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# Liquid-crystalline polyesters containing alternating alkylene and oxyalkylene spacers

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# Liquid-crystalline polyesters containing alternating alkylene and oxyalkylene spacers

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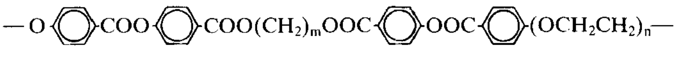
Three new series of thermotropic polyesters were prepared in which the structural units consisted of two *p*-oxybenzoyl dyads alternately flanked by a polymethylene segment and an oxyethylene oligomer. In each series the length of the oxyethylene residue was fixed ($n = 2$, 3 or 4) and the length of the alkylene segment was varied ($m = 6$–10 and 12). Details of the synthesis and characterization of the polymers are reported. The effect of the parity and length of the oxyethylene and polymethylene segments on the incidence of mesophases and on their thermodynamic parameters is stressed. The substitution of methylene groups by oxygen atoms in the polymethylene spacer of a fourth series of polymer analogues completely inhibited the nematogenicity of the polymers incorporating even powerful mesogens such as the *p*-oxybenzoyl dyads.

## 1. Introduction

The study of polymer liquid-crystalline mesophases based on macromolecules consisting of rod-like units regularly spaced by flexible segments showed the existence of several conformational states for the individual macromolecular chains affecting their relative organization in supermolecular structures [1]. In particular, the structure of the mesogenic core as well as of the flexible segments and of the bridging groups, together with the intermolecular and intramolecular cooperative constraints imposed by their macromolecular nature, constitute the fundamental elements responsible for the ultimate characteristics of the polymers [2]. In that respect the establishment of definite correlations between several structural features and the corresponding liquid-crystalline responses is of major concern in view of the potential of those polymer systems in various practical applications [3].

Following this line, in the present work we describe the mesomorphic properties of three series of polymers, ***m*-DI**, ***m*-TR**, and ***m*-TE**, whose structures are closely related, as schematically represented in the formula



| *m* | *n* | Samples |
|---|---|---|
| 6–10, 12 | 2 | ***m*-DI** |
| 6–10, 12 | 3 | ***m*-TR** |
| 6–10, 12 | 4 | ***m*-TE** |

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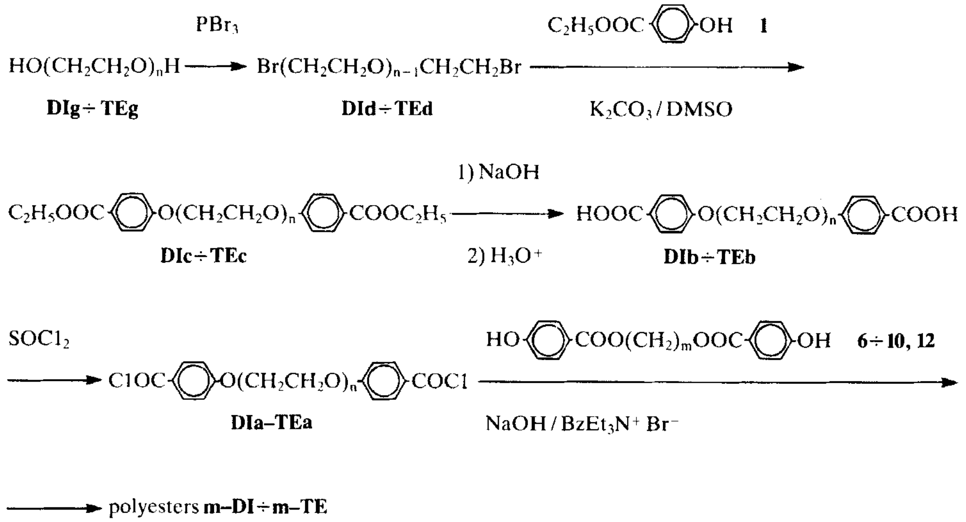
The polymer repeating units contain two mesogenic *p*-oxybenzoyl dyads separated by an oxyalkylene oligomer residue of variable length, i.e. dimer (**DI** series), trimer (**TR** series) or tetramer (**TE** series), and a polymethylene segment containing a variable number of methylene groups. The members of the three series will be designated as ***m*-DI**, ***m*-TR** and ***m*-TE** according to the number, *m*, of methylene units in the polymethylene spacer and to the number *n* of oxyethylene units in the ether segment. In a recent paper [4] some salient features of the liquid-crystalline properties of the ***m*-TR** series have already been reported, and they are considered again here for the sake of completeness.

