Synthesis and Characterization of a New Series of Semiflexible Liquid-Crystalline Polyesters with Aromatic Triad Mesogens

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ABSTRACT: A new series of semiflexible liquid-crystalline polyesters **1-n** or **2-n** based on a terephthalate–methylhydroquinone–terephthalate triad ester mesogen and a flexible spacer segment of variable number n of methylene units ($n=4$—12) was prepared and studied. Two synthetic procedures were used involving a diacid/diphenol direct polycondensation in the presence of a condensing agent (polyesters **1-n**), or a diacyl chloride/diphenolate polycondensation under phase transfer conditions (polyesters **2-n**). By the former synthetic method, high molecular weight polymers **1-n** were obtained, that were characterized by a greater thermodynamic stability and a wider persistence range of the nematic phase with respect to the corresponding low molecular weight analogues **2-n**. The mesophase behavior depended on the length and parity of the spacer segment, and the nematic–isotropic transition temperature exhibited a strong even–odd oscillation. For polyesters **1—10** and **1—12**, the nematic phase was quenched to room temperature and in the latter sample a cybotactic nematic structure was frozen-in.
KEY WORDS Liquid Crystals / Thermotropic Polyesters / Nematic Mesophase / Diacid–Diphenol Polycondensation / Aromatic Triad Mesogen /

Most examples of main-chain liquid crystalline (LC) polymers consist of aromatic diad or triad mesogens in combination with flexible spacer segments sequentially interconnected along the polymer backbone.[1] Other approaches to the development of new processable thermotropic polymers include, for instance, the introduction of lateral bulky substituents on the mesogenic core, or otherwise the insertion of rigid kinks in the repeat unit disrupting the collinearity of structural elements along the polymer backbone. Both options result in disturbing the efficient packing of the macromolecules, thereby inhibiting crystallization of the polymer and facilitating its overall processability.[2]

In the search for polyesters with high molecular weight and narrow polydispersity,[1,3] typical reactions that are conventionally used include the solution condensation of a diacyl chloride with a diphenolate with or without a phase transfer catalysts. The ester interchange reaction in the melt can also be used.

In this work we have synthesized and studied a new series of thermotropic polyesters, as shown below:

1-n or 2-n
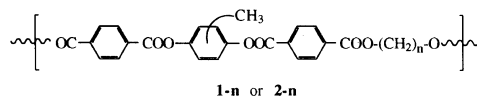
The repeat unit consisted of both a flexible methylene spacer of varying length ($n=4$, 5, 6,

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7, 8, 9, 10, or 12) and a mesogenic triad unit with a lateral substituent group, namely a terephthalate-methylhydroquinone-terephthalate unit. On occasions this mesogenic unit had been incorporated into some LC polymers, and the polyester homologues with $n=8$ or 10 have been previously described.[4,5] The main objective of this work was the elucidation of their structure-property relationships, especially the influence of the spacer length on the type and stability range of the thermotropic mesophases. One further objective was to evaluate the synthetic potential of the direct solution polycondensation of a diacid with a diphenol in the presence of a condensing agent[6-8] for the preparation of high molecular weight LC polyesters. In fact, to the best of our knowledge, this reaction has never been used before for the preparation of high molecular weight thermotropic polyesters.

Accordingly, polyesters **1-n** were prepared with this procedure, while homologue samples **2-n** were prepared by the conventional polycondensation of a diacyl chloride with a diphenolate according to the interfacial technique. The LC behavior of the polymers will be discussed and compared, with reference to the influence of their molecular weight. Indeed, the attainment of semiflexible LC polymers with high molecular weight offers good opportunities in the formulation of blends with commodity polymers in view of achieving a general property upgrading and extending their segments of application.

EXPERIMENTAL

Synthesis of Precursors

Commercially available α,ω-diols were used as received. Diacids **9-n** were prepared as outlined in Scheme 1. As a typical example, the synthesis of **9—10** is described in detail.

