Studies on thermotropic liquid crystalline polymers: 4. Synthesis and properties of poly(ether ester amide)s

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The thermotropic liquid crystalline behaviour of a series of aliphatic–aromatic poly(ether ester amide)s, which were prepared by direct polycondensation, was observed. Poly(ether ester amide)s I were prepared from 4,4′-diacrylic acid-α,ω-diphenoxyalkanes and 4-aminophenol or 4-amino-3-methylphenol in the presence of diphenylchlorophosphate (DPCP) and pyridine. Poly(ether ester amide)s II were prepared from 4,4′-dicarboxy-α,ω-diphenoxyalkanes and 4-aminophenol or 4-amino-3-methylphenol in the presence of DPCP and pyridine. The phase behaviour of the polymers was studied by differential scanning calorimetry and optical polarizing microscopy equipped with a heating stage. Poly(ether ester amide)s I exhibit thermotropic liquid crystalline characteristics, except in cases where methoxy or ethoxy groups were introduced into the benzene ring. All of the poly(ether ester amide)s II exhibit thermotropic liquid crystalline behaviour as observed by optical polarizing microscopy.

(Keywords: poly(ether ester amide); direct polycondensation; thermotropic liquid crystalline properties)

INTRODUCTION

Amide linkages are not often used to synthesize thermotropic liquid crystalline polymers because the high degree of hydrogen bonding associated with these groups increases intermolecular attraction to the point that mesomorphism usually cannot occur[1–3]. Nevertheless, there are a few reports in the literature discussing the development of thermotropic liquid crystalline polymers in which the main chain contains amide groups[4–7]. Recently, a thermotropic liquid crystalline aromatic polyamide has been reported by Ringsdorf and Tschirner[4]. The synthesis of thermotropic liquid crystalline poly(ester amide)s incorporating a flexible methylene group in the main chain was reported by Aharoni[5]. Successful preparation of aromatic thermotropic liquid crystalline poly(ester amide)s using direct polycondensation has been reported by one of the authors[6] and the preparation of poly(ether ester amide)s using melt polycondensation was reported by Khan *et al.*[7] in 1983.

The processing problems due to high melting point and large degree of interchain hydrogen bonding of aromatic polyamide–ester are expected to be overcome by: incorporation of one or two lateral substituents; incorporation of spacers in the main chain; and incorporation of vinylene units to constitute a mesogenic group. In this investigation, two series of poly(ether ester amide)s (I and II) were synthesized by direct polycondensation. The structures of the monomers and the poly(ether ester amide)s are given in *Schemes 1* and *2*. The thermotropic liquid crystalline properties of these polymers were also studied.

EXPERIMENTAL

Measurements

The i.r. spectra of the synthesized monomer and polymer solid samples were obtained on KBr discs using a Perkin–Elmer 710B spectrophotometer. Inherent viscosities were measured with a Ubbelohde viscometer in a solution of LiCl in dimethylacetamide (DMAc) at 30°C (0.5 g dl^{-1}). D.s.c. measurements were conducted on a Du Pont differential thermal analysis unit model 9900 in aluminium pans and at a heating rate of 20°C min^{-1}. Thermogravimetric analysis (t.g.a.) was carried out on a Mettler TG50 at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Observation of the thermal transitions under cross-polarized light was made with a Jenapol polarizing light microscope connected with a Jenapol SMH 400 heating stage.

Monomer synthesis

4,4′-Diformyl-α,ω-diphenoxyhexane (**1**), 4,4′-diformyl-α,ω-diphenoxydecane (**2**), 4,4′-diformyl-2,2′-methoxy-α,ω-diphenoxydecane (**3**) and 4,4′diformyl-2,2′-ethoxy-α,ω-diphenoxydecane (**4**) were synthesized by the methods reported previously[8]. Their characteristics are listed in *Table 1*.

