

THE EFFECT OF SUBSTITUENT ON THE THERMAL PROPERTIES OF POLYESTERS CONSISTING OF AROMATIC TYPE SCHIFF BASE MESOGENIC UNITS AND POLYMETHYLENE SPACERS

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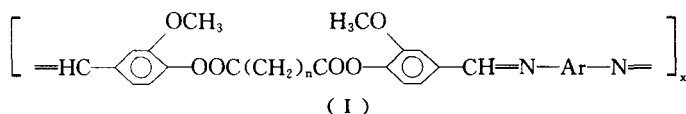
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ABSTRACT

Polyesters consisting of substituted aromatic type Schiff base mesogenic unit and polymethylene spacers were synthesized and their thermal transitions and liquid crystalline properties were studied. The liquid crystalline behaviour has been characterized by differential scanning calorimetry (DSC) and optical polarizing microscopy. Structural broadening by substitution of methoxy group in 2, 2' positions of the mesogenic core produce polymers with lower transition temperatures. Polymers synthesized from ortho and meta substituted phenylene diamine did not form a liquid crystal phase.

INTROOUCTION

In our recent articles^[1,2], we have synthesized liquid crystalline polymers containing di-(4-formylphenyl) α , ω -alkanedicarboxylates and diamines unit. Within our continuing interest in establishing basic structure-property relations in functional liquid crystalline polymers incorporating different mesogenic units, we have synthesized the polymers containing di-(4-formyl-2-methoxy phenyl) α , ω -alkane-dicarboxylates and diamine units, for the purpose of studying the substituent effect, and studied their thermotropic liquid crystalline behaviour. The polymers synthesized have the following general structural formula:



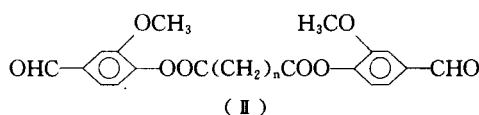
EXPERIMENTAL

Materials

Di-(4-formyl-2-methoxyphenyl) α,ω -alkanedicarboxylates of structural formula II were prepared by following the procedure already described^[2] for the preparation of di-(4-formylphenyl) α,ω -alkanedicarboxylates except that 4-hydroxy-3-methoxy benzaldehyde (vanilline) was substituted for 4-hydroxy benzaldehyde. Melting points and analytical data are presented in Table 1.

Table 1 Data for di-(4-formyl-2-methoxyphenyl) α,ω -alkanedicarboxylates monomers II

n of —(CH ₂)—	mp (°C)	Found (Calcd.) %	
		C	H
3	83	62.99 (63.00)	5.00 (5.00)
4	138	63.55 (63.76)	5.43 (5.31)
7	54	65.59 (65.78)	6.21 (6.14)
8	69	66.20 (66.38)	6.13 (6.38)



2-, 3- and 4-Phenylenediamine (Aldrich) were purified by recrystallization from benzene, their melting points were 102, 63 and 140 °C, respectively. 4,4'-diaminodiphenyl methane and 4,4'-diaminodiphenyl ether were recrystallized from benzene and tetrahydrofuran, their melting points were 93-95 and 191-194 °C, respectively^[3].

Polymerization

In a 50 ml round bottom, three-neck flask, equipped with a mechanical stirrer, reflux condenser and gas-inlet tube, a mixture of 4-phenylenediamine (0.54 g, 5 mmole), di-(4-formyl-2-methoxyphenyl) α,ω -

alkanedicarboxylates (5 mmole), ethanol (15 ml) and ethanoic acid (1 drop), was refluxed under a nitrogen atmosphere for 4 hr. The pale yellow precipitate which formed was removed by filtration, washed with methanol and acetone, and dried in a vacuum oven at 60°C.

Polymer characterization

Inherent viscosity (η) of the polymers was measured for 0.5 g/dL solutions in N,N-dimethylacetamide at 30°C using an Ubbelohde viscometer.

Differential scanning calorimetry (DSC) analysis was carried out under dry nitrogen flow on polymer samples (10-15 mg) with a Perkin-Elmer DSC-7 calorimeter equipped with a 3770 data station. Indium was employed for temperature calibration. The maxima in DSC peaks with heating rate 20K/min was taken as the phase transition temperature.

