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Free-radical ring-opening polymerization of 2-(*o*-chlorophenyl)-4-methylene-1,3-dioxolane

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Abstract

2-(o-chlorophenyl)-4-methylene-1,3-dioxolane was synthesized and polymerized in presence of AIBN or by use of benzoin methyl ether as photosensitizer. Based on the analysis of the resulting polymers, a polymerization mechanism was proposed.

Introduction

Last years, a series of papers reported the radical ring-opening polymerization of vinylcyclopropanes (1), unsaturated spiro orthoesters (2), unsaturated spiro orthocarbonates (3) and methylene derivatives of 1,3-dioxolane (4).

As for 2-phenyl-4-methylene-1,3-dioxolane (PMD), its radical ring-opening polymerization may occur in three different ways (5,6), namely (a) according to a normal vinyl polymerization, to yield macromolecular chains containing cycles, (b) according to a vinyl polymerization followed by ring-opening, and (c) according to a vinyl polymerization followed by both ring-opening and elimination of benzaldehyde. The distribution of the three types of structural units in the chain was proved to be determined by initiation and radical polymerization conditions. High solvent/monomer ratio favours the ring-opening polymerization and benzaldehyde elimination (5).

On the other hand, the photopolymerization of PMD allows the synthesis of a chemically homogeneous polymer containing only structural units having open cycles and occurs without benzaldehyde elimination (6).

The reported data thus indicate that, according to the polymerization conditions, dioxolane monomers yield polymers and/or copolymers with a large variety of structures.

The present paper is concerned with the photoinitiated and with the 2,2′-azobisisobutyronitrile (AIBN) free- radical ring-opening polymerization of 2-(o-chlorophenyl)-4-methylene-1,3-dioxolane (CPMD).

Experimental Part

A. Monomer preparation

1. Preparation of 2-(o-chlorophenyl)-4-chloromethyl-1,3-dioxolane (CPCMD)

To a solution of 70.5 g (0.5 mol) o-chlorobenzaldehyde and borontrifloride etherate (1 ml) in 100 ml carbon tetrachloride, 69.7 g (0.75 mol) epichlorohydrin was added dropwise over 1 h at a temperature below 15°C. After the addition was completed the mixture was stirred for an additional 9 h period at the same temperature. The $BF_3 \cdot OEt_2$ catalyst was then destroyed by addition of 3 ml of triethylamine. The mixture was

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washed with water and dried over anhydrous potassium carbonate. The solvent was removed under reduced pressure, and the residue was fractionally distilled to give 71.0 g (yield, 61 %) of CPCMD, b.p. 148°C/8 mm Hg.

^{1}H-NMR (CCl_4): δ=7.2 ppm (4H from o-chlorophenyl), 6.0-6.3 ppm (1H, ClPh-CH), 4.1-4.4 ppm (3H, -O-CH_2-CH(CH_2Cl)-O-), 3.7 ppm (2H, -CH_2Cl).

2. Preparation of 2-(o-chlorophenyl)-4-methylene-1.3-dioxolane (CPMD)

A solution of 29.4 g (0.15 mol) CPCMD in 50 ml THF was added dropwise into a mixture of 22.4 g (0.2 mol) of potassium t-butoxide in 100 ml THF while stirring at 60°C for 1 h. After the addition was completed, the mixture was stirred for an additional 9 h period and then poured into 150 ml water. The aqueous solution was extracted four times with ether. The organic layer was dried over anhydrous potassium carbonate and ether was removed by evaporation. The residue was fractionally distilled to obtain 24.0 g (yield, 82 %) CPMD, b.p. 134°C/8 mm Hg.

IR (KBr): 1687 cm^{-1} (-C=C-), 1080, 1065 cm^{-1} (-C-O-), 760, 700 cm^{-1} (substituted benzene ring).

^{1}H-NMR (CCl_4): δ=7.3 ppm (4H from o-chlorophenyl), 6.4 ppm (1H, ClPh-CH), 4.6 ppm (2H, -CH_2-O-), 4.3 ppm (1H, -C=C-H), 4.0 ppm (1H, -C=C-H).

B. Polymerization

1. Radical polymerization of CPMD

The polymerization was carried out in bulk, in sealed tube, in the presence of 3 mol % AIBN as initiator (see Table 1). The resulting polymers were purified by dissolution in benzene followed by precipitation in petroleum ether, then dried under reduced pressure at room temperature.