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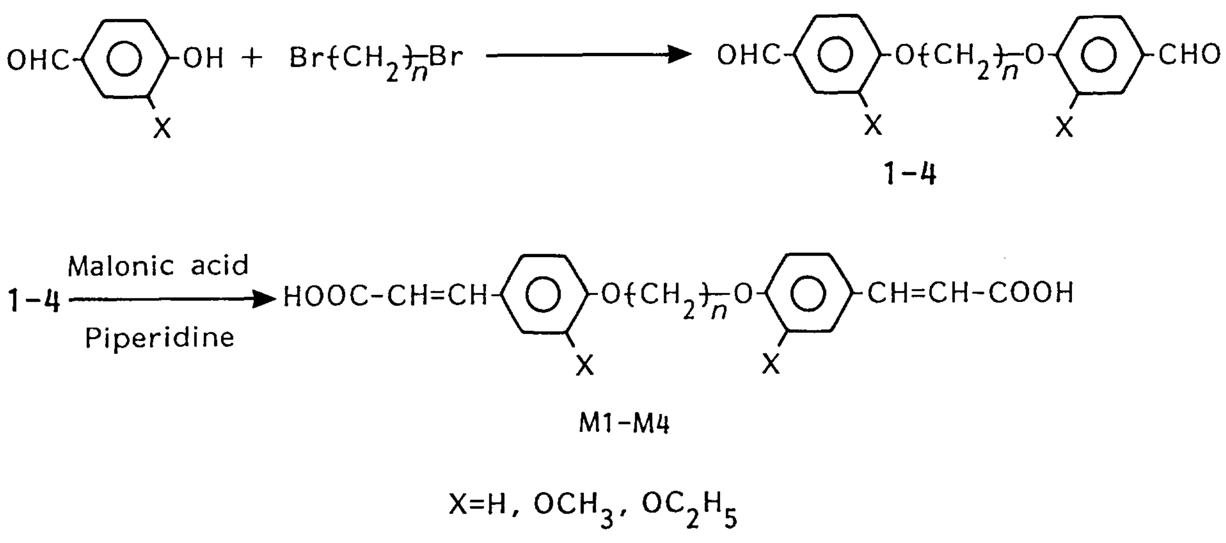
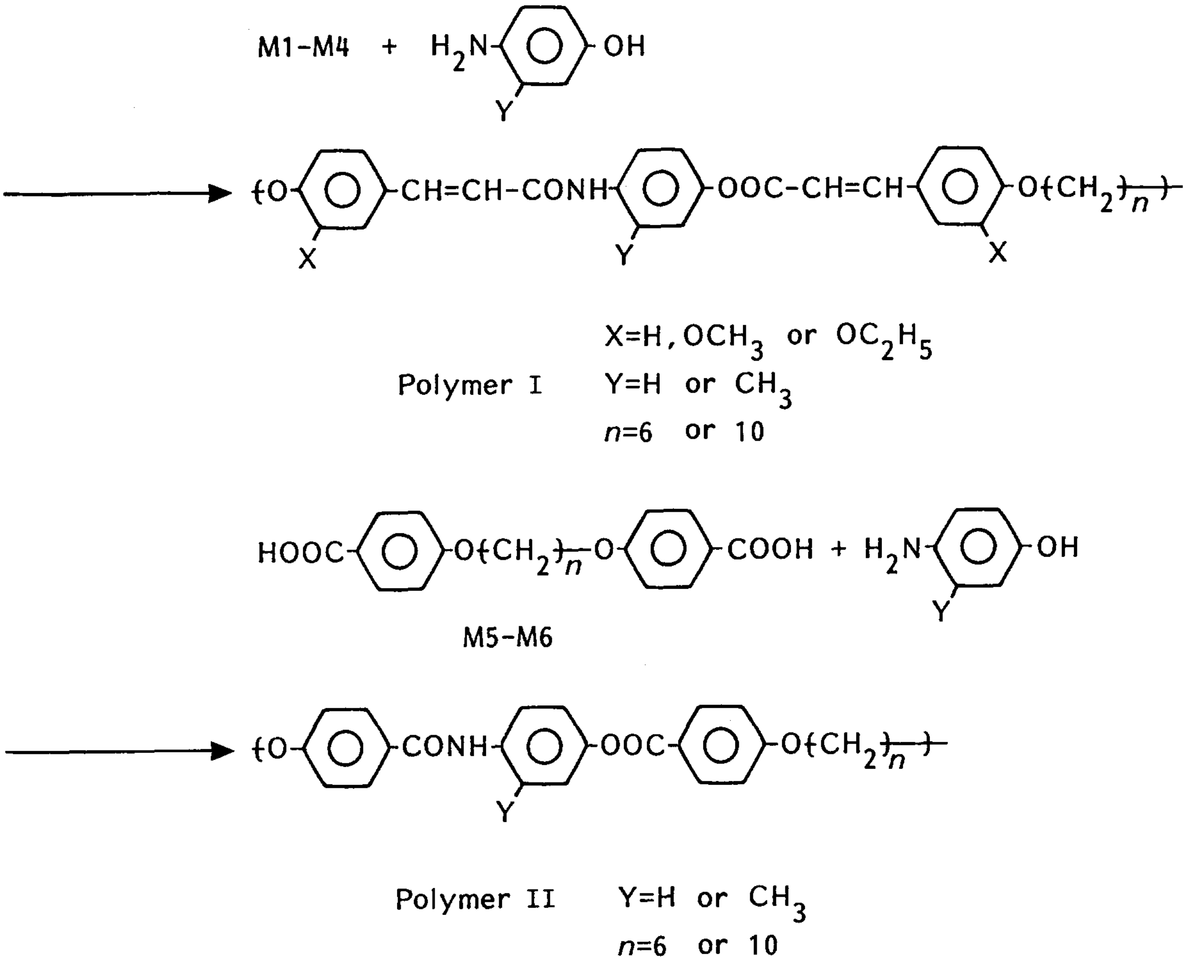


