

Liquid-crystalline copolymers of bibenzoate and terephthalate units

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Summary

The effect on the mesophase behaviour of the substitution of mesogenic bibenzoate groups by non-mesogenic terephthalate units is studied. Time-resolved synchrotron X ray and DSC experiments indicate that copolymers with an amount of terephthalate units as high as 29 mol % exhibit liquid crystalline properties, and a smectic mesophase is obtained on cooling, which further experiences a transformation into a three-dimensional crystal. The two transitions are rather sharp and well defined, in contrast to other similar copolymers.

Introduction

Liquid crystalline polymers, LCPs, are a subject of increasing interest due to the favourable combination of some characteristics such as their low density and exceptional mechanical properties, including strength, easy flow, excellent dimensional stability, ability to incorporate high levels of fillers and excellent chemical resistance [1]. Moreover, LCPs have also remarkable gas barrier properties [1,2].

In order to tailor the transition temperatures (and the final properties) the copolymerization with non-mesogenic monomers or the introduction of spacers are widely used strategies in LCPs. Thus, many publications have reported on the synthesis and characterization of LCPs with the bibenzoate group as mesogen and different methylenic and oxymethylenic spacers [3-11] with transition temperatures in a very wide range (up to 352 °C), which can be easily tailored by choosing the appropriate spacer. Smectic mesophases are usually obtained, organized in layers at the nanometric level: typically in the order of 1.5 – 2 nm. Moreover, the nature of the spacer has also a great influence on the kind of mesophase (or mesophases) obtained.

On the other hand, several reports have been published on copolymers of bibenzoate with terephthalic or isophthalic units [12-16], most of them dealing with ethylene glycol as spacer. No evidence of liquid crystallinity was found in the case of poly(ethylene terephthalate-co-4,4'-bibenzoate), although a "frustrated" liquid crystalline structure was proposed [12-14]. Copolymers with up to 20% isophthalic content were reported to possess some amount of liquid crystalline character [16], although the isotropisation endotherms were rather wide and of small intensity.

This work presents the preliminary results of a general project dedicated to study the effect on the mesophase behaviour of the substitution of part of the bibenzoate units by terephthalic groups, aiming to obtain copolymer materials with tailored properties (and reduced cost) but yet presenting the ability to exhibit liquid-crystalline phases. A relatively long and flexible spacer, composed of seven methylenes, is used here, but other different spacers are being prepared.

Experimental Part

The copolymers (and the homopolymers) were synthesised by melt transesterification of different proportions of diethyl *p,p'*-bibenzoate and dimethyl *p,p'*-terephthalate with 1,7-heptanediol, using tetraisopropyl titanate, TIPT, as catalyst. The synthetic procedure, and the molecular structure, is presented in Figure 1. The polymers were purified by precipitating into methanol their solutions in chloroform.

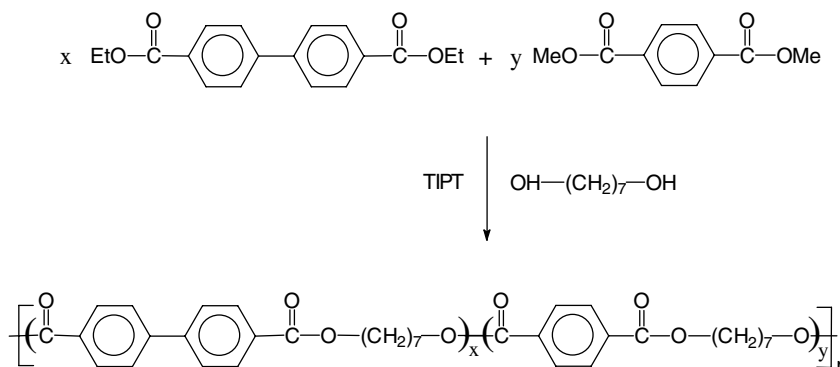


Figure 1. Synthetic procedure and molecular structure of the copolymers.

The chemical composition of the samples was analyzed by ^{13}C NMR spectroscopy, in a Varian 300 spectrometer, using deuterated chloroform as the solvent, at 40 °C. The composition was determined by integration of the corresponding protonated aromatic carbon signals arising from the bibenzoate or terephthalate units. The results are shown in Table 1, compared with the theoretical values deduced from the amount of precursors in the polymerization.