Texture observations were performed by a Leitz microscope (Laborux 2 Pol) equipped with heating stage (Leitz 350) and a photographic camera (Vario Orthomate 2).

Infrared spectra were obtained on a Pye-Unicam IR 7912 spectrophotometer. Elemental analysis was performed using Perkin-Elmer 240C elemental analyzer.

RESULTS AND DISCUSSION

Twenty kinds of poly (ester-Schiff bases) having di-(4-formyl-2-methoxyphenyl) α,ω -alkane dicarboxylates (I) and various diamine units as described in chart 1 were synthesized.

Polymer symbol	Ar (diamine unit)
nIa	
nIb	
nIc	
nId	
nIe	

where $n=3, 4, 7$, or 8

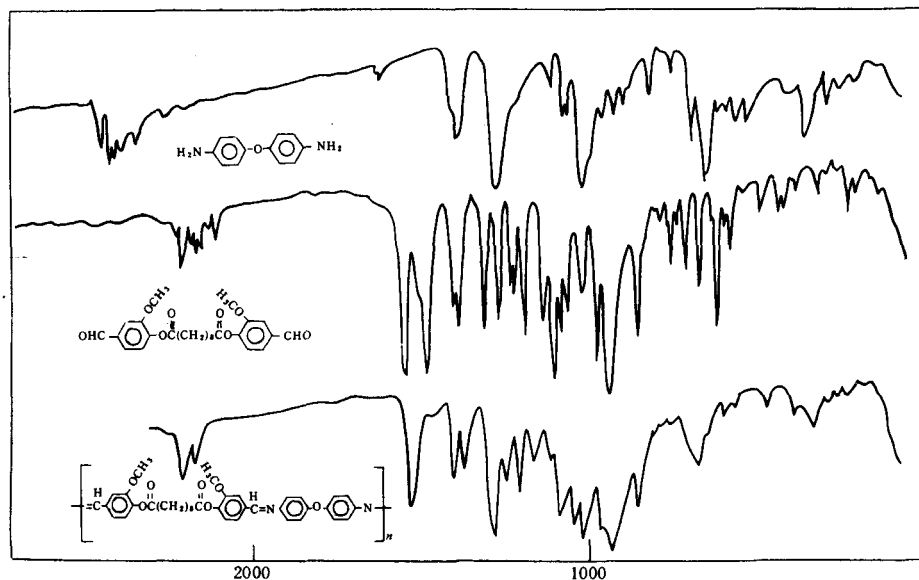


Fig. 1 Infrared spectra of (a) 4-phenylenediamine; (b) di-(4-formyl-2-methoxy phenyl) α,ω -octanedicarboxylates (II) and (c) polymer 8Ie

Table 2 The elemental analysis of poly(Schiff bases) I

Polymer	Found (Calcd.)%		
	C	H	N
3Ia	67.68(68.64)	5.62(5.08)	6.11(5.93)
3Ib	67.92(68.64)	5.11(5.08)	5.73(5.93)
3Ic	67.59	5.06	6.29
3Id	72.80(72.59)	5.60(5.33)	5.20(4.98)
3Ie	69.84(70.21)	5.19(5.31)	4.53(4.96)
4Ia	68.41(69.13)	5.44(5.34)	5.59(5.76)
4Ib	68.77(69.13)	5.12(5.34)	5.61(5.76)
4Ic	68.50(69.13)	5.15(5.34)	5.49(5.76)
4Id	72.74(72.91)	6.00(5.55)	4.61(5.86)
4Ie	70.11(70.58)	5.32(5.19)	4.49(4.84)
7Ia	70.00(70.45)	6.13(6.06)	5.02(5.30)
7Ib	69.62(70.45)	6.03(6.06)	4.91(5.30)
7Ic	69.50(70.45)	6.31(6.06)	5.00(5.30)
7Id	72.51(73.78)	6.22(6.14)	4.63(4.53)
7Ie	71.46(71.61)	5.66(5.80)	4.50(4.51)
8Ia	70.58(70.84)	6.25(6.27)	4.97(5.16)
8Ib	70.24(70.84)	6.31(6.27)	4.96(5.16)
8Ic	70.10(70.84)	5.92(6.27)	5.30(5.16)
8Id	73.00(74.05)	6.27(6.32)	4.14(4.43)
8Ie	72.10(71.92)	5.60(5.99)	4.10(4.41)