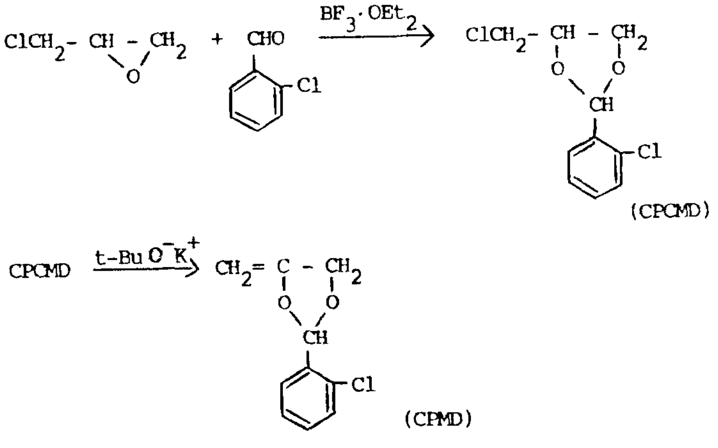
2. Photopolymerization of CPMD

The photopolymerization was carried out in bulk, in sealed Quartz tube, by use of a 280 W Hg lamp, at 50°C, during 11 h, in the presence of benzoin methyl ether (BME) as sensitizer. The distance between the lamp and the ampule was 11 cm. Following the reaction, the content was dissolved in benzene and precipitated in petroleum ether.

The proton chemical signals are listed in Table 2.

Results and Discussion

The monomer CPMD was prepared according to Scheme 1.



Scheme 1

The polymerization conditions and results are summarized in Table 1

Table 1: Polymerization of 2-(o-chlorophenyl)-4-methylene-1.3-dioxolane.

Initiator (Sensitizer) (mol %)	Temp. (°C)	Polym. duration (h)	Polymer[a] yield (%)	[η][b] (dl/g)	Units distribution in polymer[c] I	II	III	IV
AIBN (3)	70	168	35	<0.1	<15	20	<5	60
BME (1)	50	11	92	<0.1	0	45	0	55

a) insoluble in petroleum ether
b) in chloroform, at 30°C
c) as determined from the ratio of the integrated NMR peaks;
I - units with intact ring; II - ring-opening; III - elimination;
IV - ring-opening with exomethylenic group (see also Table 2).

Table 2: ^{1}H-NMR characteristic signals and attribution (units I-IV).

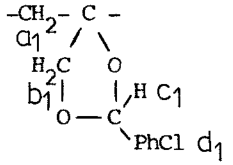
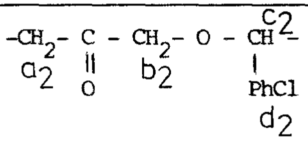
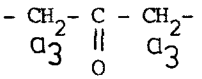
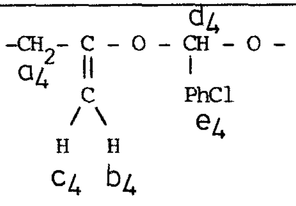
Repeating unit	Proton	δ (ppm)	Structure
I	a_1	1.2-1.5	
	b_1	3.9-4.2	
	c_1	5.1-5.5	
	d_1	7.1-7.6	
II	a_2	2.7-3.0	 $-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-O-\underset{\underset{PhCl}{\vert}}{CH}-$
	b_2	3.9-4.2	
	c_2	5.1-5.5	
	d_2	7.1-7.6	
III	a_3	2.7-3.0	 $-CH_2-\underset{\underset{O}{\|}}{C}-CH_2-$
IV	a_4	2.0-2.5	 $-CH_2-\underset{\underset{\underset{H\quad H}{/\ \backslash}}{C}}{\underset{\|}{C}}-O-\underset{\underset{PhCl}{\vert}}{CH}-O-$
	b_4	3.7-3.8	
	c_4	4.2-4.3	
	d_4	5.9-6.1	
	e_4	7.1-7.6	

Figure 1 presents the ^{1}H-NMR spectra of the obtained polymers.

The absence of a signal at $\delta=1.4$ ppm (Fig. 1,a) shows that the polymer obtained by photoinitiation doesn´t contain units with intact ring. The signals at 4.2-4.3 and 3.7-3.8 ppm (Fig. 1, a,b) indicate the existence of two protons in an exomethylenic group, while that at $\delta=2.0$-2.5 ppm is characteristic to the $-CH_2-\underset{|}{C}=CH_2$ group. These assignements justify the proposed structure IV.