Scheme 1



Scheme 2

4,4′-Diacrylic acid-α,ω-diphenoxyalkanes were synthesized from the corresponding dialdehydes and a pyridine solution of malonic acid in the presence of piperidine as a catalyst, using the method of Doebner condensation[9]. The structures of the 4,4′-diacrylic acid-α,ω-diphenoxyalkanes are shown in *Scheme 1*. The 4,4′-diacrylic acid-α,ω-diphenoxyalkanes were purified by recrystallization from ethanol to obtain 4,4′-diacrylic acid-α,ω-diphenoxyhexane (M1), as a pale yellow powder; 4,4′-diacrylic acid-α,ω-diphenoxydecane (M2), 4,4′-2,2′-methoxy-α,ω-diphenoxydecane (M3) and 4,4′-diacrylic acid-2,2′-ethoxy-α,ω-diphenoxydecane (M4) were also obtained as pale yellow powders. The yield, melting point and elemental analysis of the 4,4′-diacrylic acid-α,ω-diphenoxyalkanes are listed in *Table 2*.

4,4′-Dicarboxyl-α,ω-diphenoxyalkanes. 4,4′-Dicarboxyl-α,ω-diphenoxyhexane (M5) and 4,4′-dicarboxyl-α,ω-diphenoxydecane (M6) were prepared from the corresponding 1,n-dibromoalkanes and 4-hydroxybenzoic acid, respectively, according to the method of Griffin and Havens[10]. The yield, melting point and elemental analysis of M5 and M6 are given in *Table 2*.

Polymer synthesis

Poly(ether ester amide)s I and II. Polymers I and II were polymerized according to the procedure described in the preceding paper of this series[6]. A mixture of diphenylchlorophosphate (13 mmol), pyridine (10 ml), and LiCl (10 mmol) was stirred for 30 min. Diacid (5 mmol) in pyridine (20 ml) was added to the above solution, stirred for 20 min at room temperature, then heated to 120°C and stood for 10 min. 4-Aminophenol or 4-amino-3-methylphenol (5 mmol) in pyridine (10 ml) were added into the above hot solution dropwise for 10 min. The whole mixture was maintained at 120°C for 3 h under stirring, and then poured into methanol to precipitate the polymer. The precipitated polymer was refluxed in boiling methanol, filtered, and then dried at 80°C under vacuum. The structures of polymers I and II are shown in *Scheme 2*.

