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LIQUID CRYSTALLINE POLYMERS
III. Characterization by thermo-optometry of some copolyethers containing an oxetane ring in the main chain

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Abstract

The suitabilities of thermo-optometry and differential scanning calorimetry for the characterization of certain copolyethers were compared. Under certain conditions, such polymers do not exhibit the endotherm signal corresponding to the solid/liquid crystalline transition in the DSC curves. Thermo-optometry provides evidence of these phase transitions into the liquid crystalline state, and is a very useful additional method.

Keywords: copolyethers, DSC analysis, oxetane, phase-transfer catalysis, thermo-optometry, thermotropic liquid crystalline polymers

Introduction

The syntheses of polyesters and polyethers based on 3,3-bis-(chloromethyl)oxetane [BCMO] and some bisphenols or diacids have previously been described [1–6]. The presence of an oxetane ring in the main chain induces special properties, due to its chain geometry. In the case of polyesters, for instance, the presence of oxetane rings explains the difficulties encountered in the ordering of the polymer chains on cooling. As a consequence, the liquid crystalline [LC] properties appear only on first heating [6].

Measurement of the light transmitted in a polymer sample, either heated or cooled, at a controlled rate, has been proved to be a very useful method in the study of transition or relaxation phenomena in polymers. Thermo-optometry (TO) has been mentioned in the literature as a method suitable for the demonstration of LC transitions in polymers [7, 8], reflecting the birefringence modifications of a sample either on heating or on cooling.

The present paper studies LC behavior by TO, in comparison with the DSC analysis of some copolyethers containing an oxetane ring in the main chain.

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Experimental

Copolyethers were synthesized by phase-transfer catalysis; the main aspects of their synthesis and characterization were reported previously [4].

The compositions of the copolymers were calculated *via* ^{1}H – NMR spectroscopy in $CDCl_3$, on a JEOL-60 MHz spectrometer.

The thermo-optical analysis apparatus was built in our laboratory; details of its construction have been given elsewhere [9]. The recordings were performed in unpolarized light.

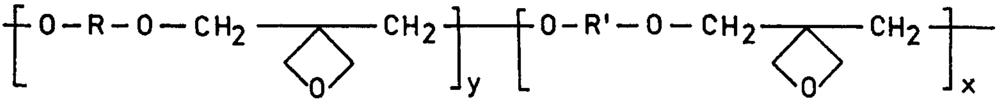
DSC curves were recorded on DuPont 2000 DSC-V4 and Perkin-Elmer DSC 7 instruments, at a heating rate of 10°C min^{-1}.

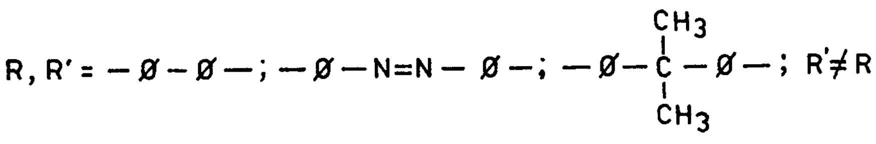
The glass transition temperature was determined as $1/2\Delta C_p$, and the isotropization temperature as the top of the corresponding peak.

Amorphous samples were preferred for the TO analyses, as crystalline polymers give more complicated curves because of the solid–solid phase transition processes. In consequence of the high ability of some copolyethers to crystallize, fast cooling was necessary to prepare amorphous samples. The polymer was placed on an uncovered glass plate, isotropized and then quenched at –5°C.

Results and discussion

Copolyethers were synthesized from 3,3-bis(chloromethyl)-oxetane [BCMO] and the following bisphenols: 4,4′-dihydroxy-azobenzene [DHAB], bisphenol-A [BPA] and 4,4′-dihydroxydiphenyl [DHD]. The copolymers have the following structure:





$$R, R' = -\varnothing-\varnothing-;\ -\varnothing-N{=}N-\varnothing-;\ -\varnothing-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-\varnothing-;\ R' \neq R$$

The first copolymer analysed was that containing DHAB and DHD (sample 1) as mesogens ($y/x=3.3$). On first heating, this copolyether exhibited a glass transition (T_g) at 101°C, followed by a solid/LC transition (the mesophase is stable between 150 and 180°C) and an isotropic phase at 210°C (Fig. 1–A). On uncontrolled cooling of the sample (at about 4°C min^{-1}) and reheating, the LC transition intensity is reduced, although it remains in the same temperature range (Fig. 1–B).