## 2. Experimental

### 2.1. *Precursors and monomers*

Commercially available, moisture free α,ω-oligoethylene diols (**DIg**, **TRg** and **TEg**) were used as obtained by azeotropic distillation from toluene solution before use. Alkylene di(4-hydroxybenzoate)s **6–10** and **12** were prepared according to [5, 6] and purified by recrystallization from ethanol : water (volume ratio 60 : 40). Diacids **DIb–TEb** were synthesized according to the general procedure outlined in Scheme 1. As a typical example, the synthesis of diacid **TRb** is described in detail in the following.



Scheme 1. General representation of the synthetic route for the preparation of polyesters ***m*-DI–*m*-TE** based on *p*-oxybenzoyl dyads and different flexible segments.

1,8-Dibromo-3,6-dioxaoctane (**TRd**): 90 g (0·332 mol) of $PBr_3$ was added dropwise with vigorous stirring to a solution of 92 g (0·613 mol) of 1,8-dihydroxy-3,6-dioxaoctane( triethylene glycol, **TRg**) and 20 g of dry pyridine at 0°C. Once the addition was completed, the reaction mixture was stirred for 12 h at room temperature and then poured into 200 ml of water. The organic layer was washed with 1 M $NaHCO_3$, with 2 M HCl and finally with water. The organic phase, after drying over sodium sulphate, was evaporated under vacuum and the oily residue was distilled: b.p. 85–86°C/0·4 mm; yield 57·5 g (34 per cent).

$^1$H-N.M.R. ($CDCl_3$): $\delta$ (in p.p.m. from tetramethylsilane (TMS)) = 4·2–3·4 (*m*, 12 H, $CH_2$).

Crude intermediates **DId** and **TEd** were distilled: b.p. 97–98°C/15 mm and b.p. 116–126°C/0·5 mm, respectively.

1,8-Di(4-carboethoxyphenoxy)-3,6-dioxaoctane (**TRc**): a mixture of 33·2 g (0·199 mol) of ethyl 4-hydroxybenzoate (**1**), 26·0 g (0·188 mol) of anhydrous potassium carbonate and 21·6 g (0·078 mol) of **TRd** in 120 ml of dimethyl sulphoxide (DMSO) was heated at 110–120°C for 4 h. After cooling, the reaction mixture was poured into 150 ml of 0·5 M NaOH. The solid product was filtered and crystallized from diisopropyl ether: m.p. 70–71°C; yield 30·4 g (87 per cent).

$^1$H-N.M.R. ($CDCl_3$): $\delta$ (in p.p.m. from TMS) = 8·0 (*d*, 4 H, aromatic); 6·9 (*d*, 4 H, aromatic); 4·4–3·4 (*m*, 16 H, $OCH_2$); 1·4 (*t*, 6 H, $CH_3$).

Crude intermediates **DIc** and **TEc** were crystallized from ethanol and diisopropyl ether, respectively.

1,8-Di(4-carboxyphenoxy)-3,6-dioxaoctane (**TRb**): a solution of 20 g (0·045 mol) of **TRc** in 225 ml of 1 M NaOH and 80 ml of ethanol was refluxed for 4 h. Then 100 ml of solvent was distilled off and the solution refluxed for an additional 10 min. The reaction mixture was filtered and the solution was poured into 150 ml of 2 M HCl. The solid product was filtered and then washed with 100 ml of 95 per cent ethanol, dried under vacuum and crystallized from ethylene glycol monomethyl ether: m.p. 235–237°C; yield 15·7 g (90 per cent).

$^1$H-N.M.R. (DMSO-$d_6$): $\delta$ (in p.p.m. from TMS) = 11·8 (*bs*, 2 H, COOH), 7·9 (*d*, 4 H, aromatic); 7·0 (*d*, 4 H, aromatic); 4·3–3·1 (*m*, 12 H, $OCH_2$).

Crude intermediates **DIb** and **TEb** were crystallized from ethylene glycol monomethyl ether and ethanol, respectively.