Dibenzyl Terephthalate (**5**). A solution of 50 g (0.25 mol) of terephthaloyl chloride (**4**) in 300 ml of dry tetrahydrofuran was added dropwise under mechanical stirring to a solution of
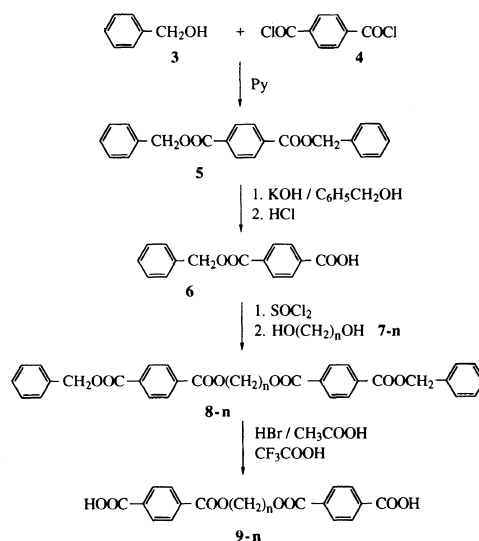
Scheme 1. Synthetic pathway for the synthesis of the diacids **9-n**.

78 ml (0.75 mol) of benzyl alcohol (**3**) in 61 ml (0.75 mol) of dry pyridine. After reacting overnight at room temperature, half of the solvent was removed by distillation and the residue was poured into 750 ml of 5% Na_2CO_3 at 0°C. The precipitate was filtered and washed with 5% HCl, water and then dried. The crude product was crystallized in 95% ethanol. Yield 91%; mp 96°C.

^1H NMR ($CDCl_3$): δ (ppm) 8.1 (s, 4H, terephthalate), 7.5—7.4 (m, 10H, benzyl), 5.4 (s, 4H, CH_2).

Monobenzyl Terephthalate (**6**). A solution of 5.4 g (96.1 mmol) of KOH in 60 ml of benzyl alcohol was added to a solution of 35 g (96.1 mmol) of (**5**) in 350 ml of benzyl alcohol over 45 min under vigorous stirring. The reaction mixture was maintained at 60°C for 1 h and then it was cooled to 5°C and 30 ml of toluene were added to it. The precipitate was filtered, washed twice with toluene and dried under vacuum at 120°C. The salt was purified by first dissolving it in excess water, filtering the insoluble residue, and titrating the solution with 0.1N HCl to pH 5.3. After 30 min the pH of the solution was adjusted to 5.25, and the solution was left overnight at 0°C. The isolated

precipitate was vacuum dried and crystallized in toluene. Yield 66%; mp 178—180°C.

^{1}H NMR (DMSO-d_6): δ (ppm) 13.4 (s, 1H, COOH), 8.2 (s, 4H, terephthalate), 7.5—7.4 (m, 5H, benzyl), 5.4 (s, 2H, CH$_2$).

1,10-Bis{4-(benzyloxycarbonyl)benzoyloxy}-decane (8—10). 30.1 g (118 mmol) of **6** was converted into the corresponding acid chloride by treating with 45 ml of freshly distilled SOCl$_2$ in the presence of pyridine at reflux for 2 h. The excess SOCl$_2$ was removed by azeotropic distillation with benzene. The crystalline acid chloride was dried under vacuum and then dissolved in 350 ml of dry dioxane. A solution of 9.6 g (55 mmol) of 1,10-decanediol (7—10) in 35 ml of dioxane and 17 ml of pyridine was added dropwise with stirring. The reaction mixture was refluxed for 4 h. After cooling to room temperature the solution was poured into 5% HCl. The precipitate was filtered, washed with 5% NaHCO$_3$, water and then dried. The crude product was crystallized in 95% ethanol. Yield 79%; mp 98°C.

^{1}H NMR (CDCl$_3$): δ (ppm) 8.3 (s, 8H, terephthalate), 7.5—7.4 (m, 10H, benzyl), 5.4 (s, 4H, CH$_2$ benzyl), 4.4 (t, 4H, COOCH$_2$), 2.2—1.2 (m, 16H, aliphatic).

1,10-Bis{4-(carboxy)benzoyloxy}decane (9—10). 10 ml of 33% HBr in acetic acid was added to a solution of 28.2 g of **8—10** in 300 ml of trifluoroacetic acid under vigorous stirring over 30 min at room temperature. The reaction mixture was left to react overnight and then poured into 2 l of acetone. The precipitate formed was washed several times with acetone, filtered and dried under vacuum. The crude product was crystallized in ethanol–dioxane (3 : 1, v/v). Yield 98%; mp 217°C.

