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# Thermotropic liquid crystalline block copolyesters with PET as flexible spacers

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## Summary

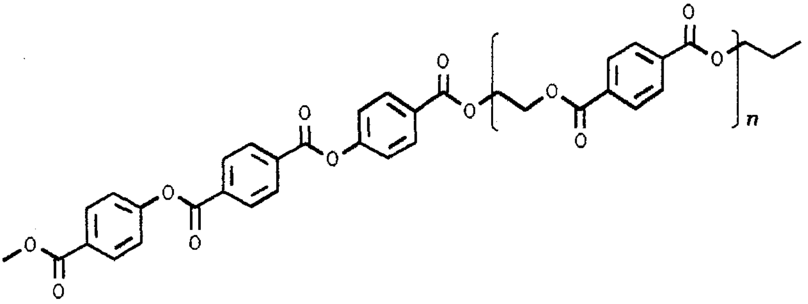
PET oligomers with different degrees of polymerization containing PHB as end groups were synthesized by melt condensation of bis(2-hydroxyethyl) terephthalate (BHET) in the presence of ethyl *p*-hydroxybenzoate (EtPHB). Coupling the oligomers with terephthaloyl chloride, a series of block copolymers with identical triad aromatic ester "hard" segments as mesogen and different lengths of PET "soft" segments as spacer were obtained. Observation with a cross-polarized optical microscope shows that these copolymers are thermotropic in a certain range of the spacer length (*n*). As *n* increases, the melting point ($T_m$) of the copolymer also increases, following the increasing molecular weight. The isotropic transition temperature ($T_i$) and the LC phase range ($\Delta T$), on the other hand, decrease with the increasing *n*. When *n* exceeds a critical value, the LC phase disappears.

## Introduction

The most natural approach from low molecular weight liquid crystals (LC's) to liquid crystalline polymers (LCP's) is, probably, to connect the small molecules, which usually contain a rigid mesogenic "core" with flexible "tails" at either or both sides, together to form a polymer backbone. The resulted macromolecule has a semi-rigid main chain with flexible segments as spacers between mesogenic groups. A mesophase above melting point was theoretically predicted for these polymers [1]. Since Roviello and Sirigu experimentally synthesized the first of such kind LCP in 1975 [2], extensive studies followed [3-9]. It was found that with increasing spacer length, the isotropic transition temperature ($T_i$) decreases and the temperature range of nematic state ($\Delta T$) becomes narrow. This class of polymers provides a possibility for molecular design to obtain a thermotropic LCP with a desired melting point and hence a processing temperature range well below the decomposition temperature.

A well-known phenomenon observed in these LCP's is the odd-even effect of the spacer length, which implies the flexible chain segments are not completely random coils in the LC state. Entropy study from DSC analysis confirmed that the nematic state in a LCP is more ordered than in a small LC with similar structure [7,10]. Moreover, it is observed that only two *para* conjoined benzene rings are sufficient to be a mesogen, which has an aspect ratio x≈3, far less than what Flory's lattice theory predicted x≥6.42 for small LC [11].

In this work, a series of block copolymers (referred as $P_n$) with structures showed below are prepared:



(I)

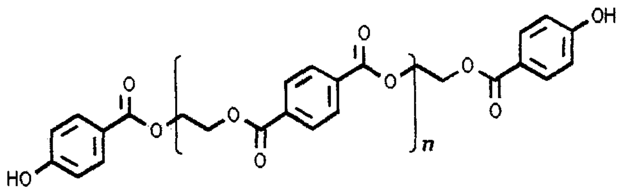
in which, a series of poly(ethylene terephthalate) (PET) oligomers ($S_n$) with $n \approx 1, 2, 3, 6$, or 10 are used as spacers. The PET spacer in these synthesized LCP's may control the transition temperatures as reported in previous works. However, the main purpose to introduce PET segments into the LCP chain lies on our interest in "*in-situ* composite" of this LCP's with PET: It is believed that the alignment of LCP molecules in a flow field can be utilized for so-called self-reinforced composite, where the reinforcement comes from the fibrils of LCP formed *in situ* during processing, e.g. extrusion or injection molding. If the LCP is partially compatible with the other component (say, matrix) in a blend, like PET spacers with PET matrix in this specific case, a fine phase separation morphology with only little voids at the interface is expected. Therefore, efficient stress transfer and thus good mechanical properties can be achieved. If the more or less aligned PET spacers in the LCP can induce the orientation of PET matrix molecules, it will enhance the performance further more.

This paper delivers some synthetic results briefly. Further investigation on the resulted materials is under way.

