

STUDY ON LIQUID CRYSTAL POLYMERS WITH TWO-DIMENSIONAL MESOGENIC UNITS

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ABSTRACT

A series of liquid crystalline polymers with two-dimensional mesogenic units were synthesized by solution polycondensation at low temperature. All the polymers were liquid crystalline. The melting temperature T_m (except that with substituent of methoxy) and the clearing temperature T_i of the polymers change regularly with varying of the length of the alkyl substituent groups.

INTRODUCTION

It is a new field to introduce two-dimensional mesogenic units into polymer chains to obtain "liquid crystalline polymers with two-dimensional mesogenic units"^[1]. Some reports about this aspect have already been published in recent years^[2-4]. Since this type of polymers are expected to have not only extended chain conformation as that of a rigid main chain liquid crystal polymer, but also stronger lateral molecular interactions between the molecules, a new type of materials may be formed with good but less-anisotropic mechanical properties. It is therefore valuable to further study the relations between molecular structure and properties of this type of liquid crystal polymers. In this paper, we report the synthesis and properties of a new series of liquid crystal polymers with the emphasis on the substituent effect.

EXPERIMENTAL

1. Characterization

The monomers and polymers were characterized by the following techniques:

Melting point measuring: WRS-1 apparatus, Shanghai Physical and Optical Instrument Factory.

Elemental analysis: MOD 1106 (Italy),

H-NMR: Varian FT-80A with CDCl_3 as solvent.

DSC: Perkin-Elmer DSC-4, heating and cooling rate: 20 °C / min in N_2 .

TG: Rigaku, 20 °C / min in N_2 .

Intrinsic viscosity measurement: Ubbelohde type, at 40 °C with 25/35/45 (by

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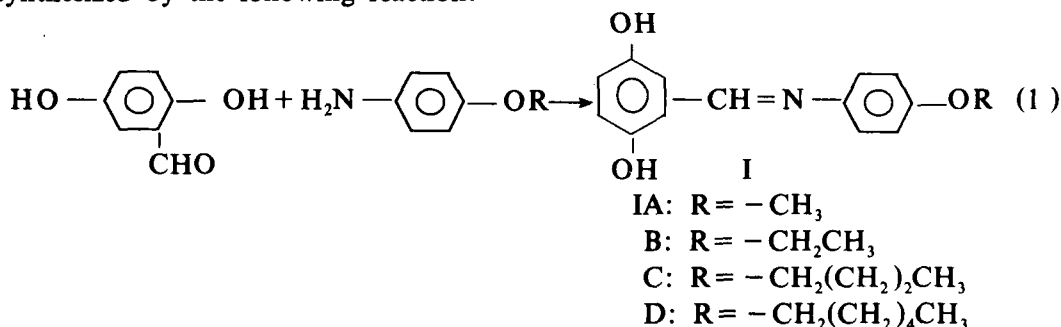
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volume) phenol/tetrachloroethane/4-chlorophenol as solvent in a concentration of 0.5g/dl.

2. Synthesis of the monomers

The monomers N-2', 5'-dihydroxybenzylidene-4-alkoxyanilines were synthesized by the following reaction:



Equal mole of 2,5-dihydroxybenzaldehyde and a p-alkoxyaniline were dissolved in absolute ethanol, several drops of acetic acid were added. The solution was stirred for 6 hours at room temperature. The alcohol was distilled off by vacuum. After recrystallization of the remains from chloroform/n-hexane and dried in vacuum, compound I was obtained as a yellowish powder. Four monomers with different alkoxy groups were thus synthesized with yields for IA 85%, IB 87%, IC 83% and ID 86%.

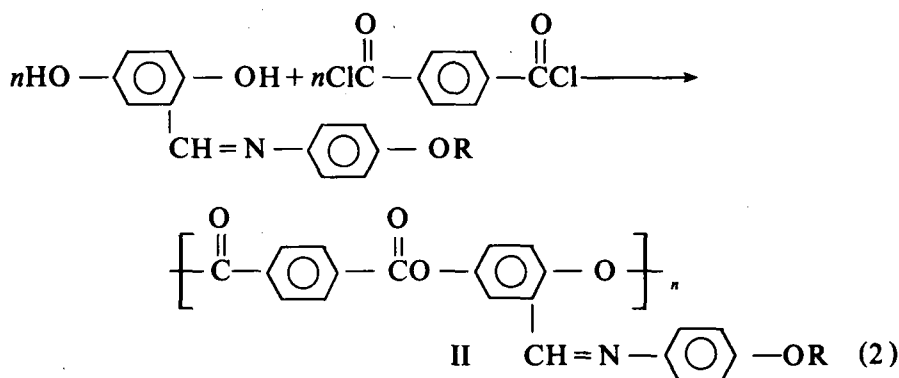
The results of the characterization of compounds IA-ID were collected in Table 1.