^{1}H NMR (DMSO-d_6): δ (ppm) 13.8 (s, 2H, COOH), 8.0 (s, 8H, terephthalate), 4.2 (t, 4H, COOCH$_2$), 1.8—1.0 (m, 16H, aliphatic).

IR (KBr) $\bar{\nu} = 3655$ (νCOOH), 2925—2855 (νCH$_2$), 1947 (νC=C), 1716 (νC=O ester), 1282 (νC–O–C), 798 (γCH aromatic), 730 (γCH$_2$ chain) in cm^{-1}.

Elemental analysis (C$_{26}$H$_{30}$O$_8$)

Found: C, 66.21%; H 6.33%
Calcd: C, 66.37%; H 6.43%

Synthesis of Polymers

Polymer samples were prepared according to the synthetic route outlined in Scheme 2 by direct polycondensation of a diacid and methylhydroquinone in the presence of a condensing agent (polyesters **1-n**) and/or interfacial polycondensation of a diacyl chloride with the methylhydroquinone disodium salt in the presence of a phase transfer agent (polyesters **2-n**). As typical examples of each polymerization procedure, the syntheses of **1—10** and **2—10** are described in detail.

Direct Polycondensation. A solution of 9.7 g (51.0 mmol) of *p*-tosyl chloride in 20 ml of dry pyridine and 0.8 ml of dimethylformamide was kept for 30 min at room temperature. After addition of 8.0 g (17.0 mmol) of **9—10**, the mixture was maintained for an additional 30 min at room temperature and at 120°C for 30 min. A solution of 2.1 g (17.0 mmol) of methylhydroquinone in 10 ml of pyridine was added dropwise at 120°C in 15 min, and the mixture was let to react at 120°C for 3 h. The polymer **1—10** was precipitated with methanol, filtered and washed with 5% HCl, water and methanol, and finally precipitated from chloroform solution into methanol. Yield 98%.

^{1}H NMR (CDCl$_3$): δ (ppm) 8.2 (m, 8H, terephthalate), 7.3—7.2 (m, 3H, hydroquinone), 4.3 (t, 4H, COOCH$_2$), 2.2 (s, 3H, CH$_3$), 2.0—1.2 (m, 16H, aliphatic).

Interfacial Polycondensation. 2.0 g (4.3 mmol) of **9—10** was refluxed for 2 h with 15 ml of SOCl$_2$ and several drops of DMF. The excess SOCl$_2$ was removed under vacuum by azeotropic distillation with benzene. The white crystalline diacid chloride residue was dissolved in 50 ml of anhydrous 1,2-dichloroethane. This solution was added, under vigorous stirring, to a solution of 0.52 g (4.2 mmol) of methylhydroquinone, 0.6 g (15 mmol) of NaOH, and 1 g (3.1 mmol) of tetrabutylammonium bromide (TBAB), in 50 ml of water. The mixture was

stirred for an additional 45 min and then poured into 400 ml of methanol. The precipitated polymer **2**—**10** was washed with 5% HCl, water, methanol, extracted in a Kumagawa apparatus with boiling chloroform and finally precipitated from chloroform solution into methanol. Yield 72%.

^{1}H NMR (CDCl$_3$): δ (ppm) 8.3 (m, 8H, terephthalate), 7.4—7.3 (m, 3H, hydroquinone), 4.4 (t, 4H, COOCH$_2$), 2.3 (s, 3H, CH$_3$), 2.0—1.0 (m, 16H, aliphatic).

Characterization

NMR and IR spectra were recorded on a Varian Gemini 200 MHz spectrometer and a Perkin-Elmer FT-IR Mod. 1600 spectrophotometer, respectively. Average molecular weights of polymers were determined by size exclusion chromatography (SEC) with a Perkin Elmer chromatography equipped with Shodex A 802/S and A 803/S columns with tetrahydrofuran as the eluent (1 ml min^{-1}). The measurements were performed at room temperature using a Perkin Elmer LC75 UV detector. Monodisperse polystryrene samples were employed for calibration. Light scattering measurements were performed using a Sofica 4200 photogoniometer equipped with a cylindrical cell immersed in a toluene bath with He-Ne laser source at a wavelength of 633 nm. The refractive index increments of the polymers were also measured with KMX 16 laser differential refractometer at the same wavelength. Differential scanning calorimetry (DSC) analysis was carried out under nitrogen flow with a Mettler TA 4000 system. The apparatus was calibrated with a reference standard of high purity indium. Transition temperatures were taken from DSC traces of second cycle as corresponding to the maximum of enthalpic peaks at heating-cooling rate of 10 K min^{-1}. Thermogravimetric analysis (TGA) was performed with a Mettler TG50 thermobalance equipped with a Mettler M3 balance, under air or nitrogen flow. Optical microscopy was done on polymer films between glass slides with a

