

SYNTHESIS OF MESOGENIC POLYESTERS WITH 2-DICHLOROMETHYLHYDROQUINONE MOIETIES*

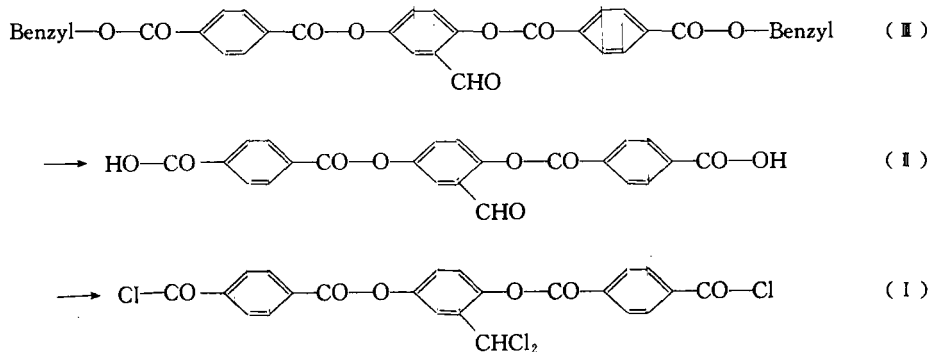
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ABSTRACT

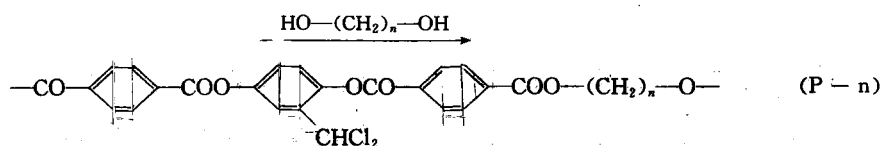
A series of novel mesogenic polyesters with 2-dichloromethylhydroquinone moieties were synthesized by polycondensation of the novel diacyl chloride monomer 2-dichloromethyl-1,4-bis(4'-chloroformylbenzoyl)oxybenzene (I) with α, ω -polymethylenediols including ethylene glycol, 1,4-butanediol, 1,6-hexanediol and 1,10-decanediol. The diacyl chloride monomer was synthesized by simultaneous transformations of both the carboxy and formaldehyde groups of 2-formyl-1,4-bis(4'-carboxybenzoyl)oxybenzene into acyl chloride and dichloromethyl groups respectively. The syntheses of the monomer (I) and the polymers were reported.

In the synthesis of novel mesogenic polymers with strong electron-pulling groups laterally substituted at the mesogenic units and with potential negative dielectric anisotropy, polyesters with 2-dichloromethylhydroquinone moieties were prepared through the following reactions:



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where $n=2, 4, 6, 10$ for the four polymers.

The structures and properties of the monomer (I), the polymers and the intermediates were characterized by using ST-02 or Heraeus instrument for elemental analyses, VG-IBA-HS for mass spectra, ARX400 for NMR analyses, Leitz Laborlux 12 Pol for melting and liquid crystal phase transitions, Waters 201 instrument with polystyrene standards for polymer molecular weight determination and Shimadzu DSC-50 for the thermal behavior of the polymers. The results for compound (I) and the monomer (I) are shown in Table 1.

Table 1 Key data for the synthesized compounds I and I

Compound	I		I	
Yield	89%		78%	
Mol. wt. (by MS)	434		526	
Melt. point (°C)	320*		164—166	
C,H anals. calcd. (%)	C:63.6	H:3.25	C:52.51	H:2.27
found	C:63.6	H:3.29	C:52.34	H:2.20
NMR results(ppm)	7.6—8.3;	11 H for benzene	6.89;	1H for —CHCl ₂
	10.12;	1H for—CHO	7.42—7.77;	3 H for
	13.50	2H for—COOH		central ring
			8.27—8.40;	8 H for
				terminal rings

* as determined by polarizing microscope. Compound I is also thermotropic with a clearing temperature of 377°C of the nematic liquid crystal phase.