### 2.2. *Polymers*

In a typical polymerization experiment 2·00 g (0·005 mol) of the diacid **TRb** was refluxed for 4 h with 2 ml (0·027 mol) of $SOCl_2$, 50 ml of 1,2-dichloroethane and several drops of pyridine. The solvent and the excess $SOCl_2$ were removed under vacuum by azeotropic distillation with benzene. The solid 1,8-di(4-chloroformylphenoxy)-3,6-dioxaoctane (**TRa**) was dissolved in 50 ml of 1,2-dichloroethane and the solution was transferred into an appropriate flask containing 1·83 g (0·005 mol) of hexamethylene di(4-hydroxybenzoate) (**6**), 0·60 g (0·015 mol) of NaOH and 1 g (0·003 mol) of benzyl tributylammonium bromide. The mixture was stirred for 20 min and then poured into 300 ml of acetone. The precipitated polymer was washed with acetone and purified by precipitation from chloroform solution into methanol. Yield 3·3 g (91 per cent).

$^1$H-N.M.R. ($CDCl_3$): $\delta$ (in p.p.m. from TMS) = 8·1 (*d*, 8 H, aromatic); 7·4–6·7 (*m*, 8 H, aromatic); 4·5–3·6 (*bm*, 16 H, $OCH_2$); 2·0–1·2 (*m*, 8 H, $CH_2$).

All of the other samples of the three series were prepared according to the same synthetic procedure.

### 2.3. *Physico-chemical characterizations*

$^1$H-N.M.R. and $^{13}$C-N.M.R. spectra were recorded on a Varian XL-100 spectrometer. Intrinsic viscosity measurements were performed in chloroform at 30°C. Average molecular weights of the polymer samples were obtained by gel permeation chromatography with a liquid chromatograph consisting of a Waters pump, a Waters U6K injector and a Waters R-401 differential refractometer, equipped with a Shodex KF-804 column. Monodisperse polystyrene standard samples were used for calibration.

Calorimetric analyses were carried out under dry nitrogen flow with a Perkin-Elmer DSC-7 apparatus, equipped with a 3700 data station using Delta series standard programs, on polymer samples of 8–12 mg. The transition temperatures were taken as corresponding to the maximum in the enthalpic peaks obtained with a heating/cooling rate of 10 K min$^{-1}$. Indium standards were used for temperature calibration and enthalpy change evaluation.

Thermal-optical observations were performed on a Reichert Polyvar polarizing microscope equipped with a Mettler FP-52 programmable heating stage at a scanning rate of 10 K min$^{-1}$.

X-ray diffraction measurements were performed in a transmission mode by means of a conventional X-ray powder diffractometer. Nickel-filtered Cu-$K_\alpha$ radiation ($\lambda$ = 1·54 Å) was used.

## 3. Results and discussion

All of the polymer samples of the three series were obtained with yields greater than 90 per cent by a polycondensation reaction between the sodium salt of the diphenols **6–10** and **12** and the diacid chlorides **DIa–TEa** in the presence of catalytic amounts of benzyl tributylammonium bromide, acting as a phase transfer agent, following the route outlined in Scheme 1. The polymer samples were characterized by intrinsic viscosities in the range 0·20–0·40 dl g$^{-1}$ to which average molecular weights of $4 \times 10^3$ to $1{\cdot}5 \times 10^4$ corresponded (tables 1–3). The structure of the polymers was confirmed by $^1$H-N.M.R. and $^{13}$C-N.M.R. analyses. Their mesophase behaviour was investigated by differential scanning calorimetry (D.S.C.), by observation of birefringent textures and, in a few cases, by X-ray diffraction. The phase transition temperatures, corresponding to the extremum of an endotherm (heating mode) or of an exotherm (cooling mode), and the relevant enthalpies were taken from D.S.C. curves on samples annealed by cooling at 10 K min$^{-1}$ from the isotropic melt. Results of the D.S.C. measurements on the different polymer series are collected in tables 1–3.