Reichert Polyvar microscope equipped with a programmable Mettler FP52 heating stage, at a scanning rate of 10 K min^{-1}. X-ray diffraction measurements were performed on powder as well as fiber specimens with a pinhole camera operating under vacuum, using Ni-filtered Cu-radiation ($\lambda = 1.54$ Å) from room temperature up to the isotropization point. Fibers were oriented pulling the polymer with tweezers from its mesomorphic melt at different temperatures.

RESULTS AND DISCUSSION

Diacids **9-n** containing flexible methylene segments of different length ($n = 5$, 6, 7, 8, 9, 10, or 12) were prepared as outlined in Scheme 1. According to this procedure, terephthaloyl chloride (**4**) was esterified with benzyl alcohol (**3**), and the resulting terephthalate ester **5** was deprotected by selective hydrolysis under controlled pH conditions.[9] The monoprotected terephthalic acid **6** was then converted into its acid chloride that was coupled with aliphatic diols **7-n** to yield the corresponding α,ω-bis{4-(benzyloxycarbonyl)benzoyloxy}alkanes (**8-n**). Finally, they were deprotected to the respective diacids **9-n** with HBr in acetic acid, which were then purified by crystallization in dioxane–ethanol (1 : 3, vol/vol). The yields for the

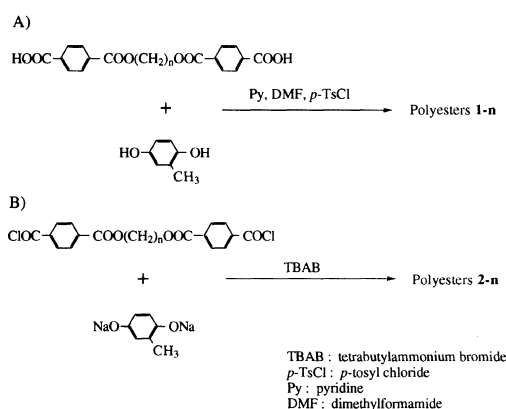**Table I.** Yields and melting points of diesters **8-n** and diacids **9-n**

n	8-n		8-n	
	Yield/%	mp/°C[a]	Yield/%	mp/°C[b]
4	69	135	71	290
5	81	113	60	250
6	67	106	87	246
7	71	104	69	218
8	91	106	81	236
9	82	105	45	215
10	79	98	98	217
12	69	108	91	210

[a] After crystallization in 95% ethanol.
[b] After crystallization in dioxane–ethanol (1 : 3, vol/vol).

synthesis of **8-n** and **9-n** and their melting points are collected in Table I.

The polyesters were prepared by following two different procedures. According to the first procedure (Scheme 2A), polyesters **1-n** ($n = 4$, 5, 6, 7, 8, 10, or 12) were prepared by the direct polycondensation of a diacid **9-n** with methylhydroquinone in pyridine solution in the presence of dimethylformamide as an activator and *p*-tosyl chloride as a condensing agent. Investigations on model systems have sug-

gested[6] that this reaction should proceed (Scheme 3) by the *in situ* formation of a mixed sulfonate-carboxylate anhydride (II), *via* the intermediate Vilsmeier-type adduct (I). Subsequent attack of a biphenol on (II) would lead to the final phenyl ester product. In agreement with this mechanism, best results in our polycondensation experiments were obtained by first mixing *p*-tosyl chloride with dimethylformamide at room temperature in pyridine solution, followed by the reaction with the diacid at 120°C, and finally by reaction with methylhydroquinone.