Table 1. Molar composition of the different samples

Sample	Mol % terephthalate units	
	theoretical	experimental
P7MB	0	0
C7TB1	11	10
C7TB2	31	29
P7MT	100	100

The thermal transitions were analyzed in a Perkin-Elmer DSC7 calorimeter connected to a cooling system and calibrated with different standards. A sample weight in the range from 7 to 11 mg was used, with a scanning rate of 20 °C/min.

Variable-temperature X ray scattering experiments were performed by employing synchrotron radiation ($\lambda=0.150$ nm) in the beam-line A2 at HASYLAB (Hamburg, Germany). Two linear position-sensitive detectors were used simultaneously, covering two different spacing intervals: the first one covers the region from around 6 to 1 nm (Middle-Angle X ray Scattering, MAXS, region). The second detector covers the spacings from around 1 to 0.3 nm (Wide-Angle X ray Scattering, WAXS, region). A cooling rate of 4 °C/min was used. The calibration of the spacings for the detectors was made as follows: the diffractions of a crystalline PET sample were used for the WAXS detector, and a sample of silver behenate (giving a well-defined diffraction at a spacing of 5.838 nm, and several orders) was used for the MAXS detector.

The polymer films for DSC and synchrotron measurements were prepared by moulding the material in a Collin press above the melting temperature and then cooling down to room temperature.

Results and Discussion

Figure 2 shows the DSC curves of the different samples cooled from the isotropic melt. The upper curve, corresponding to P7MB homopolymer, presents two exotherms, centred at 138 and 95 °C, with enthalpies of 18 and 15 J/g, respectively. As it is well known [5,17,18] the exotherm at higher temperature corresponds to the transition, T_{I-S} , from the isotropic melt to a smectic mesophase of the type SmCalt (the spacer in P7MB includes an odd number of methylene groups). The second exotherm, at lower temperature, represents the transition from the smectic mesophase to a three-dimensional crystal, T_{S-C} .

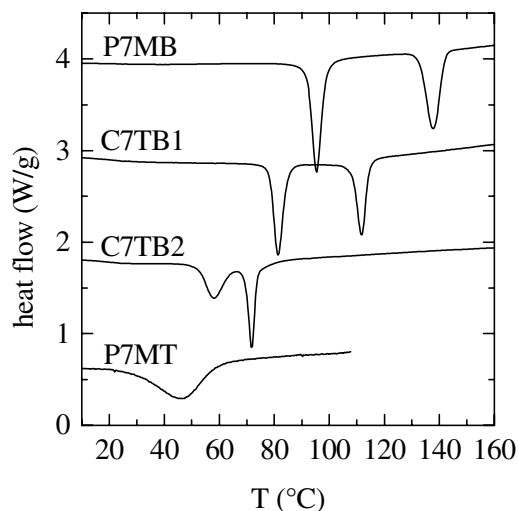


Figure 2. DSC cooling curves from the isotropic melt of the different samples.

Copolymer C7TB1 shows a DSC curve rather similar to the one of P7MB, but with somewhat lower transition temperatures (and enthalpies): 112 and 81 °C, with 15 and 14 J/g, respectively. In principle, and as it will be demonstrated below, these two transitions have the same origin than those for P7MB, i.e. they represent the

transitions $T_{I,S}$ and $T_{S,C}$, respectively. It is important to note that the two transitions are rather sharp and perfectly well defined, in contrast to other similar copolymers.

In the case of C7TB2, where the content in terephthalate units is as high as 29 mol%, the depression of those transition temperatures is considerably higher, since they appear at 72 and 58 °C, respectively (with enthalpies of 13 and 13 J/g, respectively). But, more importantly, the interval of stability of the mesophase, represented by the difference $T_{I,S} - T_{S,C}$, has been considerably reduced, passing from the 43 °C for P7MB and the 31 °C for C7TB1 to only 14 °C for C7TB2. These results were expected, since the terephthalate units do not have the ability to act as mesogenic groups.

Finally, the lower curve in Figure 2 shows the behaviour of P7MT homopolymer. In this case, a single wide exotherm is observed, characteristic of the direct crystallisation from the isotropic melt. It appears centred at 46 °C, with an enthalpy of 26 J/g.