The molecular structure of the synthesized polymers was established

from IR spectra and elemental analysis. The spectra of the polymers was confirmed by the complete disappearance of the IR absorption band at $3200 - 3500 \text{ cm}^{-1}$ of diamine monomers and the appearance of a very strong absorption band at $1600-1800 \text{ cm}^{-1}$ corresponding to the di-(4-formyl-2-methoxy phenyl) α,ω -alkanediacycloxyates (I). Fig. 1 show IR spectra of the monomer and the resultant polymer. Typical results of the elemental analysis of the synthesized polymers are listed in Table 2.

Properties of polymers, including their inherent viscosities, glass transition temperatures T_g , melting temperature, T_m , and clearing temperatures, T_c , as determined by DSC, are summarized in Table 3, and typical DSC scan is shown in Fig. 2. All the polymers synthesized were insoluble in the reaction medium and precipitated out as they were formed during polymerization before reaching high molecular weight. As a result, their molecular weights were not expected to be very high, and this is reflected by the relatively low η_{inh} obtained for all samples (Column 2, Table 3).

Table 3 Characterization of poly (ester-Schiff bases)

Polymer	η_{inh}	$T_g(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$	$T_c(^{\circ}\text{C})$	T_m^a for unsubstituted polymers
3Ia	0.22		b		
3Ib	0.20			243	
3Ic	0.27		138	280	175
3Id	0.52		145	250	290
3Ie	0.46		141(166) ^c	280	323
4Ia	0.43		b		
4Ib	0.41	75		290	
4Ic	0.45	68	196(187) ^c	247	225
4Id	0.64		153	220	350
4Ie	0.57		100	174	368
7Ia	0.17	70	b		
7Ib	0.18	70		d	
7Ic	0.41	70	141	200	160
7Id	0.54	72	220(260) ^c	325	280
7Ie	0.63		135	229	350
8Ia	0.30	65		175	
8Ib	0.30	55		180	
8Ic	0.32		179(195) ^c	236	170
8Id	0.37		190	210	275
8Ie	0.46		115	276	260

a data taken from ref. [1,2] for comparison

b decomposition

c multiple endothermic peak occurs at first heating

d broad peak could not be detected accurately

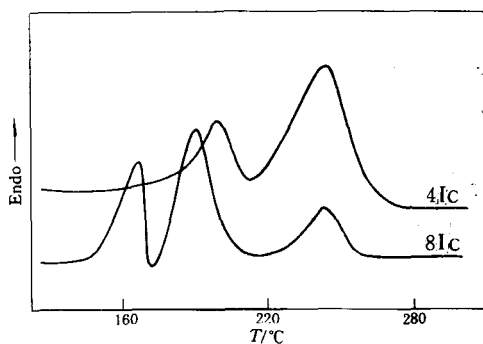


Fig. 2 DSC thermograms of polymers 4Ic and 8Ic

In this work, we have examined the substituent effect (the methoxy group in 2, 2'' positions) on the polymer properties of poly (ester-Schiff bases). By comparison between unsubstituted^[2] and substituted polymers, it was found that the transition temperatures were lowered. However, the temperature of isotropization appears to be much less affected. Therefore the temperature range of the stable mesophase in this polymer series were broadened by the presence of the methoxy group. It has been shown^[4,5] that the introduction of substituent groups into the backbone of liquid crystalline polymers in 2, 2'' or 3, 3'' positions caused two major effects on the geometry of the polymer, first the coplanarity will be disrupted and second the overall breadth will be increased.

