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Characterization of side-chain liquid crystal polymers using dynamic mechanical thermal analysis and dielectric thermal analysis

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Ten members of a homologous series of side-chain liquid crystal polymers, the poly[[α-(4-methoxybiphenylyl-4′-oxy)-ω-alkyl]methacrylate]s, have been characterized using dynamic mechanical thermal analysis (DMTA) and dielectric thermal analysis (DETA). For the undecyl and dodecyl homologues both techniques revealed a smectic–smectic transition not detected in previous studies either by differential scanning calorimetry or by optical microscopy. It is proposed that this corresponds to a monolayer–bilayer smectic A transition. A weak transition at ca. − 30 °C is detected using DMTA for polymers with spacer lengths 4–8 and by analogy with poly(methyl methacrylate) may indicate the absorption of small amounts of water. DMTA also proved to be particularly effective in deconvoluting transitions and for the propyl homologue established the existence of a smectic phase suggested by optical microscopy.

1. Introduction

Side-chain liquid crystal polymers (SCLCPs) are an important class of new materials with considerable application potential in a wide range of advanced electro-optic technologies including, for example, optical information storage [1], non-linear optics [2] and holographic imaging [3]. Their importance, however, is not restricted only to the development of new devices but in addition, these materials provide a demanding challenge to our fundamental understanding of the structural factors that promote self-organization in polymeric systems [4]. The thermal characterization of new SCLCPs is normally performed using differential scanning calorimetry (DSC) while polarized light microscopy is used to characterize phase types. On the basis of these studies SCLCPs may be studied further using a range of advanced techniques. Thus, the initial thermal characterization by DSC serves, in many instances, as a screening method for the selection of SCLCPs for further research and development. In this paper we discuss the merits of employing dynamic mechanical thermal analysis (DMTA) and dielectric thermal analysis (DETA) in the routine thermal characterization of SCLCPs. In principle, these techniques offer many advantages over DSC including a much enhanced sensitivity for detecting weak second order transitions, such as glass transitions, and also the ability to detect secondary transitions occurring below the glass transition. These sub-T_g processes which cannot be detected using DSC could limit the suitability of a SCLCP in a given application such as information storage [1] and therefore, it is important both to characterize and understand these relaxations. We should note that the dielectric behaviour of SCLCPs has been extensively characterized [5]. By contrast, the rheological properties of SCLCPs have received surprisingly little attention [6–10]. This situation has arisen principally for two reasons: first, considerable research effort has focused on the application potential of SCLCPs in electro-optic devices and clearly an understanding of the material's dielectric behaviour underpins such technologies; second, the field of SCLCPs has, to a large extent, overlapped that of low molar mass liquid crystals in which rheological techniques are rarely used. Thus, DMTA has been sparingly employed for the thermal characterization of SCLCPs [11]. This technique, however, has found widespread application in polymer science and our objective was to establish its value in characterizing SCLCPs. A major problem with these materials is that they can exhibit a large change in modulus and often over a short temperature range. This can make the measurements challenging to even those familiar with

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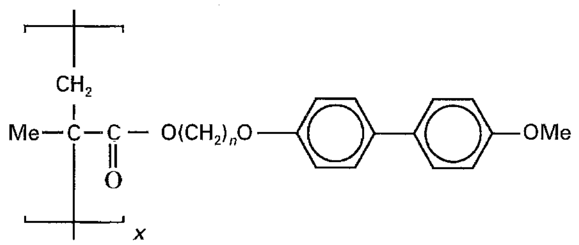
the technique. In this paper, however, we show that both mechanical and dielectric measurements can be made routinely using unmodified commercial equipment yielding valuable data which complements that obtained by DSC and optical microscopy. The homologous series, the poly[[α-(4-methoxybiphenylyl-4′-oxy)-ω-alkyl]methacrylate]s [12], **1**, was chosen for study in these investigations and the acronym used to refer to these polymers is *n*-OMe where *n* refers to the number of methylene units in the flexible spacer. This particular series has been chosen primarily because within the series many differing phase transitions have been observed using DSC and optical microscopy [12] and thus will provide a demanding test for DMTA and DETA.