## Experimental

Materials The monomer of PET, bis(2-hydroxyethyl) terephthalate (BHET), was prepared by controlled transesterification between dimethyl terephthalate and ethylene glycol [12]. Pure product was obtained after recrystallization from hot water (yield 70%). Terephthaloyl chloride was prepared by terephthalic acid with thionyl chloride in the presence of catalyst amount of DMF [13] (yield 90%). The purity was about 94% according to element analysis of Cl. Other reagents were used as received without special treatment.

Oligomers A series of oligomers with structures (II) were synthesized by melt condensation of BHET in the presence of ethyl *p*-hydroxybenzoate (EtPHB). The degree of condensation was controlled by the feed ratio of BHET/EtPHB, suppose EtPHB acts as a mono-functional reactant and forms end-groups in the products.


(II)

Typical experimental procedure is as follows for $S_1$: BHET 10.16g (0.04 mol), EtPHB 9.28g (0.08 mol), together with catalysts of $Mn(OAc)_2 \cdot 4H_2O$ 45.6mg and $Sb_2O_3$ 3.1mg were heated in $N_2$ for 30 min at 160°C, 60 min at 200°C, 30 min at 220°C, 120 min at 240°C, and in vacuum for 60 min at 240°C to give a clear melt which solidified after poured into ice water. It was then carefully ground, washed with water, filtered and vacuum dried at room temperature. Results are listed in Table 1.

Polymerization Block copolymers with structures (I) were prepared by Schotten-Baumann reaction of the respective oligomers with equimolar terephthaloyl chloride in 1,1,2,2-tetrachloroethane solution. Two folds pyridine was added as catalyst and HCl acceptor. The reaction mixture was refluxed at 140°C over 24 hours before precipitated in excessive methanol. The products were washed successively with 3% $Na_2CO_3$, 3% HCl, water and acetone. Results are listed in Table 2.

Measurements Inherent viscosities $\eta_{inh.}$ of the copolymers were measured at 25°C with an Ubbelhode type viscometer on solutions of 0.5 g/dl in 1:1 (wt) phenol/*o*-dichlorobenzene. $^1H$-NMR spectra were recorded in deuterized trifluoroacetic acid solution on a Varian UNITY200 spectrometer. The optical texture was observed on a hot-stage with a Carl-Zeiss PHMK 80/2603 cross-polarized microscope. The thermal behaviors were studied on a Perkin-Elmer DSC7 differential scanning calorimeter.

## Results and Discussion

### Characterization

*Table 1.* Characterization of the oligomers

| Sample | Feed ratio BHET/EtPHB | $n$ a) | End group ratio phenol/alcohol | Conversion of EtPHB (%) | Polymerization of EtPHB (%) | $T_m$ b) (°C) |
|---|---|---|---|---|---|---|
| $S_1$ | 1 : 2 | 1.7 | 8.7 : 1 | ~ 100 | 0 | 72 |
| $S_2$ | 1 : 1 | 2.2 | 6.0 : 1 | ~ 100 | 0 | 82 |
| $S_3$ | 3 : 2 | 2.4 | 2.1 : 1 | ~ 100 | 0 | 88 |
| $S_6$ | 3 : 1 | 4.4 | 2.2 : 1 | ~ 100 | 0 | 195 |
| $S_{10}$ | 5 : 1 | 7.7 | 1.2 : 1 | ~ 75 | 0 | 235 |

a) Calculated from end groups in quantitative 1H-NMR spectra.
b) Visual measurement on a hot-stage.

The oligomers were characterized as shown in Table 1. Quantitative results are mainly calculated from $^1H$-NMR analyses (Figure 1). Chemical shift assignments come from spectra of monomers in an identical environment (i.e. solvent, concentration, temperature, etc.).

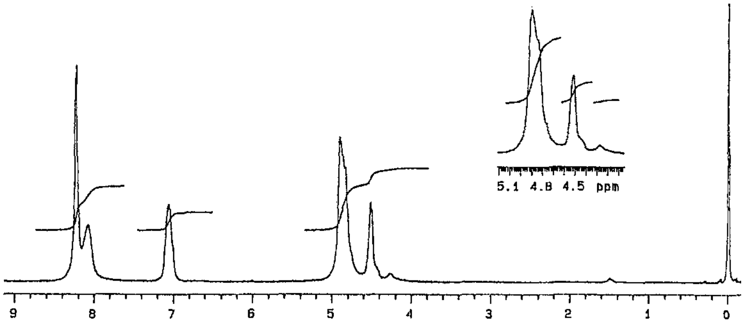


*Figure 1.* $^1$H-NMR spectrum of $S_1$ in deuterized trifluoroacetic acid.