A)

Scheme 2. Outline of the polycondensation procedures for the preparation of polyesters **1-n** and **2-n**.
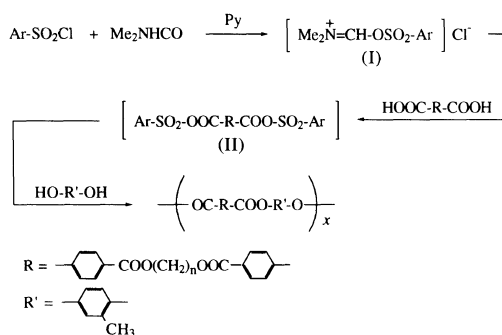
Scheme 3. Proposed mechanism for the diacid/diphenol polycondensation (after ref 6).

Table II. Physicochemical and mesomorphic properties[a] of polyesters **1-n** prepared by direct polycondensation

Sample	M_w^b	M_w/M_n^b	T_m	ΔH_m	T_i	ΔH_i	ΔS_i
			K	kJ mol^{-1}	K	kJ mol^{-1}	J mol^{-1} K
1—4	12500	1.2	462	8.2	>580[c]	nd[d]	nd[d]
1—5	42000	1.4	469	2.3	—[e]	—[e]	—[e]
1—6	14500	1.6	473	13.0	553	5.0	9.0
1—7	23500	1.1	423	12.9	—[e]	—[e]	—[e]
1—8	27000	1.8	481	12.9	507	3.4	6.9
1—10	66000[f]	2.8	435	4.2	486	5.5	11.3
1—12	62000[g]	2.6	432[h]	9.3	463	5.3	11.4

[a] Temperature, enthalpy, and entropy $(T, \Delta H, \Delta S)$ of melting (m) and isotropization (i), by DSC.
[b] By SEC in tetrahydrofuran (THF).
[c] With partial decomposition.
[d] Not determined with accuracy.
[e] Not mesomorphic.
[f] $M_w = 60000$ (by light scattering).
[g] $M_w = 50000$ (by light scattering).
[h] Additional transition at 421 K ($\Delta H = 4.1$ kJ mol^{-1}) on cooling from the isotropic state.

According to the second procedure (Scheme 2B), polyesters **2-n** ($n = 4$ to 10) were obtained by converting a diacid **9-n** into its diacyl chloride that was then reacted with the disodium salt of methylhydroquinone under phase transfer conditions in the presence of tetrabutylammonium bromide (TBAB) as a catalyst. In both cases, the terephthalate-methylhydroquinone-terephthalate mesogenic triad unit was formed during the polycondensation reaction.

Samples **1-n** were prepared with yields typically greater than 80%, and had rather high molecular weights ($M_w = 12000$—66000) with narrow molecular weight dispersities ($M_w/M_n = 1.1$—2.8) (Table II). While SEC measurements may not be very accurate for the evaluation of molecular weights of polyesters, when referenced to polystyrene standards, the above values were confirmed by light scattering measurements for representative polymer samples ($M_w = 60000$ for **1—10** and 50000 for **1—12**). In contrast, samples **2-n** were obtained in 60—80% yields and were characterized by rather low molecular weights and wide molecular weight dispersities (Table III), corresponding in fact to oligomers with average degrees of polymerization in the range 5—10.

In a previous work,[10] this synthetic approach was used for the preparation of distantly related thermotropic polyesters, but materials with much lower molecular weights were obtained as estimated by the low values of their intrinsic viscosities or ^{1}H NMR analysis of the terminal groups. The high molecular weight and very narrow molecular weight dispersity determined for some of the present polyesters are surprising. This polycondensation process must rely on the quantitative formation and reaction with the hydroquinone nucleophile of an intermediate mixed dianhydride, such as (II) in Scheme 3, that easily forms on sterically not hindered carboxyl groups. In addition, the condensation process should be able to discriminate selectively on the kinetic chain length thus enabling the production and recovery of high molecular weight fractions only. We obtained[11] very similar results with closely related polyesters to those of this work thus confirming the suitability of this procedure for the preparation of high molecular weight, narrow molecular weight polydispersity LC polyesters, in spite of the variable and in some cases significant length of the aliphatic component in the repeat unit. An interpretation of this behavior supported by specific experi-

Table III. Physicochemical and mesomorphic properties[a] of polyesters **2-n** prepared by interfacial polycondensation