The liquid-crystalline behaviour in the three series is amazingly similar within members of the same parity, independent of the length of the oligo oxyethylene residues. Polymers containing an even number of methylene groups showed one mesophase, either enantiotropic or monotropic, which was identified as nematic by unequivocal observations of Schieren textures with disclinations of $|S| = 1$ and 1/2. X-ray diffraction spectra, recorded on representative unoriented samples **6-DI**, **8-DI**, **6-TR** and **6-TE** in the temperature range between melting and isotropization, were constituted only by an outer broad halo, thus supporting the assignment of a nematic structure to the present mesophases. In complete contrast, polymers having odd values of $m$ did not display mesomorphic properties even in the supercooled state. The trends of the melting and isotropization temperatures as a function of the number of methylene units in the $\alpha,\omega$-alkylene spacers are represented in figure 1. Within each series the isotropization temperatures lay on a smooth curve with a descending trend as the series was ascended. The major effect exerted by the increase in the number of oxyethylene units was the shift of the nematic–isotropic temperature curves toward lower values along the temperature scale without changing so much their shape. In going from series ***m*-DI** to ***m*-TR** and from ***m*-TR** to ***m*-TE**, average drops in the corresponding isotropization temperatures of 23 and 32 K, respectively, could be evaluated. The melting temperatures exhibited within the series a rather irregular even–odd alternation, even members possessing higher transition temperatures than the adjacent odd member(s). The increase in the number of oxyethylene units produced a decrease of the melting temperature, analogous to the isotropization

Table 1. Structural and thermal properties of ***m*-DI** polyesters based on a dioxyethylene ($n = 2$) segment and polymethylene segments of different length.

| Sample | $m$ | $[\eta]$† $(\mathrm{dl\,g^{-1}})$ | $\bar{M}_n$‡ | $\bar{M}_w/\bar{M}_n$‡ | $T_m$/°C | $T_i$/°C | $\Delta H_i/\mathrm{kJ\,mol^{-1}}$ | $\Delta S_i/\mathrm{J\,mol^{-1}\,K^{-1}}$ |
|---|---|---|---|---|---|---|---|---|
| **6-DI** | 6 | 0·29 | 10 300 | 1·76 | 163 | 201 | 8·83 | 18·6 |
| **7-DI** | 7 | 0·28 | 3 900 | 1·95 | 150 | N.M. | N.M. | N.M. |
| **8-DI** | 8 | 0·38 | 12 000 | 1·85 | 165 | 179 | 9·27 | 20·5 |
| **9-DI** | 9 | 0·33 | 6 900 | 1·83 | 144 | N.M. | N.M. | N.M. |
| **10-DI** | 10 | 0·30 | 6 800 | 1·90 | 146 | 153 | 9·34 | 21·9 |
| **12-DI** | 12 | 0·36 | 9 200 | 1·95 | 142 | 146 | 9·52 | 22·7 |

† In chloroform, at 30°C.
‡ By gel permeation chromatography, in chloroform.
N.M., Not mesomorphic.

Table 2. Structural and thermal properties of ***m*-TR** polyesters based on a trioxyethylene ($n = 3$) segment and polymethylene segments of different length.

| Sample | $m$ | $[\eta]$† ($\mathrm{dl\,g^{-1}}$) | $\bar{M}_n$‡ | $\bar{M}_w/\bar{M}_n$‡ | $T_m$/°C | $T_i$/°C | $\Delta H_i$/$\mathrm{kJ\,mol^{-1}}$ | $\Delta S_i$/$\mathrm{J\,mol^{-1}\,K^{-1}}$ |
|---|---|---|---|---|---|---|---|---|
| **6-TR** | 6 | 0·33 | 9 000 | 1·91 | 120 | 177 | 6·66 | 14·8 |
| **7-TR** | 7 | 0·35 | 7 100 | 1·86 | 93 | N.M. | N.M. | N.M. |
| **8-TR** | 8 | 0·39 | 14 100 | 1·94 | 103 | 151 | 8·14 | 19·2 |
| **9-TR** | 9 | 0·27 | 8 800 | 1·95 | 92 | N.M. | N.M. | N.M. |
| **10-TR** | 10 | 0·32 | 7 700 | 2·00 | 114 | 135 | 8·65 | 21·2 |
| **12-TR** | 12 | 0·34 | 9 900 | 1·87 | 120 | 125 | 10·01 | 25·1 |

† In chloroform, at 30°C.

‡ By gel permeation chromatography, in chloroform.

N.M., Not mesomorphic.