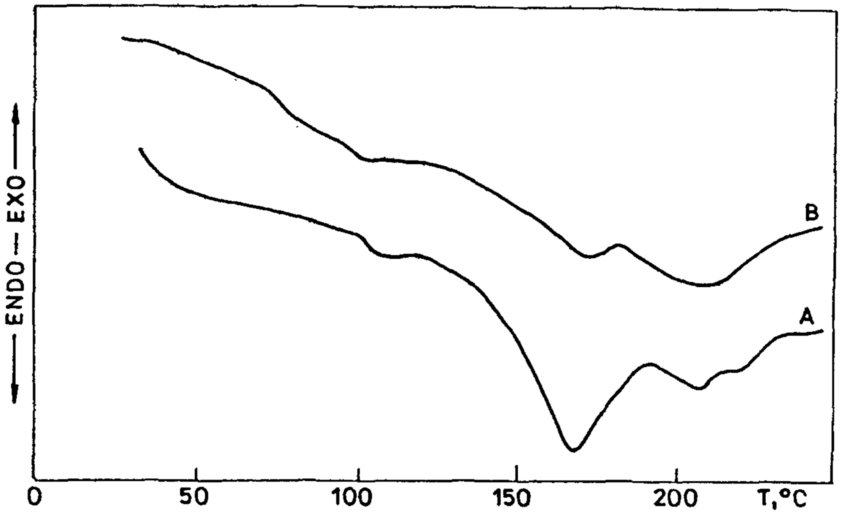


Fig. 1 DSC curves of sample 1: A – first heating; B – second heating

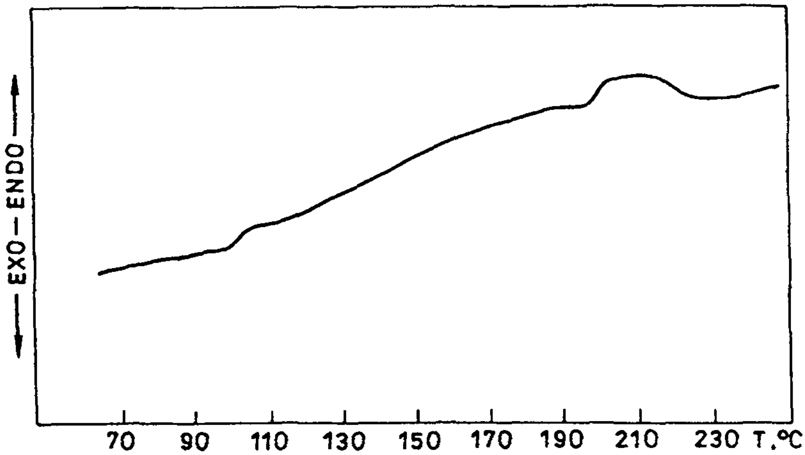


Fig. 2 DSC curve of sample 1 after isotropization and controlled cooling with 10°C min^{-1}

If the rate of cooling is controlled (10°C min^{-1}), the solid/LC transition disappears, and only glass and isotropization transitions are present (Fig. 2). The endo effect in Fig. 2 is upwards because the recording was made with a Perkin-Elmer apparatus. All other DSC curves were recorded with a DuPont 2000 instrument.

Disappearance of the DSC peak corresponding to the solid/LC phase transition has been mentioned by other authors. Thus, Ringsdorf [12] reported on LC polymers with mesogens in both the main chain and the side-chain, whose peaks corresponding to the solid/LC transitions diminished and eventually disappeared as the content of mesogenic side-groups was increased. This was due to the crystallization temperature being close to, or below the glass transition, the system being 'frozen' below T_g.