2-Formyl-1,4-bis(4'-carboxybenzoyl)oxybenzene (I) is a new liquid crystal compound which has been synthesized through a series of reactions by following a general procedure used by Hasslin et al.^[1]. In short, terephthaloyl chloride was reacted with benzyl alcohol in the presence of THF as the solvent and pyridine as the HCl acceptor. The obtained dibenzyl terephthalate was partially hydrolyzed by a controlled addition of KOH to yield the desired monobenzyl ester of terephthalic acid, which was then

reacted with thionyl chloride and transformed into its acid chloride. The reaction of this acid chloride and 2, 5-dihydroxybenzaldehyde (gentisaldehyde) gave the product (III), yield 80%. M.P. 122-124 °C. The molecular structure of (III) was confirmed by routine analysis including the Mass Spectroscopy, the elemental analysis and high resolution NMR. The benzyl protected ester was then treated with HBr/glacial acetic acid with trifluoroacetic acid as the solvent to give the product (II).

The one step transformation of (II) into monomer (I) is an interesting one, the synthesis is described as follows: Into 1.0 g of the compound (II) an excess amount of thionyl chloride was added. The mixture was refluxed for 1 hour to obtain a clear solution. The excess thionyl chloride was removed using a rotary evaporator and a white solid product was obtained. The product was washed several times with cold toluene and dried in a vacuum oven. The yield was 78%. By routine analysis this product was proved to be the monomer (I). As described here this monomer was obtained by the simultaneous transformations of both the carboxy and the formaldehyde groups of the molecule (II) to acyl chloride and dichloromethyl groups respectively.

It has been known that O-sulfinylation of carbonyl compounds by thionyl chloride can lead to gem-dichlorides. A review of these reactions was given by Oka [2]. However, our synthesis reported here is the first example to prepare a monomer with two acyl chloride and one dichloromethyl groups in one single step by using this reagent.

Solution polymerization of equal molar (I) and a diol was used to synthesize the polymers. As an example, 0.44 g (0.84 mmol) of (I) was dissolved in 5 ml 1, 1, 2, 2-tetrachloroethane and 1 ml pyridine at room temperature, into which a solution of 0.174 g (0.84 mmol) 1,10-decanediol in 1 ml pyridine and 5 ml tetrachloroethane was added under nitrogen. The mixture was stirred at room temperature for two days, at 80°C for two hours and then poured into methanol to obtain the polymer as a white mass. After filtration, it was washed in turn with dilute hydrochloric acid, dilute solution of sodium carbonate, de-ionized water and acetone. The product was further purified by repeated dissolution-precipitation using THF as the solvent and methanol as the precipitant before characterization.

The molecular weights and thermal properties of the polymers are enumerated in Table 2. The molecular weights are low in general and it might be attributed to the low reactivity of the diols [3]. The properties of

the polyester polymers will be discussed later but suffice it to mention here that all the polymers are liquid crystalline with phase transition temperatures as shown also in Table 2. Values for T_m and T_i of the polymers were obtained by polarizing microscopic observations and confirmed by DSC measurements.

Table 2 Data for the synthesized polyester polymers

Polymer	M_n	M_w	$T_m(^{\circ}\text{C})$	$T_i(^{\circ}\text{C})$
P-2	3100	5900	130—170	186—200
P-4	3000	6300	150—175	210—250(with decompn.)
P-6	8400	18000	112—136	160—170
P-10	11000	21000	90—110	116

Keywords :

2-dichloromethylhydroquinone; 2-dichloromethyl-1,4-bis(4'-carboxybenzoyl)oxybenzene; 2-dichloromethyl-1,4-bis(4'-chloroformylbenzoyl)oxybenzene; Liquid crystalline polymer; Polyesters

REFERENCES

- [1] Hasslin, H. W. ; Droescher, M. and Wegner, G. , *Makromól. Chem.* , **1980**, 181, 301
- [2] Oka, K. , *Synthesis* , **1981**, p. 661
- [3] Odian, G. "Principles of Polymerization", 3rd ed. , John Wiley and Sons, New York, **1991**, p. 96