Table 1 The characterization of compounds I

	¹ H-NMR (CDCl ₃)		Element analysis			MP(°C)
			C%	H%	N%	
IA	3.84(3H, s)					
	6.84 — 7.36 (7H, m)	Calcd.	69.12%	5.39	5.76	144.2 — 144.5
	8.51 (1H, s)	Found.	69.00	5.93	5.17	
IB	1.34 — 1.52 (3H, t)					
	3.93 — 4.19 (2H, q)	Calcd:	70.02	5.88	5.44	139.0 — 139.4
	6.87 — 7.32 (7H, m)					
	8.51 (1H, s)	Found:	69.91	5.96	5.28	
IC	0.69 — 1.06 (3H, t)					
	1.28 — 1.95 (4H, m)	Calcd:	71.56	6.71	4.91	123.7 — 123.9
	3.83 — 4.06 (2H, t)					
	6.87 — 7.31 (7H, m)	Found:	71.60	6.80	5.15	
	8.50 (1H, s)					
ID	0.91 (3H, t)	Calcd:	72.82	7.40	4.71	
	1.28 — 1.79 (8H, m)					
	3.88 — 4.04 (2H, t)	Found:	72.73	5.54	4.61	118.4 — 119.1
	6.85 — 7.28 (7H, m)					
	8.46 (1H, s)					

3. Synthesis of the polymers

The polymers were synthesized according to the following reaction:



IIA: R = -CH₃

B: R = -CH₂CH₃

C: R = -CH₂(CH₂)₂CH₃

D: R = -CH₂(CH₂)₄CH₃

0.0019mol of a compound I was dissolved in 1ml pyridine and 4ml THF. Equal mol of terephthaloyl chloride was dissolved in 4ml THF and added dropwise into the former solution at 0 °C. After stirred for 48 hours at the same temperature, the reaction solution was poured into methanol to precipitate the polymer which was then filtered and dried. By the same procedure four powder samples of the polymers with different R chains were obtained. The samples were all purified by redissolution in DMF and reprecipitation in methanol.

RESULTS AND DISCUSSION

The structures of compounds I were confirmed by the results of characterization (Table 1).

All the four polymer samples were pale yellowish powder in appearance and insoluble in THF and other common organic solvents. Because of the poor solubility, the molecular weights of the polymers were not examined, but intrinsic viscosities were determined and listed in Table 2.

Table 2 Intrinsic viscosities of the polymers

Polymer	IIA	IIB	IIC	IID
[η] g/dl	0.26	0.31	0.32	0.35

As shown in Table 2, the intrinsic viscosity of the polymer samples was not high (0.26 — 0.35). This is considered to be the result of the low reactivity of the substituted hydroquinone monomers. First of all, the nucleophilicity of the phenolic oxygen is lowered by delocalization of the p-electrons of the oxygen ortho to the azomethine bond over the large conjugated benzyldeneaniline structure. In addition, intramolecular hydrogen bonding between the hydroxyl group and the nitrogen of the azomethine structure of the phenolic monomer is possible, which would make the leaving of the hydrogen atom more difficult. A further factor might also responsible for the low reactivity of the phenolic monomer is the considerable bulkiness of the substituent on the hydroquinone ring, which would hinder the approaching of the phenolic oxygen to the acyl chloride. The low

reactivity has made it very difficult to obtain high molecular weight polymers. Very pure monomers (as may be judged from the elemental analysis) had been used, the polymerization time had been lengthened, yet only low molecular weight samples were obtained.

From DSC, TG and the observation by polarizing microscope with a heating stage, the thermal properties of the polymers were studied and the parameters were shown in Table 3.

Table 3 Thermal properties of the polymers*

Polymer	R	Transition point		Decomposition T_d
		T_m	T_i	
IIA	methyl	185	312	300
IIB	ethyl	276	290	287
IIC	n-butyl	252	270	265
IID	n-hexyl	234	215**	280

* Temperatures are in $^{\circ}\text{C}$. T_m : melting point; T_i : clearing temperature; both are from DSC.

T_d : initial decomposition temperature from TG.

** See the text for interpretation.

It is well known that properties of LCPs are dependent on molecular weight and molecular structure of the polymers. In general, the melting and clearing points will rise with the rising of molecular weight and reach a plateau value when the molecular weight becomes high enough. It is thus desirable to compare properties of polymers with wimilar molecular weights especially when the latter are still low. For the present series of polymers, the intrinsic viscosities, though relatively low, were similar for polymers IIB, IIC and IID. It is therefore possible to compare the properties of these polymers, and to interpret the property difference in view of the molecular structure variation. A significant decrease in melting temperature was observed from polymer B to D, with the increase of the number of carbon atoms in the substituent groups of the polymer molecules. The increase of the number of carbon atoms (thus the bulkiness) of the substituents would lower the packing efficiency of the molecules in the crystal lattice. The intermolecular interactions among the molecules of chain segments will be weakened also. One thus expects a lower crystallinity and a lower stability of the crystal lattice, and in turn a lower melting point for the polymer with longer alkyl substituents. Besides, the conformational entropy would also contribute to the lowering of the melting point.