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2. Experimental procedure

The polymers were prepared according to methods described in detail elsewhere [12]. DMTA was performed using a PC-controlled Rheometric Scientific DMTA system comprising a 706 temperature programmer and a MkIII analyser; both the MkII and MkIII heads were used. The MkIII head was used for experiments over the range − 100 to 200 °C while the MkII head was restricted to the range 30 to 200 °C. The ramping rate used was 3 °C min^{-1}. A frequency of 1 Hz was used for all the measurements and the strain was set at a fixed value corresponding to an amplitude of approximately 5 μm, i.e., ± 0.71% strain. The shear mode was used to characterize the polymers; samples were prepared by heating the polymer to approximately 200 °C, i.e. into the isotropic phase, and moulding into bars approximately 2 mm wide and 0.5 mm thick. These bars were cut to a suitable length for the shear plates. It was found that a slight compressive force on the fixed plates was necessary to locate the polymer correctly and to provide sufficient adhesion between the plates and the polymer. Attempts to use either the bending or compression deformation modes to study these polymers were unsuccessful.

DETA was performed using a PC-controlled Rheometric Scientific DETA system comprising a 706 temperature programmer, a MkI DETA head and a Hewlett Packard 4284A bridge. Each sample was heated at 1 °C min^{-1} from 30 to 200 °C. Three measuring frequencies were used, 1, 10 and 100 kHz, and the applied voltage was 200 mV r.m.s. The cell was prepared by sandwiching the polymer between 20 mm plates, heating to 200 °C and compressing the plates so that their separation was 0.1 mm. Excess polymer was removed from the edge of the plates.

3. Results and discussion

Fig. 1 shows the combined analyses of 8-OMe using DMTA, DETA and DSC. The two features in these traces common to all the polymers studied are (i) the electrical permittivity increases with increasing temperature while (ii) the shear modulus decreases with increasing temperature. The former effect results from the increase in mobility of the dipolar components of the polymer on increasing temperature while the latter effect reflects that the polymer chains are more mobile at higher temperatures and hence the resistance to deformation is reduced. We will discuss the analysis of 8-OMe in more detail later but it should be noted that the phase transitions are detected by each of the three techniques. Also, it was generally found that the clearing temperature was independent of the measuring frequency as would be expected for a strong first order transition.

A single peak is evident in the DSC trace for 3-OMe (see Fig. 2), although this has a reproducible low temperature shoulder. Microscopy revealed an arced focal conic fan texture indicative of a crystal E phase [12]. However, such a texture is paramorphotic and implies the presence of a smectic A (S_A) phase at higher temperatures although this was not observed optically. The presence of an E-S_A transition is supported by the DMTA analysis of 3-OMe; specifically, two transitions are clearly observed (see Fig. 2), the lower temperature one corresponding in temperature to the shoulder on the DSC endotherm. Indeed, DMTA allows a transition temperature to be assigned to the E-S_A transition, namely, 171 °C. A closer inspection of the DMTA trace reveals that the onset of the modulus decrease is at approximately 165 °C and corresponds with a change in the permittivity; it is possible that this corresponds to a glass transition. The E-S_A transition was not observed using DETA implying that the transition is either dielectrically inactive or that the

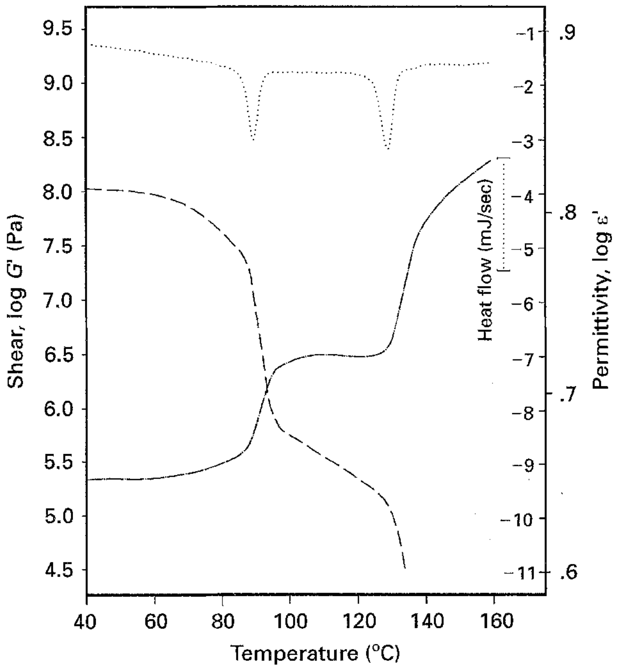

Figure 1 DMTA, DETA (measured at 1 kHz) and DSC traces for 8-OMe. Shear (– – –); permittivity (—·—).