Table 1 Monomer characteristics

Compound	Yield (%)	Melting point (°C)
1	90	112–113
2	90	80–81
3	92	98–99
4	87	102–104

RESULTS AND DISCUSSION

Polymer synthesis

In this investigation, two new series of semiaromatic poly(ether ester amide)s were synthesized by direct polycondensation. The inherent viscosities and thermal analyses of these polymers are listed in *Tables 3* and *4*. The inherent viscosities of poly(ether ester amide)s I and II were in the range of 0.25–0.31 and 0.39–0.96 dl g^{-1}, respectively. The lower inherent viscosities of the series I

Table 2 Yield and properties of the synthesized monomers

Compound	Formula	Yield (%)	Melting point (°C)	Analysis		
					C (%)	H (%)
M1	$C_{24}H_{26}O_6$	86	208–210	Found	70.36	6.26
				Calc.	70.02	6.34
M2	$C_{28}H_{34}O_6$	86	195–197	Found	72.14	7.74
				Calc.	72.10	7.30
M3	$C_{30}H_{38}O_8$	83	155–157	Found	68.41	7.43
				Calc.	68.44	7.22
M4	$C_{32}H_{42}O_8$	82	145–146	Found	70.01	7.65
				Calc.	69.31	7.58
M5	$C_{20}H_{22}O_6$	53	298–300[a]	Found	66.87	6.02
				Calc.	67.04	6.15
M6	$C_{24}H_{30}O_6$	31	276–278[b]	Found	69.59	7.30
				Calc.	69.57	7.25

[a] Reference 11, 298°C
[b] Reference 11, 277°C

Table 3 Transition behaviour of poly(ether ester amide)s I

Polymer	n	X	Y	Inherent viscosity[a]	Stirred opalescence	Transition temp.[b]			Loss of weight temp. (°C)[d]	
						$T_m - T_i$ (°C)	ΔT (°C)	T_m[c] (°C)	5%	10%
Ia	6	H	H	0.29	Yes	140–302	162	117	328	378
Ib	6	H	CH_3	0.27	Yes	115–205	90	112	320	364
Ic	10	H	H	0.27	Yes	118–287	169	112	302	354
Id	10	H	CH_3	0.29	Yes	110–200	90	120	310	345
Ie	10	OCH_3	H	0.31	Yes	108–180	72	129	344	392
If	10	OCH_3	CH_3	0.29	None	105	0	124	–	–
Ig	10	OC_2H_5	CH_3	0.25	None	95	0	–	317	368

[a] Concentration 0.5 g dl^{-1} of 5 wt% LiCl in DMAc at 30°C
[b] Measured by a polarizing microscope equipped with a heating stage
[c] Measured by d.s.c. (20°C min^{-1})
[d] From t.g.a., under N_2 (10°C min^{-1})

Table 4 Transition behaviour of poly(ether ester amide)s II

Polymer	n	Y	Inherent viscosity[a]	Stirred opalescence	Anisotropic melt[b] $T_m - T_i$ (°C)	Anisotropic melt[b] ΔT (°C)	Loss of weight temp. (°C)[c] 5%	Loss of weight temp. (°C)[c] 10%
IIa	6	H	0.39	Yes	290–340	50	374	385
IIb	6	CH_3	0.76	Yes	242–340	98	372	388
IIc	10	H	0.71	Yes	260–306	46	348	360
IId	10	CH_3	0.96	Yes	140–282	142	364	380

[a] Concentration 0.5 g dl^{-1} of 5 wt% LiCl in DMAc at 30°C
[b] Measured by a polarizing microscope
[c] From t.g.a., under N_2 (10°C min^{-1})

polymers suggest that the direct polycondensation method is less suitable for their synthesis than for the series II polymers.

Thermotropic liquid crystalline properties of poly(ether ester amide)s

The phase behaviour of the polymers measured by optical microscopy and d.s.c. are summarized in *Tables 3* and *4*. The melting points of poly(ether ester amide)s I measured by d.s.c. were confirmed by microscopic observation. The poly(ether ester amide)s I and II, except If and Ig, exhibit melt birefringence and stirred opalescence while observed under a polarizing microscope equipped with a heating stage. Therefore, it is concluded that poly(ether ester amide)s I and II, except If and Ig, exhibit thermotropic liquid crystalline properties. The mesophase–isotropic phase transition temperature could not be determined by d.s.c. analysis. The isotropic temperature of these polymers was observed by using a polarizing microscope equipped with a heating stage in the temperature range of 180–302°C.