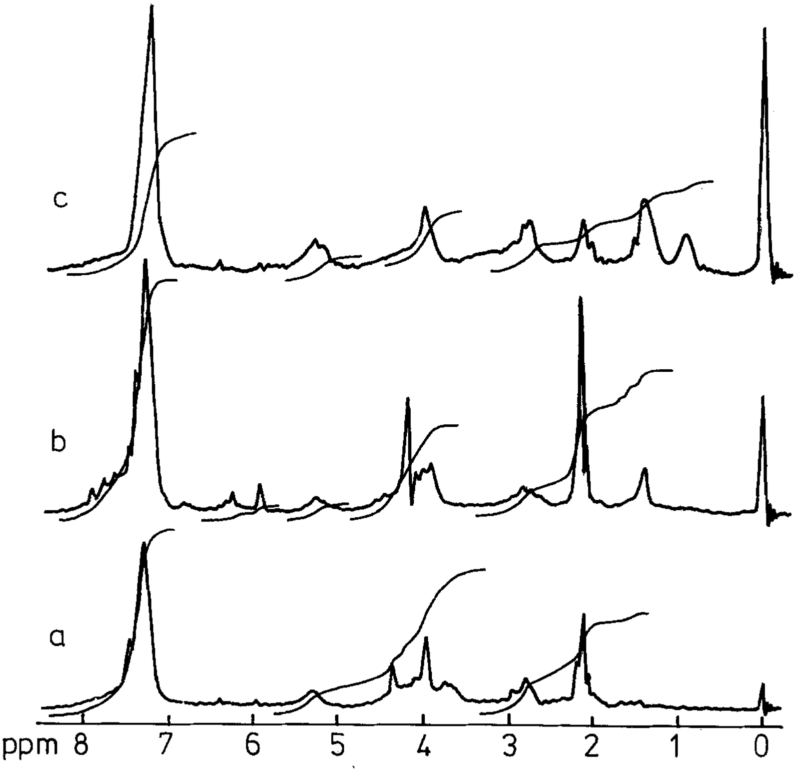


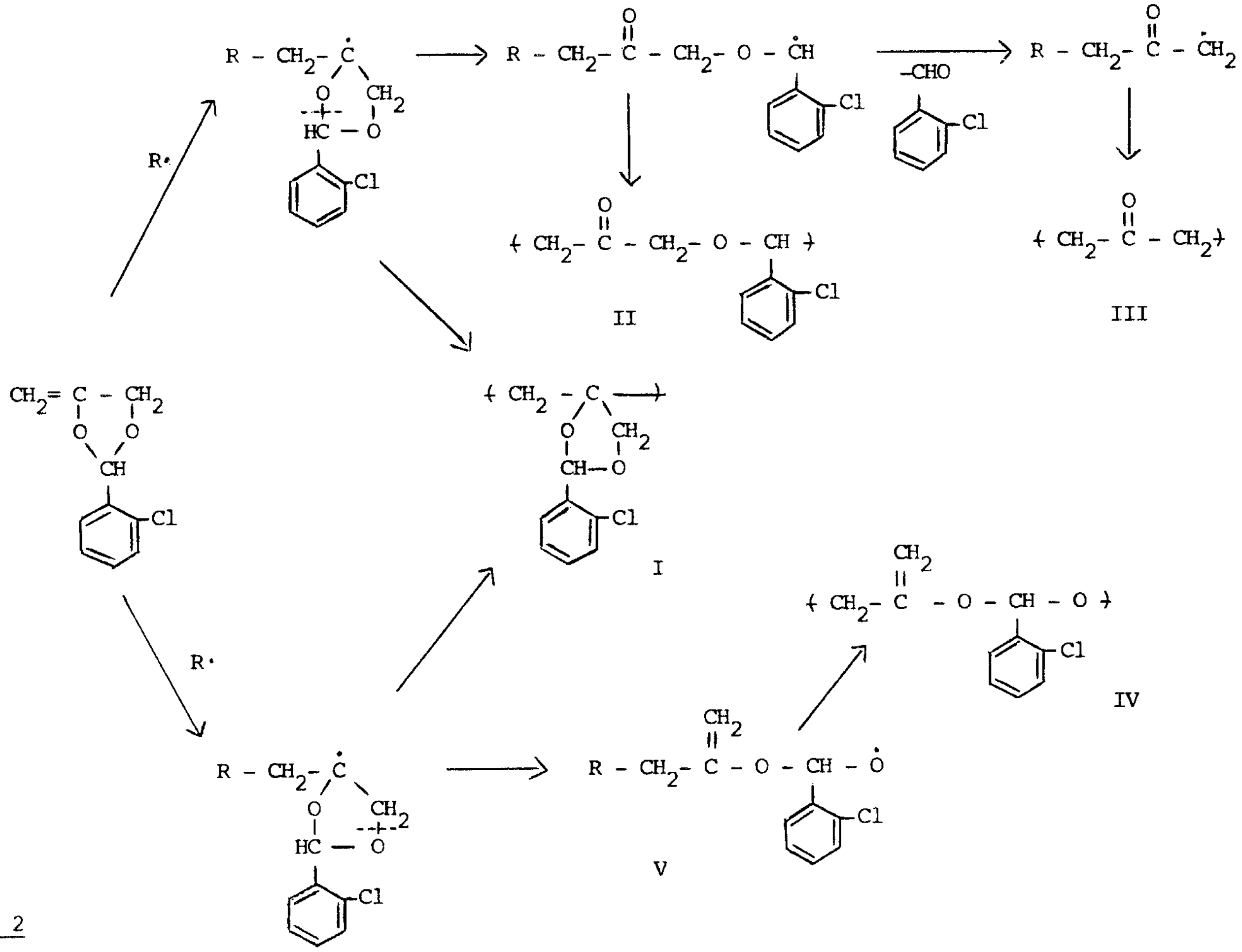
Figure 1. ^{1}H-NMR spectra of the polymer obtained (a) by photoinitiation, (b) by chemical initiation with AIBN, and (c) of the polymer reprecipitated following the addition of Br_2 at the $\gt C{=}CH_2$ double bond.