Sample	M_w[b]	M_w/M_n[b]	T_m	ΔH_m	T_i	ΔH_i	ΔS_i
			K	kJ mol^{-1}	K	kJ mol^{-1}	J mol^{-1} K
2—4	2500	2.4	463	7.8	>465[c]	nd[d]	nd[d]
2—5	2000	3.9	442	6.1	—[e]	—[e]	—[e]
2—6	2000	4.4	461	11.6	486	0.4	0.7
2—7	5000	4.3	433	7.3	—[e]	—[e]	—[e]
2—8	3000	5.2	453	nd[d]	≈470	nd[d]	nd[d]
2—9	9300	2.4	402	8.4	404[f]	1.8[f]	4.5[f]
2—10	4000	3.9	429	7.3	466	4.3	9.2

[a] Temperature, enthalpy, and entropy (T, ΔH, ΔS) of melting (m) and isotropization (i), by DSC.
[b] By SEC in THF.
[c] With partial decomposition.
[d] Not determined with accuracy.
[e] Not mesomorphic.
[f] Determined on cooling from the isotropic melt.

mental evidence is still pending, and an extension of the reported procedure to other polyesters and model compounds is needed.

To evaluate the thermal stability of the polyesters prepared, a thermogravimetric analysis was carried out in both air and nitrogen atmospheres from room temperature up to the total degradation of the polymers at a heating rate of $10°C \min^{-1}$. Under nitrogen flow, two successive degradation stages were observed, the first beginning at 350°C and the second at 450°C. In air atmosphere, there existed an additional degradation stage at 420—430°C. In any case the weight loss was 10% at about 365°C. There were no substantial differences in the loss pattern of the various homologues on increasing the length of the flexible spacer, thus indicating a general thermal stability of these polyesters.

The LC behavior of the polyesters greatly depended upon the chemical structure of the repeat unit, i.e. the length and the parity of the spacer segment (n). In homologous polyesters 1-n and 2-n comprising a spacer segment of the same number n, the LC properties were also much affected by the molecular weight. Polyesters may suffer from melt-phase ester interchange reactions,[12,13] which in turn could affect their LC properties. However, we had no evidence of transesterification by our NMR or SEC studies of the polymers after different thermal treatments. Furthermore, the LC behavior of the polymers was highly reproducible in subsequent cycles, and was not influenced to any appreciable extent by undesired side-reactions.

Samples 1-n having even spacers (n = 4, 6, 8, 10, or 12) exhibited a mesophase between the melting (T_m) and isotropization (T_i) temperatures (Table II). In some cases the DSC melting process was composed of several transitions (Figure 1A) including sometimes exothermic transitions. This was due to a crystalline polymorphism involving the cold-crystallization of amorphous or defective regions; the upper temperature transition was due to the
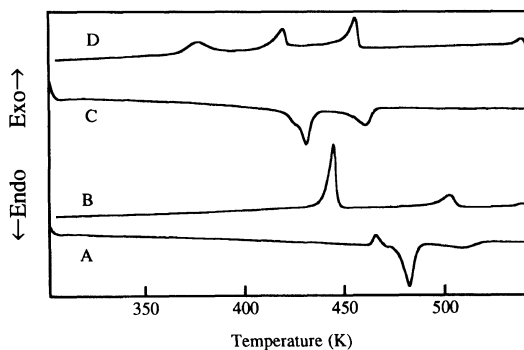

Figure 1. DSC second heating and cooling curves of polyesters 1—8 (A, B) and 1—12 (C, D).

final melting of the most stable semicrystalline phase. Such phenomenom is quite common in thermotropic polyesters and makes it difficult to determine the thermodynamic melting temperature.[14] The measured melting enthalpies (ΔH_m) were apparent values as the degree of crystallinity was not known. The isotropization transitions were relatively sharp and resulted, therefore, in a narrow biphasic region in which isotropic and anisotropic melts coexisted, in agreement with previous findings on related polyesters.[15] On cooling from the isotropic phase, the isotropic-nematic transition occurred with a few degrees of supercooling (3—5 K) (Figures 1B and 1D), whereas the crystallization was rather supercooled because of the kinetic control of the nematic–crystal transition. This allowed to detect another phase transition in polyester 1—12 around 421 K, possibly due to the onset of an additional mesophase which was therefore monotropic or metastable in character (Figure 1D).