Table 3. Structural and thermal properties of ***m*-TE** polyesters based on a tetraoxyethylene ($n = 4$) segment and polymethylene segments of different length.

| Sample | *m* | $[\eta]$† ($\mathrm{dl\,g^{-1}}$) | $\bar{M}_n$‡ | $\bar{M}_w/\bar{M}_n$‡ | $T_m$/°C | $T_i$/°C | $\Delta H_i$/kJ mol$^{-1}$ | $\Delta S_i$/J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|---|---|---|---|
| **6-TE** | 6 | 0·24 | 6900 | 1·72 | 75 | 140 | 5·69 | 13·8 |
| **7-TE** | 7 | 0·26 | 7900 | 1·72 | 62 | N.M. | N.M. | N.M. |
| **8-TE** | 8 | 0·42 | 7200 | 1·96 | 94 | 122 | 5·73 | 14·5 |
| **9-TE** | 9 | 0·29 | 7600 | 1·72 | 75 | N.M. | N.M. | N.M. |
| **10-TE** | 10 | 0·30 | 6600 | 2·10 | 105 | (102)§ | 5·17 | 15·0 |
| **12-TE** | 12 | 0·22 | 5600 | 2·07 | 106 | (96)§ | N.D. | N.D. |

† In chloroform, at 30°C.
‡ By gel permeation chromatography, in chloroform.
§ Monotropic transition.
N.M., Not mesomorphic; N.D., D.S.C. peaks not resolvable.

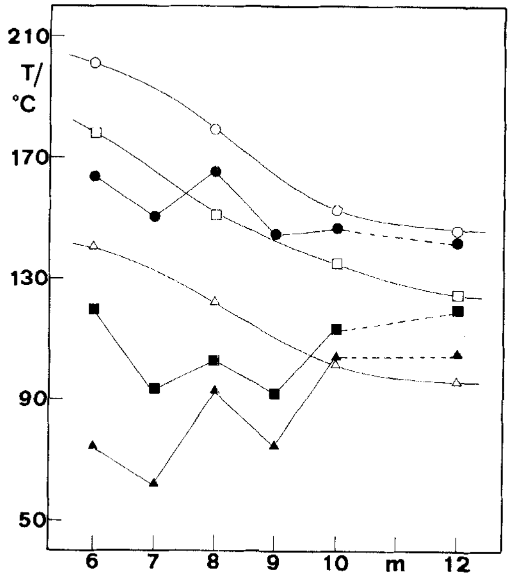


Figure 1. Melting (filled symbols) and isotropization (open symbols) temperatures for polyesters ***m*-DI** (circles), ***m*-TR** (squares) and ***m*-TE** (triangles) as a function of the number, *m*, of methylene groups in the polymethylene segment.

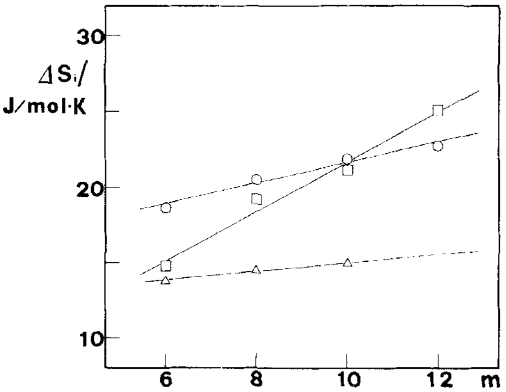
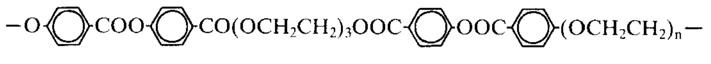


Figure 2. Isotropization entropies for polyesters ***m*-DI** (○), ***m*-TR** (□) and ***m*-TE** (△) as a function of the number, *m*, of methylene units in the polymethylene segment.

temperature. However, the series characterized by the presence of the trimer and tetramer oxyethylene units showed an ascending tendency in the melting temperatures with lengthening polymethylene spacer, whereas a descending trend was detected in the ***m*-DI** series.