Figure 3 presents the TO curve corresponding to sample 1. The decrease in light transmission intensity is due to the transition from the solid to the LC

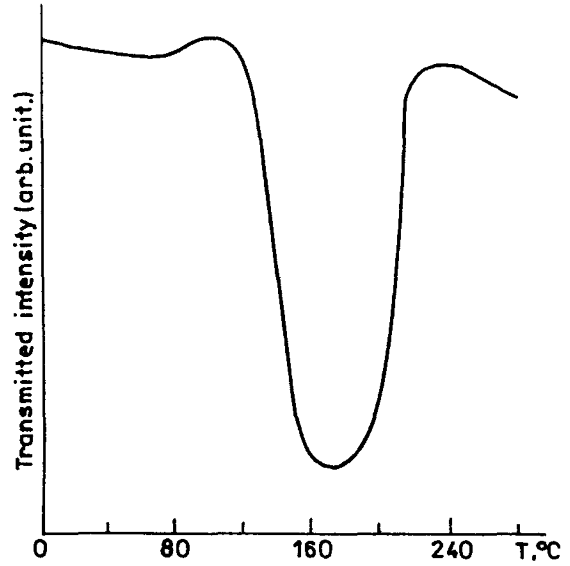


Fig. 3 TO curve of sample 1

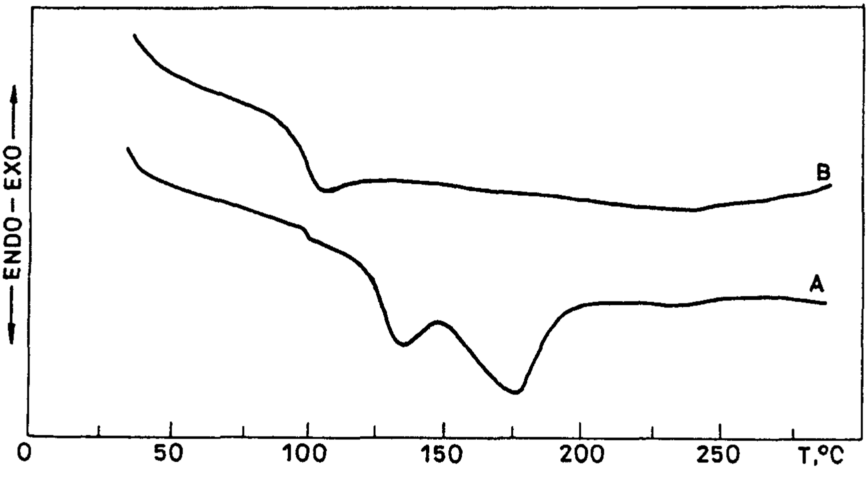


Fig. 4 DSC curves of sample 2: A – first heating; B – second heating

state, which takes place at 150–170°C. The isotropization is marked by an enhancement in the light transmission intensity, due to the passage from an anisotropic to an isotropic system (200–225°C). Thus, TO provides evidence of the solid/LC transition, which is absent from (Fig. 2) or reduced (Fig. 1–B) in the DSC curves. As already mentioned, this behavior is due to the occurrence of a crystallization temperature close to the glass transition. If the system is cooled at 4°C min^{-1}, it is able to crystallize partially, and as a consequence an endothermic peak is present at 160°C (on second heating), but it does not have the same magnitude as for the first heating (Fig. 1). If the cooling rate is 10°C min^{-1}, the system does not have enough time to crystallize at all. As a consequence, only the glass and isotropization transitions are observed (Fig. 2). The particular geometry of these semi-rigid chains, with the oxetane rings linked asymmetrically, is probably responsible for the shifting of the crystallization temperature close to the glass transition.

The second sample analysed was a copolymer with LC properties only on first heating. After isotropization, the sample displayed ordering difficulties on cooling, and thus an amorphous polymer resulted. Ordering in the polymer was attained again after an annealing process (72 h) at a temperature above T_g. The copolymer contains the same type of mesogens (DHAB and DHD), but the copolymerization ratio is $x/y=0.66$ (sample 2). For this sample, no thermal treatment (isotropization and fast cooling) was applied, the polymer being used as it was obtained from synthesis.

The DSC curves reveal that, on first heating, the sample affords T_g at 100°C and two phase transitions, at 120–140 and 140–195°C, the latter being that of isotropization (Fig. 4–A). On second heating, only T_g is present (Fig. 4–B).