It is fairly satisfactory that the end groups of the oligomers are rather dominated by PHB, except for those in $S_{10}$ which was prepared over a shorter reaction time. The reaction temperature was limited to 240°C in all case to restrain the polymerization of EtPHB. The results show no PHB segments exist in the middle of the chains in all circumstances. But under such conditions, the conversion of EtPHB is not completed,as indicated by the residual peaks at $\delta \approx 1.5$ in the NMR spectra (Fig. 1). It seems to increase the ultimate temperature to 250–260°C is favorable to assure a better result.

### Thermotropic behaviors

*Table 2.* Properties of the block copolymers

| Sample | $\eta_{inh.}$[a) (dl/g) | Visual (°C)[b) | | Thermal Analyses (°C)[c) | | | |
|---|---|---|---|---|---|---|---|
| | | $T_m$ | $T_i$ | $T_g$ | $T_m$(1st) | $T_c$ | $T_m$(2nd) |
| $P_1$ | 0.108 | 110 | >300 | 69 | 100 | --- | --- |
| $P_2$ | 0.155 | 130 | 240 | 74 | 130 | --- | --- |
| $P_3$ | 0.181 | 160 | 230 | 71 | 170 | --- | --- |
| $P_6$ | 0.239 | 205 | --- | 74 | 205 | 160 | 199 |
| $P_{10}$ | 0.142 | 235 | --- | 71 | 230 | 181 | 226 |

a) 0.5 g/dl in 1:1 (wt) phenol/o-dichlorobenzene at 25°C.

b) Observed in optical microscope.

c) DSC 1st scan is heating at 20°C/min, cooling at 10°C/min; 2nd scan is heating at 50°C/min.

The texture of oligomers and resulted polymers were observed under a cross-polarized optical microscope on a hot stage. None of the oligomers are thermotropic. For the polymers of $P_1$–$P_3$, a birefringence appears above the melting temperature ($T_m$). It is a typical bi-phase state, which is composed of bright domains of mesophase in the dark background of isotropic melt. The fraction of the birefringent domain decreases with the increasing temperature until the isotropic temperature ($T_i$) is reached, when the melt becomes totally isotropic.

The properties of the block copolymers are listed in Table 2. When the length of PET spacer in the copolymer increases, $T_i$ decreases as expected from over 300°C for $P_1$ to 230°C for $P_3$. But the melting point is steadily increased. A reasonable interpretation contributes this increase of melting point to the increase of the molecular weight when $M_w$<10,000 [9], as reflected from the viscosities ($\eta_{inh.}$). When the spacer length increases further on, the $T_i$ and $T_m$ meet each other and no mesophase forms from $P_6$ and $P_{10}$ (Fig. 2).

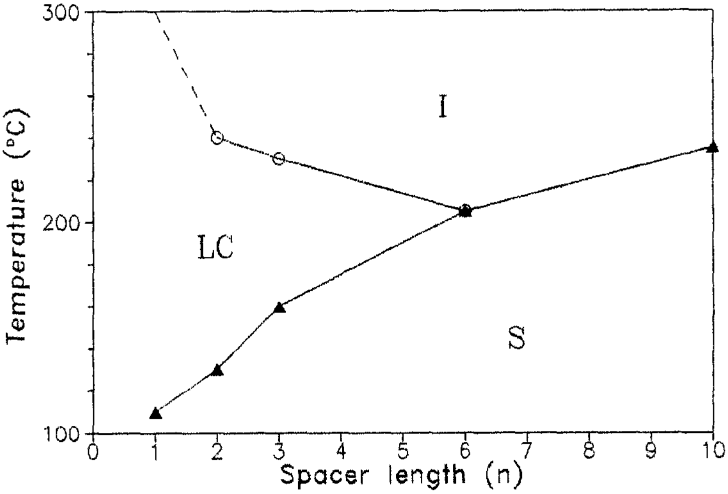


*Figure 2.* Phase diagram of block copolymers containing triad aromatic ester mesogens and PET spacers

Thermal analyses of DSC give a good complement, but the available information is rather limited. The first heating scan gives a too complex thermogram due to the complicated thermal history of the as-synthesized samples. The following scans, however, are little informative except the $T_g$, because the crystallization window ($T_m$-$T_g$) is too narrow for those with low melting point (i.e. $P_1$ - $P_3$) to recrystallize from the melt in the time scale of -10°C/min on DSC. Moreover, because the mesophase disappears gradually over the whole range from $T_m$ to $T_i$, the endothermal peaks corresponding to $T_i$ failed to be detected.

## Conclusion

The block copolymer with triad aromatic ester hard segments as mesogen and PET segments as spacer can be thermotropic in a certain range of the spacer length. With increasing length of PET, the $T_m$ increases while the $T_i$ decreases. For further studies in the future, it is critical to find an appropriate way to increase the molecular weight of the copolymers.

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