The effect of spacer length on the thermal properties of poly(ether ester amide)s Ia and Ic is shown in *Table 3*; both the melting point and isotropic temperature decreased as the length of the flexible aliphatic segment in the polymer chain increased.

The effect of substituents on the mesogenic unit on the thermal properties of poly(ether ester amide)s I is shown in *Table 3*; both the melting point and the isotropic temperature decreased when methoxy, ethoxy or methyl groups were introduced into the mesogenic units. When the number of substituents on the mesogenic unit was less than three, the polymers, such as Ia–Ie, exhibited thermotropic liquid crystalline properties. However, when the number of substituents was increased to three, the polymer, for example If or Ig, was not favourable for the formation of a thermotropic liquid crystalline polymer.

The sizes of the substituents (X) of Id, If and Ig are in the order: H < OCH_3 < OC_2H_5. Polymer Id (X = H) exhibited thermotropic liquid crystalline properties. However, as the size of the substituent is increased from polymers If to Ig, the isotropic temperature of If and Ig could be depressed to the extent that it equals the melting point. Therefore, polymers If and Ig are incapable of forming a mesophase. It is already known that substituents can reduce the coplanarity of the adjacent mesogenic group and increase the diameter or decrease the axial ratio of mesogens[11]. Therefore, the phase transition temperature decreases as the number and size of the substituents increase. Generally, the transition temperature and mesophase range decrease with increasing spacer length. However, the transition temperatures decreased with increasing spacer length but the mesophase range increased with increasing spacer length for polymers Ia, Ic and IIb, IId, respectively (*Tables 3* and *4*). These results may be explained by the fact that the longer aliphatic chain in the flexible element of the macromolecule has a stronger influence on the melting temperature than on the isotropic temperature and causes the mesophase range to be wider[12].

Poly(ether ester amide)s I have vinylene units incorporated in the main chain unlike poly(ether ester amide)s II. The transition temperatures of the series I polymers are always lower than those of the series II polymers, as shown in *Tables 3* and *4*. Dewar and Riddle[13] have suggested that an important factor in mesophase stability may be the presence of molecules which are not only rigid and rod-shaped but have a more or less uniform cross-section. The decrease in the transition temperatures of poly(ether ester amide)s I was possibly due to the presence of vinylene units leading to a local decrease in thickness, ascribed to the formation of a 'waist'. Thermogravimetric analysis indicates that poly(ether ester amide)s I and II might show a 5% weight loss over the temperature ranges of 302–344 and 348–374°C, respectively. Polymers with vinylene units incorporated in the main chain have a decreased thermal stability.

As reported in our previous study[14], poly(ether amide)s prepared from 4,4'-diacrylic acid-α,ω-diphenoxyalkane with various diamines, such as 1,4-phenylene diamine, do not exhibit thermotropic liquid crystallinity due to the presence of a high degree of interchain hydrogen bonds. However, in the present study, poly(ether ester amide)s I exhibit thermotropic liquid crystalline properties. They differ in structure only in that poly(ether ester amide)s contain one amide group while the poly(ether amide)s contain two amide groups as repeat units. The increased melting temperatures of poly(ether amide)s are due to the higher degree of intermolecular hydrogen bonding induced by the amide group on the polymer chain. Thus, these poly(ether amide)s decomposed before the thermotropic liquid crystalline phase can be observed on melting. Therefore, this study suggests that the number of amide groups on the mesogenic group affects the thermotropic liquid crystalline properties of the polymer.

Birefringence texture

The character of the texture at a given temperature was fixed by quenching it in liquid nitrogen. Micrographs were then obtained on heating to room temperature (not shown). Micrographs of Ia obtained at 145°C, show intense birefringence and exhibited no obvious batonnet texture. This suggests that polymer Ia was in the smectic phase at 145°C. Similar textures for Ic, IIa and IIc were also measured. In most cases, the polymer containing very long spacers (approximately eight or more atoms)[11] or the amide group will enhance the occurrence of the smectic phase[7]. Consequently, the structure of poly(ether ester amide)s I and II which have very long spacers ($n = 10$) and an amide group, favours the occurrence of the smectic phase.

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