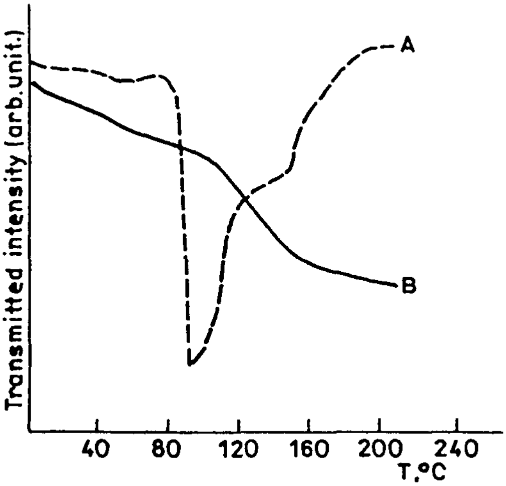


Fig. 5 TO curves of sample 2: A – first heating; B – second heating

The TO curves (Fig. 5–A) demonstrate a decrease in light intensity, followed by a two-step increase, at 120 and 160–200°C, respectively. No explanation is available for the decrease in transmitted light intensity at about 80°C, before the glass transition. However, the other two signals (the increases in light intensity) correspond to the transitions indicated by DSC analysis on first heating. On sec-

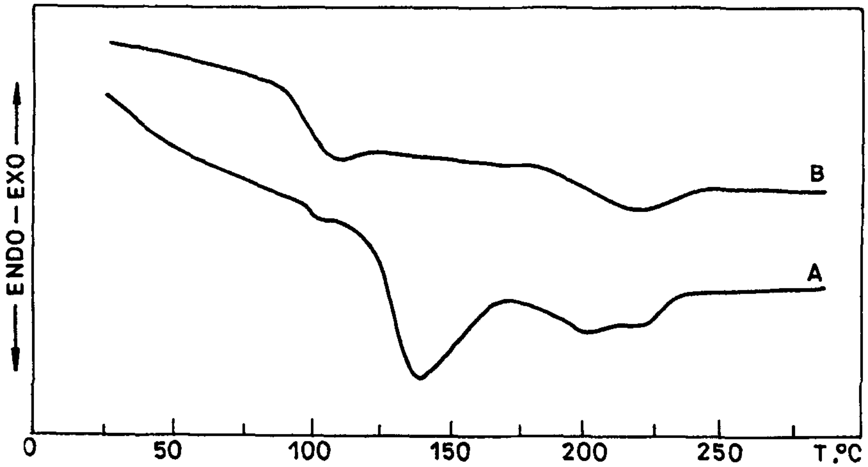


Fig. 6 DSC curves of sample 3: A – first heating; B – second heating

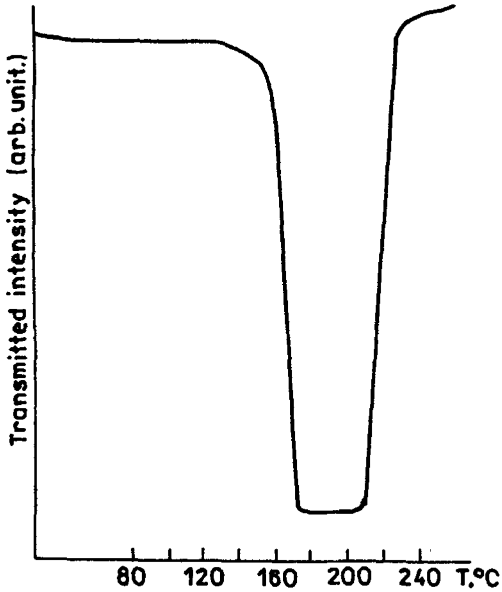


Fig. 7 TO curve of sample 3

ond heating, the TO curve shows no signals corresponding to a phase transition (Fig. 5–B), which is in agreement with DSC analysis (Fig. 4–B).

The third type of polymer analysed was ternary copolyether containing three bisphenols: DHAB, DHD and BPA (sample 3). In this case, the signal corresponding to the solid/LC transition (130–160°C) disappeared after the first heating – cooling cycle (Fig. 6). However, the mesophase was present between 160 and 200°C. On second heating, only T_g (100°C) and T_i (200–225°C) were present. Nevertheless, the TO method even yields evidence of this solid/LC phase transition. Figure 7 reveals two signals, at 160–170°C and 200–220°C, corresponding to the solid/LC and isotropization transitions, respectively.

Conclusions

It has been observed that thermo-optometry provides evidence of LC phase transitions undetected by DSC analysis on second heating. Consequently, in the event of a particular behavior of LC polymers, TO can offer additional information, and is therefore an excellent complementary analysis technique to DSC and optical polarized microscopy.

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