In any case the nature of the stable mesophase was identified as nematic by textural observations at the optical microscope and by X-ray diffraction studies (see below). The isotropization enthalpies (ΔH_i) and entropies (ΔS_i) were rather small ($\Delta H_i = 3.4$—$5.5 \mathrm{kJ}$ mol^{-1}, $\Delta S_i = 6.9$—$11.4 \mathrm{J \, mol}^{-1} \mathrm{K}$) (Table II), consistent with the low degree of order of the nematic phase.

In contrast, 1-n homologues with odd

spacers ($n = 5$ or 7) did not present mesomorphic behavior, even in their supercooled melt. This finding reflects the markedly different propensities of the even and odd members of a series of polyesters to form a nematic phase, only the even homologues giving rise to mesophases. This so-called "even–odd" effect is rather common in LC polymers[16–18] as well as in low molar mass liquid crystals.[19] It can be explained by considering the configurational character of the extended conformers of the even and odd membered spacers of main chain LC polymers.[20] The even spacers force the mesogenic groups to adopt a collinear disposition thus leading to a favorable packing of the polymer chains in the nematic phase and resulting in higher transition temperatures and larger entropies. In contrast, the odd spacers place the mesogenic groups in angled orientations which determines a mesophase with greatly depressed transition temperatures and entropies.[21,22] In the present polymer systems, short odd spacers were especially unfavorable to the onset of the nematic phase.

On increasing n, T_i gradually decreased in a significant way, whereas T_m varied rather irregularly (Figure 2). Consequently, the persistence range of the mesophase was very
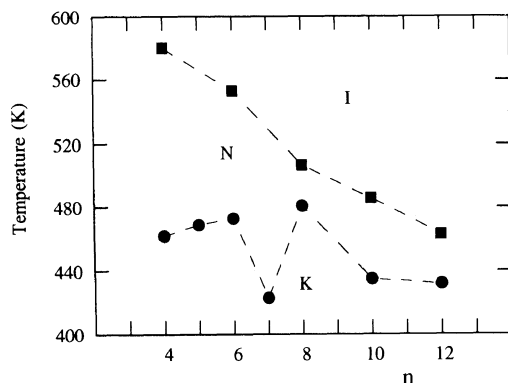

Figure 2. Trends of the melting (●) and isotropization (■) temperatures as a function of the spacer length (n) for polyesters 1-n (K, semicrystalline; N, nematic; I, isotropic).

broad for polyesters with short spacers (≈ 110 K for **1—4**) and narrow for those with longer spacers (31 K for **1—12**). In particular for the former sample, T_i was very high ($> \approx 580$ K) and the isotropization transition occurred with partial thermal degradation.

Samples **2-n** exhibited LC properties (Table III) analogous to the corresponding samples **1-n** with the same general trend as discussed above, but with notable differences due to molecular weight effects. The nematic phase of samples **2-n** exhibited sensibly lower isotropization thermodynamic parameters. As a striking example, T_i and ΔH_i were 553 K and 5.0 kJ mol^{-1} for **1—6**, whereas they were 486 K and 0.4 kJ mol^{-1} for **2—6**. In addition, the phase transition temperature ranges were rather broad, which in a few cases did not permit an accurate evaluation of the relevant parameters. Thus, the low molecular weight of samples **2-n** resulted in a ill-defined thermotropic behavior with lower transition temperatures and enthalpies relative to high molecular weight analogues **1-n**. It is well known[23–25] that in thermotropic polyesters both T_i and ΔH_i increase with increasing degree of polymerization up to a saturation value, usually corresponding to $M_n \approx 6000$—8000, and then level off. The increase in T_i and ΔH_i with increasing molecular weight of polymers has been attributed[26] to the substantial cooperative effects among mesogenic units along the polymer backbone. The mutual orientation of not consecutive units belonging to the same macromolecular chain, mediated by the ordering field of the surrounding nematic phase, would provide a polymer mesophase endowed with improved thermodynamic stability (T_i) and degree of order (ΔS_i) with respect to the corresponding oligomers and low molar mass liquid crystals. Finally, we note that **2—9** incorporating an odd, relatively long spacer segment did form a nematic phase extending over a rather wide temperature range. This finding suggests that in the present polyester series odd spacers longer than a critical
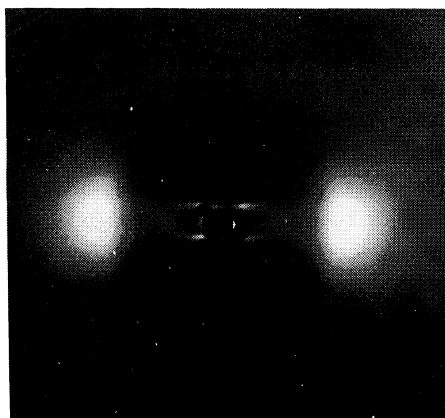
Figure 3. X-Ray diffraction diagram at room temperature of the nematic phase of polyester **1—12** (fiber pulled at 465 K; vertical fiber axis).