The intrinsic viscosity of IIA is much lower than that of the other three polymers in the series. This indicates an even lower molecular weight for this polymer, and may have offered an explanation for its lowest melting point in the series.

Also in Table 3 one finds the decrease of the clearing point T_i with the increase of carbon number in the substituents. The polymer IIA has the highest T_i though its viscosity is the lowest. It seems that the molecular diameter of the polymer chain is now a decisive parameter for the thermal stability of the liquid crystal phase of the four polymer samples. For oligomers, a bigger diameter means a lower axial ratio of the molecular rods; for higher molecules, a bigger diameter would result in a lower ratio of the Kuhn segment length to the diameter,

depending on the nature of the chains. Whatever it is will have influence on the stability of a mesophase, and in the same series of polymers a lower T_i is expected for the one with bigger molecular diameter.

The transition temperatures observed from polarizing microscope with a heating stage were the same as that obtained from DSC. All the polymers but IID go into liquid crystal phase after melting. The textures of the mesophases were nematic (Figure 1). When the polymer samples were heated at the temperature

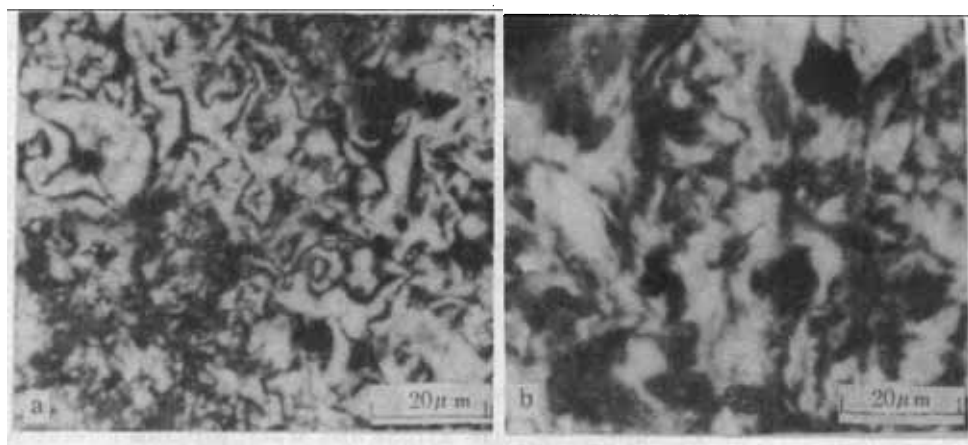


Fig.1 Polarizing photomicrographs of the polymers
a) polymer IIA at 300 °C b) polymer IID at 193 °C

close to T_i , a slight decomposition appeared. It was observed that the polymer IID exhibited a transient schlieren texture in the melting process. The birefringence of IID recurred when it was cooled from its isotropic melt to 202 °C but disappeared again after reheated to 215 °C. The heating and cooling curves of polymer IID from DSC (Figure 2) showed that there is just one endothermal peak (234 °C) in the heating course, but two exothermal peaks (202 and 185 °C) in the process of cooling. The peak in cooling curves at 202 °C represented the thermal transitions of IID from isotropic phase to anisotropic liquid crystal phase of which the texture is shown also in Figure 1. The peak at 185 °C exhibits the crystallization of IID from its liquid crystal state. If IID is first melted and cooled down only to its liquid crystal state, and then heated, the isotropization temperature of the mesophase is observed. Curve c of Figure 2 shows this process. The T_i thus obtained for IID is 215 °C comparable with the value observed optically. It can be concluded that IID is a monotropic liquid crystal polymer.

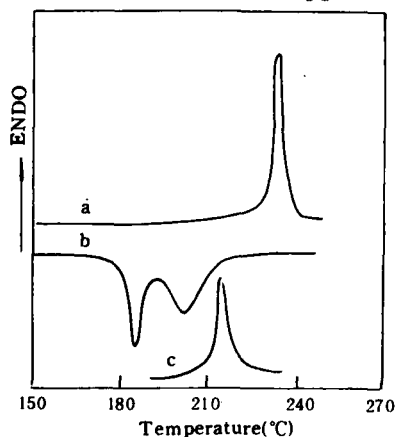


Fig.2 DSC curves of polymer IID
a) first heating scan;
b) first cooling scan;
c) second heating scan (the melt had been cooled only to 190 °C before this heating)

CONCLUSION

A new series of polymers with two-dimensional mesogenic units were

synthesized. All the polymers are liquid crystalline with one monotropic and three enantiotropic. The liquid crystal phases are nematic. The melting temperature T_m (except that with substituent of methoxy) and the clearing temperature T_i of the polymers studied change regularly with varying of the length of the alkyl substituent groups.

Keywords:

Liquid crystal polymer; Two-dimensional mesogenic unit; N-2', 5'-dihydroxy benzylidene-4-alkoxyaniline; Monotropic nematics

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