Polymers derived from the 4-phenylenediamine (nIc), 4, 4''-diaminodiphenylmethane, nId and 4, 4''-diaminodiphenyl ether, nIe, exhibit thermotropic liquid crystalline behaviour. The others derived from 2- and 3-phenylenediamine did not show such behaviour. In spite of the presence of 2- or 3- substituted phenyl ring which maintain the rigidity of the polymer chain, but its presence induces a bend of 120° along the backbone of the polymer chains, destroying the linearity. This nonlinearity is expected to reduce the parallel association of the polymer chains in liquid crystalline state and thereby diminish the stability of the the mesophase^[6]. It is worth mentioning here that the glass transition, melting and clearing temperatures (T_g , T_m and T_c) decrease in a zig-zag fashion as the number of methylene groups increases, with a certain diamine moiety. Both T_m and T_c temperatures are higher for the polymers having an even number of the methylene groups than for neighbours with an odd number of methylene groups. DSC results also show that thermal stability of the synthesized

polymers decreases with increasing the number of methylene units. These characteristics are features of main-chain liquid crystalline polymers^[7].

Observations with a polarizing microscope for a small amount of polymers (4Id) placed between glass slide and cover slip show that this polymer become mobile at above 135°C and with increasing temperature the polymer spontaneously give rise to an anisotropic fluid that exhibits a typical threaded texture (Fig. 3) which is consistent with a nematic phase. Some of these polymers as they reach the liquid crystalline temperature, they are in an homeotropic state. The homeotropic region appears black when viewed between crossed polars because the molecular axis of the polymer molecules are perpendicular to the surface of the glass slide, i. e. the molecular axis is aligned in the same direction as the incident light-beam. Thus, under crossed polars, this texture appears dark, resembling a pseudo-isotropic phase; however, slight shearing of the sample disrupt the homeotropic texture and produce bright flow lines with extreme birefringent region.

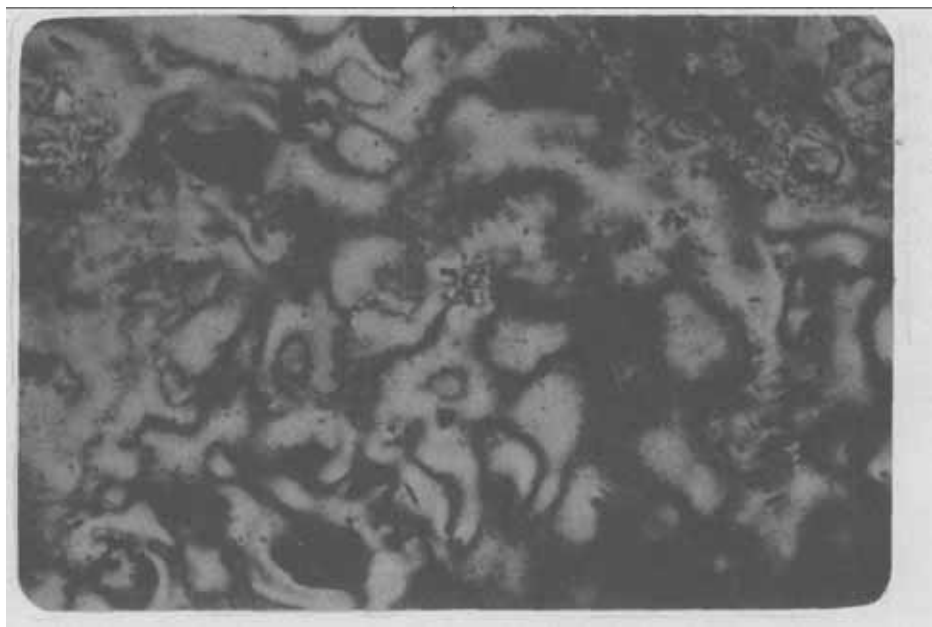


Fig. 3 Thread-like texture of polymer 4Id between crossed polars ($\times 250$)

CONCLUSIONS

The following conclusions can be drawn from this investigation. Among the series of polymers synthesized, only those containing diamine moieties substituted in 4-position are thermotropic liquid crystal. While, those substituted in 2- and 3- positions are not. The introduction of a methoxy group into the mesogenic moieties lower the transition temperatures of the synthesized polymer compared with unsubstituted counterparts.

Keywords:

Liquid crystal polymer; Polyesters; Aromatic type schiff base; Mesogenic units; Spacers

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