The following reaction mechanism can explain the coexistence of four different structural units in the obtained products (Scheme 2).

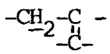
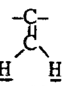
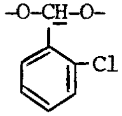
As can be seen from Table 1, both polymers have a high content of type IV structural units. The amount of units containing exomethylenic groups was determined by use of the $KBrO_3$/KBr method. After an addition duration of 24 h of Br_2 at the double bonds, the results indicated 0.255 unsaturated groups/100 g polymer, as compared to 0.32 unsaturated groups/100 g polymer from NMR spectrum. The difference between the two values can be explained by the incomplete addition of Br_2 at the $\gt C{=}CH_2$ bond.

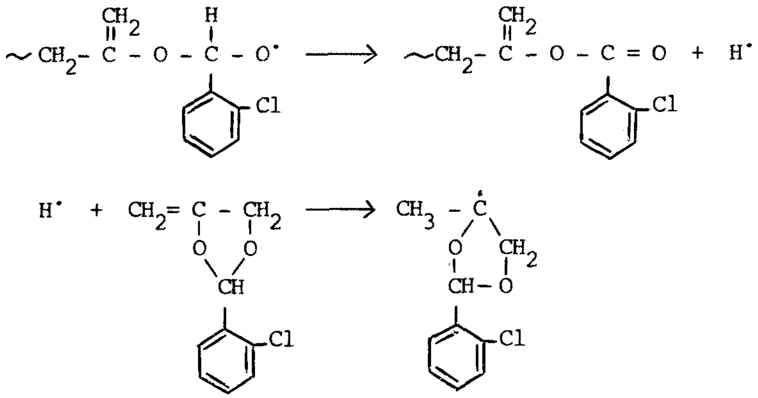
The bromurated polymer was reprecipitated, and its ^{1}H-NMR spectrum is given in Fig. 1,c. The disappearance of the signals at 4.2-4.3 ppm and 3.7-3.8 ppm, corresponding to the $\gt C{=}\underline{CH_2}$ protons, as well as the decrease of the signal corresponding to the $-\underline{CH_2}-\underset{\underset{CH_2}{\|}}{C}-$ protons prove the existence in the original polymer of type IV structural units.

A disagreement was observed in the ^{1}H-NMR spectra (Fig. 1,a,b) between



Scheme 2

the integrals of the signals corresponding to  $-CH_2-\underset{\underset{-C-}{\|}}{C}-$ and  $-\underset{\underset{\underset{\underline{H}\quad\underline{H}}{C}}{\|}}{C}-$ protons (structural unit IV) and the integral of the signal corresponding to the  $-O-\underline{C}H-O-$ proton of the same structural unit. This was explained by the presence, in the structure of radical V (Scheme 2), of a benzylic hydrogen able to stabilize the radical according to Scheme 3.



Scheme 3

This transfer reaction could also explain the low values of the determined intrinsic viscosities (molecular weights) of the resulting polymers.

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