The trends of the isotropization entropies for the even members of the three series as a function of the number of methylene groups in the alkylene spacers are illustrated in figure 2. The isotropization entropies increased in a linear fashion with increasing aliphatic spacer length, but although the nematic–isotropic entropy curves of the ***m*-DI** and ***m*-TE** series possessed almost the same slope, the nematic–isotropic entropy curve of the ***m*-TR** series showed a substantially more marked rising trend. The increase of isotropization entropy with the number of methylene units reflected an increasing flexibility of the polymer chain in the isotropic state with respect to the mesomorphic one. The difference in the slope of the nematic–isotropic entropy plots for the ***m*-DI** and ***m*-TE** series with respect to the corresponding curve for the ***m*-TR** series has to be related to the different parity of the oligo oxyethylene segments. The oxyalkylene residues of the ***m*-DI** and ***m*-TE** polymers, consisting of sequences of 5 and 11 atoms, respectively, should possess in fact an 'odd' type geometry disrupting the collinearity of the mesogen array. On the contrary, the oxyalkylene residue of the ***m*-TR** polymers, consisting of 8 atoms in a sequence, was of 'even' type, allowing for a better collinearity and packing of the mesogens in the nematic phase. It is implicit that the above interpretations stand on the assumption of a prevalently *trans* conformation of the flexible spacers. Consequently, the active participation can be stressed of the oxyalkylene segments in favouring the adoption by the alkylene segments of conformations particularly suitable to the establishment of mesomorphic properties. The lack of long range orientational correlation along the chain backbone of the odd ***m*-DI** and ***m*-TE** polymers made less severe the conformational constraints of the alklylene segments in the nematic state.

To further substantiate the key role played by the ether oxygen atoms within the skeleton of the flexible segments in affecting the mesogenic strength of main-chain polymers, three polymer samples **O8-DI–O8-TE** were prepared.



| *n* | Sample |
|---|---|
| 2 | **O8-DI** |
| 3 | **O8-TR** |
| 4 | **O8-TE** |

The three polymers are analogues of polymers **8-DI**, **8-TR** and **8-TE** in which the methylenes in the 3,6 positions have been replaced by oxygen atoms. Some physicochemical characteristics of the polymers are collected in table 4. None showed liquid-crystalline properties, thus suggesting that the substitution of oxygen atoms for methylene groups favoured the occurrence of conformers not compliant with the mesomorphic order. This finding is in accordance with previous data [7, 8] and theoretical calculations [9]. It should be mentioned, however, that a stereochemical equivalence between oxygen atoms and methylene groups was inferred for polymeric systems containing mesogens with a much greater axial ratio [10, 11].

Table 4. Structural and thermal properties of **O8-DI–O8-TE** polyesters based on a trioxyethylene segment and oxyethylene segments of different length.

| Sample | *n* | $[\eta]$†/dl g$^{-1}$ | $\bar{M}_n$‡ | $\bar{M}_w/\bar{M}_n$‡ | $T_m$§/°C |
|---|---|---|---|---|---|
| **O8-DI** | 2 | 0·15 | 4500 | 1·64 | 128 |
| **O8-TR** | 3 | 0·10 | 5300 | 1·62 | 85 |
| **O8-TE** | 4 | 0·03 | 2300 | 1·42 | 74 |

† In chloroform, at 30°C.

‡ By gel permeation chromatography, in chloroform.

§ Not mesomorphic.

## 4. Conclusions

The preparation of segmented polyesters characterized by a rigorous alternation of *p*-oxybenzoyl dyads with polymethylene ($m = 6$–$10$ and 12) and oxyethylene ($n = 2$–$4$) spacers can be carried out by a polycondensation reaction of $\alpha,\omega$-di(4-chloroformylphenoxy)alkanes with the disodium salt of $\alpha,\omega$-di(4-hydroxybenzoate)alkanes under phase transfer conditions. Accordingly, molecular weights variable from 4000 to 15 000, corresponding to degrees of polymerization of 8–20, are obtained such as to guarantee for a practical independence of the bulk properties of molecular weight of the polymers.

Oxyalkylene and polymethylene flexible segments both affect the mesomorphic behaviour of the polymers, the variation of the latter producing dramatic odd–even alternations. The parity of the oligo oxyethylene spacer also plays an important role in affecting the overall array of the mesogenic cores, permitting a tighter ordering in the nematic state. We conclude that cooperative effects of the two spacers connecting the *p*-oxybenzoyl dyads along the polymer backbone favour the onset of liquid-crystalline order, through the adoption of conformations endowed with increasing entropy contents. However, the oxyethylene residues show an inherently low mesogenic propensity relative to the polymethylene segments, and the mesomorphic properties can be fully extinguished in polyesters containing only alternating oxyethylene spacers.

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