It seems, therefore, that the two studied copolymers are able to exhibit mesophases, although the interval of mesophase stability is reducing considerably.

The subsequent melting curves are presented in Figure 3. The upper curve indicates that P7MB shows monotropic behaviour: the crystal melts directly into the isotropic phase and a single endotherm is observed, centred at 168 °C, with an enthalpy of 33 J/g (the isotropisation of the mesophase can be observed, at 160 °C, if the sample is heated after cooling from the melt down only to a temperature where the crystal is not yet formed [5]).

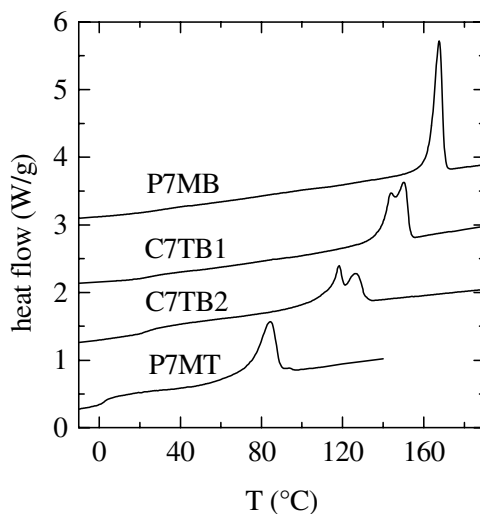


Figure 3. DSC heating curves after cooling from the melt of the different samples.

In the case of C7TB1, two overlapped endotherms are observed (at 144 and 150 °C) with a total enthalpy of 29 J/g. These two peaks may be due either to enantiotropic behaviour or to melting/recrystallisation processes. Copolymer C7TB2 exhibits a rather similar behaviour: two overlapped peaks are observed, at 118 and 126 °C, with a total enthalpy of 27 J/g.

Finally, P7MT homopolymer shows a single main endotherm at 84 °C, with a small shoulder at higher temperature. Since no mesophase is expected to be present in this

case, the shoulder is interpreted as arising from melting/recrystallisation phenomena, rather general in polyesters.

Another aspect from Figure 3 is the observation of the glass transition. Its value decreases from P7MB to P7MT, but the increment of the specific heat at the transition increases, indicating, most probably, that the total crystallinity decreases.

The variation of the different transition temperatures as function of the comonomer content is plotted in Figure 4. In all cases, a clear decrease is observed as the content in terephthalate units increases. The decrease is particularly important for the value of T_{I-S} , i.e. the transition from the isotropic melt to the smectic mesophase. The interpretation is that the terephthalate groups have a rather profound influence on the formation of the mesophase.

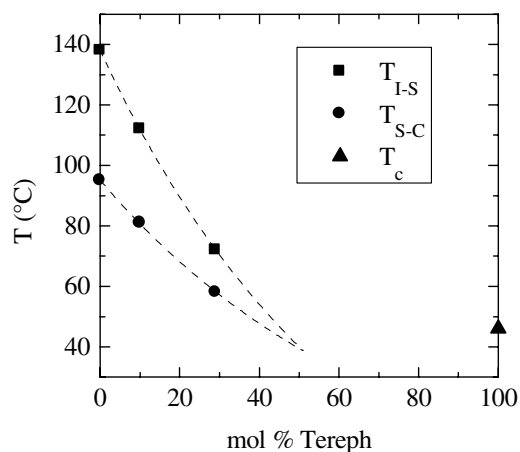


Figure 4. Variation of the indicated transition temperatures with the molar composition of terephthalate units in the sample.

A rough extrapolation (considering that the errors involved may be important, owing to the small number of samples) seems to indicate that the line for T_{I-S} crosses the one for T_{S-C} at a composition around 50 mol% terephthalate units. It follows, therefore, that the mesophase can be observed only for compositions below such approximate value (under the conditions studied here).

Attempts were made in order to identify, by polarised optical microscopy, the textures corresponding to the different phases. Unfortunately, and as it happens with LCPs of high or relatively high molecular weights, no revealing textures were obtained: thus, rather small birefringent "spherulites" are observed, on cooling the copolymers from the isotropic melt, when the first transition occurs, and this texture remains the same after the second transition, with only a certain increase of the transmitted light. The texture is compatible with both smectic or crystalline structures.

