of this unexpected peak in the IR spectrum means that the polymerization process is not a simple one. Probably there is some rearrangement occurred during the polymerization. The absorption peak looks like the lactone carbonyl peak in five member ring cyclic acrylates^[2] (see the IR spectra of A and B showed below). However more satisfactory explanation has not got yet. Since the

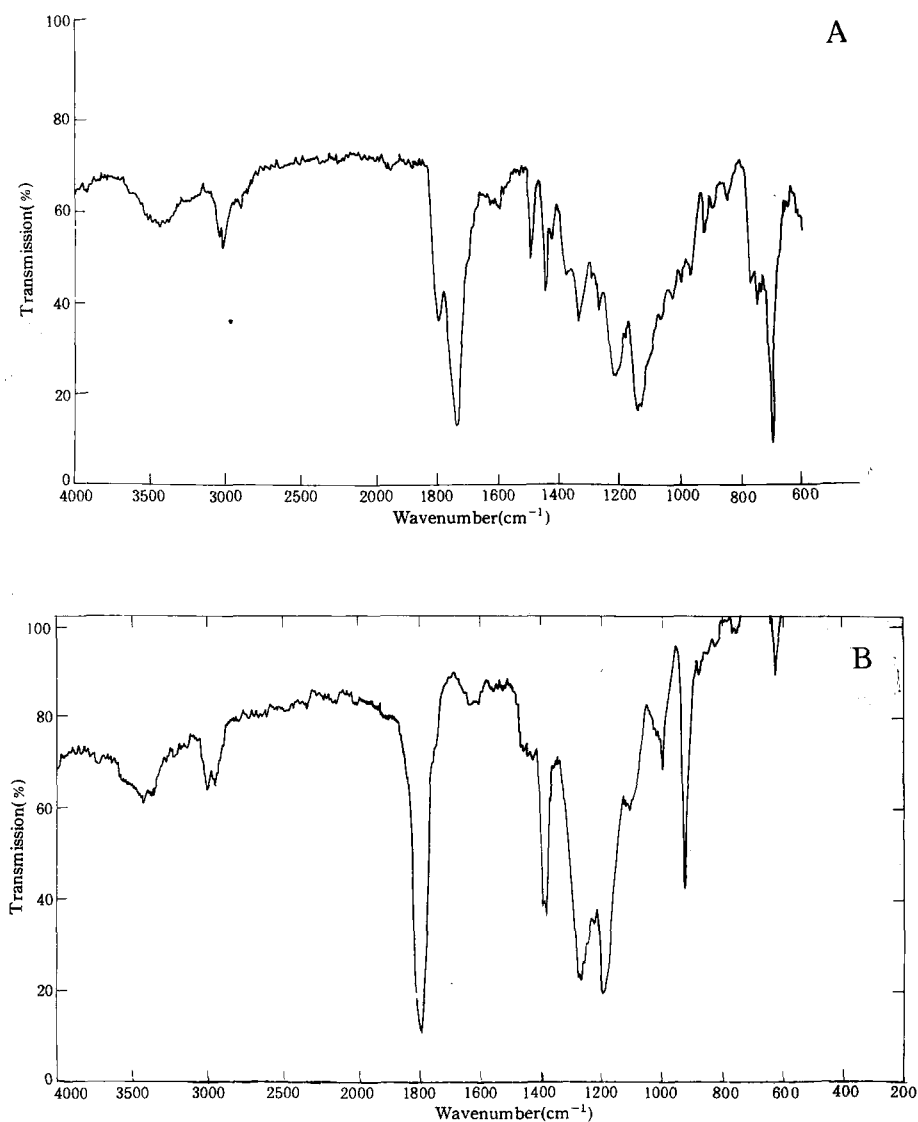
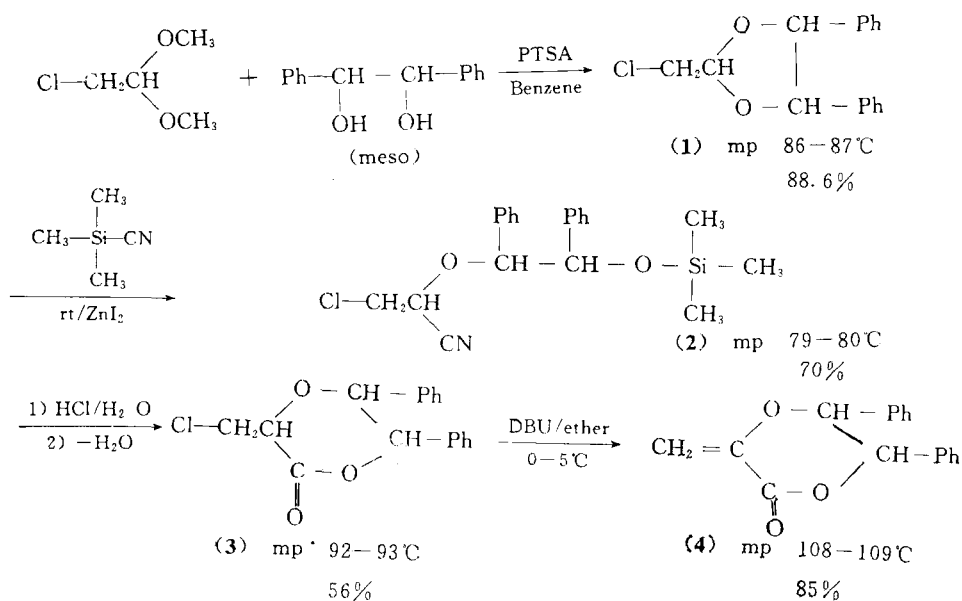


Fig. 1 IR spectra of the polymers

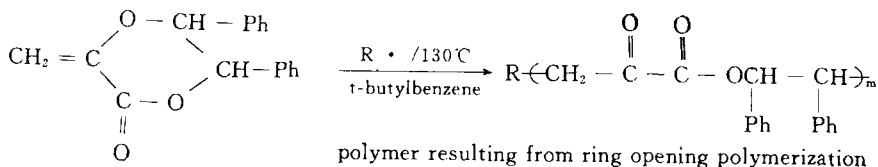
A is the IR spectrum of the polymer from the new monomer.

B is the IR spectrum of the polymer from five member ring cyclic acrylate^[2] without ring opening.

result of the elemental analysis of the polymer is the same as the formula of $(C_{17}H_{14}O_3)_n$, there is nothing to be split out during the polymerization. The probable process of the polymerization was showed in scheme II.



Scheme I



Scheme II

Keywords:

Free radical; Ring opening polymerization; Cyclic acrylate; 1,4-Dioxan

Acknowledgment The authors are grateful to the Third World Academy of Science and The University of Science and Technology of China for financial support of this work.

REFERENCES

- [1] Bailey, W. J.; Chou, J. L.; Feng, P. Z. et al. *J. Macromol. Sci. Chem.*, **1988**, A25, 781.
- [2] Feng, P. Z., *Chinese J. Polymer Science*, **1992**, 10(4), 350.
- [3] Feng, P. Z., *Chinese J. Polymer Science*, **1993**, 11(2), 154.