Figure 4. Schematic representations of the X-ray diffraction diagram (top) and cybotactic nematic structure (bottom) of polyester **1—12**.

threshold ($n \geq 9$) should have in fact sufficient flexibility and conformational freedom such as to permit the onset of the nematic phase. This could be assisted even by the concomitant depression of the melting temperature relative to homologues **2—5** and **2—7**.

The nematic nature of the mesophase of polyesters **1-n** was further identified by X-ray diffraction measurements on powder samples. Furthermore, drawing fibers in the nematic phase of polyesters **1—10** and **1—12** allowed us to freeze-in the nematic structure down to room temperature. This was not possible with polymers containing shorter spacers ($n < 10$), in that poorly oriented crystalline fibers were obtained. The former polymer gave fiber diffraction patterns exhibiting only two large equatorial spots in the wide angle region typical of an oriented nematic structure. In addition, **1—12** displayed in the low angle region four rather sharp off-meridian spots (Figure 3). These features are characteristic of a cybotactic nematic phase[27] with smectic C fluctuations involving a skewing of the mesogenic groups between polymer chains,[28,29] as schematically shown in Figure 4. The position of the central spots allowed to evaluate a thickness (d) of the *pseudo*-lamellae of approximately 25 Å and a tilt angle (β) of *ca.* 50° of the fiber axis with
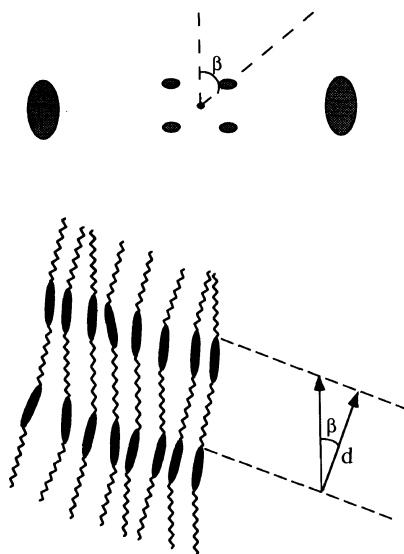
respect to the layer normal. The average intermolecular distance (D) among polymer chains was 4.8 Å, as evaluated from the wide angle diffraction signals. The presence of long flexible spacers usually favors the formation of a smectic phase rather than a nematic phase in LC polymers.[30] Probably, in polyester **1—12** the lateral methyl substituents prevent the mesogenic units from registering in well defined layers and a cybotactic nematic structure can be adopted.

CONCLUSIONS

Thermotropic LC polyesters were synthesized in which the chemical structure was designed to provide a mesophase in easily accessible temperature ranges. This consisted in incorporating in the repeat unit both a flexible spacer ($n = 4 \div 12$) and a mesogenic triad unit with a lateral methyl substituent on the central phenylene ring. The preparation of two series of polyester samples with very different molecular weights allowed to highlight the effects of the chemical structure and

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the degree of polymerization on both the stability and degree of order of the nematic phase in the thermotropic polyesters. High molecular weight samples were obtained by the diphenol–diacid polycondensation in the presence of p-tosyl chloride as a condensing agent. This procedure seems to have a good synthetic value for the easy preparation of LC polyesters with reliable T_i and ΔS_i values. These polyesters appear to have appropriate intrinsic characters for blending with commercially available polyolefins (PE) and polyesters (PET), and an investigation is in progress on these LC polymer blends.

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