Additional variable-temperature synchrotron experiments have been performed, in order to ascertain the nature of the transitions involved. The short acquisition times required for the synchrotron experiments make this technique particularly useful for the characterization of liquid crystal systems where more than one mesophase are formed, or where the mesophases present a short interval of existence.

Figure 5 shows the diffractograms in the MAXS and WAXS regions at selected temperatures in a cooling experiment (at 4 °C/min) from the isotropic melt for copolymer C7TB1. The diffractograms at high temperature (150 °C) show a wide amorphous-like peak in the WAXS region and no peaks in the MAXS channels, as corresponds to an isotropic molten sample. At lower temperature (115 °C) the WAXS diagram is rather similar to the one for the isotropic melt, but the MAXS region shows a rather prominent peak (centred at 1.72 nm): these features are characteristic of a low-order smectic mesophase, with a layer spacing of 1.72 nm and with a laterally-disordered disposition of the polymer chains. At this temperature, and considering the lower cooling rate used in the synchrotron experiments, the first transition observed in the DSC has already occurred, corresponding, as supposed above, to the formation of the smectic mesophase from the isotropic melt.

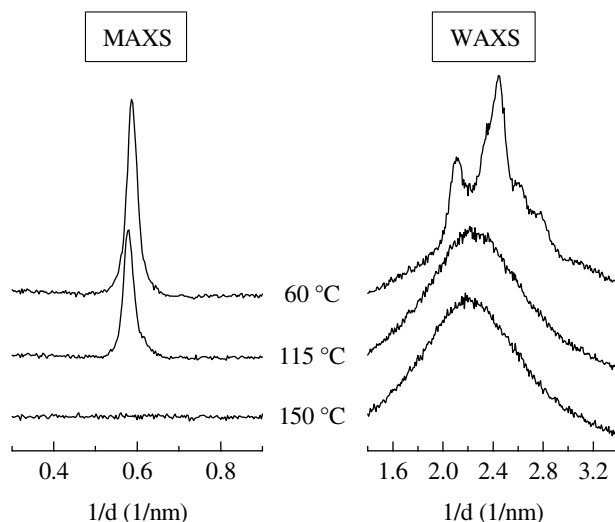


Figure 5. MAXS and WAXS diffractograms representing the three phases observed in C7TB1 when cooling from the melt. 150 °C: isotropic melt; 115 °C: smectic mesophase; 60 °C: crystalline phase.

At lower temperatures, and below the second DSC exotherm, several diffraction peaks are observed in the WAXS diffractogram acquired at 60 °C, as corresponds, most probably, to the formation of a three-dimensional crystal. Moreover, the MAXS peak appears now at 1.70 nm, and with a higher intensity.

This behaviour is similar to the one reported for P7MB homopolymer (with the evident variations in temperatures and spacings involved [5,17,18]). It follows, therefore, that smectic mesophases are also obtained in these copolymers, with similar ordering characteristics as those found in the SmCalt mesophase of P7MB. Moreover, no evidence of "frustrated" chain packing is found in these copolymers, since a single diffraction peak is obtained in the MAXS region, as observed in Figure 5, while "frustrated" structures use to exhibit two different periodicities [6,19].

A similar synchrotron experiment has been also performed on sample P7MT, cooling from the melt. No mesophase was observed, as expected, and the results show a direct transition from the isotropic melt to a three-dimensional crystal.

In conclusion, these preliminary experiments indicate that a considerable amount of terephthalate units can be copolymerized with bibenzoate groups, yet exhibiting liquid crystalline properties. Thus, a copolymer with an amount of terephthalate units as high as 29 mol % shows a smectic mesophase on cooling, which further experiences a transformation into a three-dimensional crystal. The two transitions are rather sharp and well defined, in contrast to other similar copolymers. It has to be taken into account that the two units (bibenzoate and terephthalate) are quite different in size. Nevertheless, it is not unusual that copolymer C7TB2 can exhibit a liquid crystalline character, due to the low packing requirements of low-ordered mesophases. But it is surprising that a crystal structure with a relatively high enthalpy (27 J/g compared to the 33 J/g of the homopolymer P7MB) is obtained for this 29 mol % copolymer. An extensive cocrystallisation should occur.

We are preparing and analyzing new copolymer compositions (and other systems with different spacers) in order to check the extrapolation results here advanced.

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