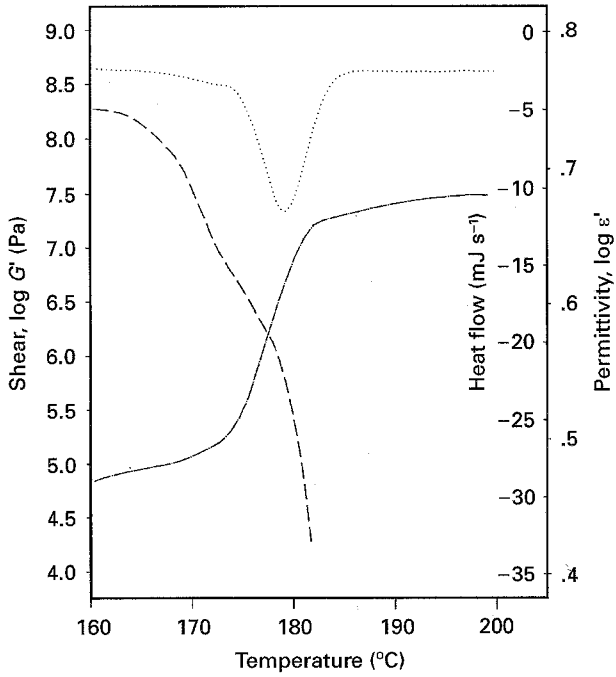

Figure 2 DMTA, DETA (measured at 1 kHz) and DSC traces for 3-OMe. Shear (– – –); permittivity (–·–·); heat flow (···).

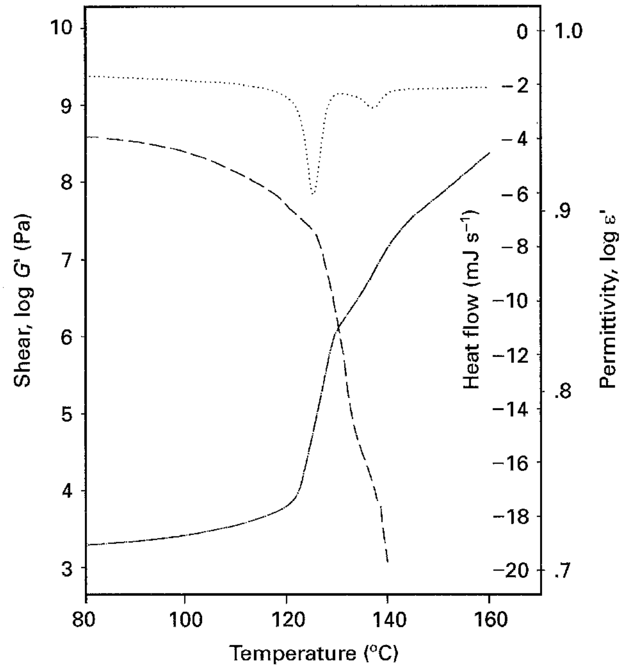

Figure 3 DMTA, DETA (measured at 1 kHz) and DSC traces for 4-OMe. Shear (– – –); permittivity (–·–·); heat flow (···).

smectic A range is too narrow to separate the E-S_A and S_A-isotropic (I) transitions.

The DSC trace for 4-OMe (see Fig. 3), contains two endotherms which were assigned as smectic C (S_C)–nematic (N) and N–I transitions. These transitions are also evident in the shear modulus and permittivity plots (see Fig. 3). The modulus is considerably lower in the nematic phase than in the smectic C phase as would be expected. The S_C–N transition is the more dielectrically active and this reflects enhanced motions in the side-chains. The shear modulus indicates a broad, weak transition with an onset at approximately 90 °C and may correspond to the glass

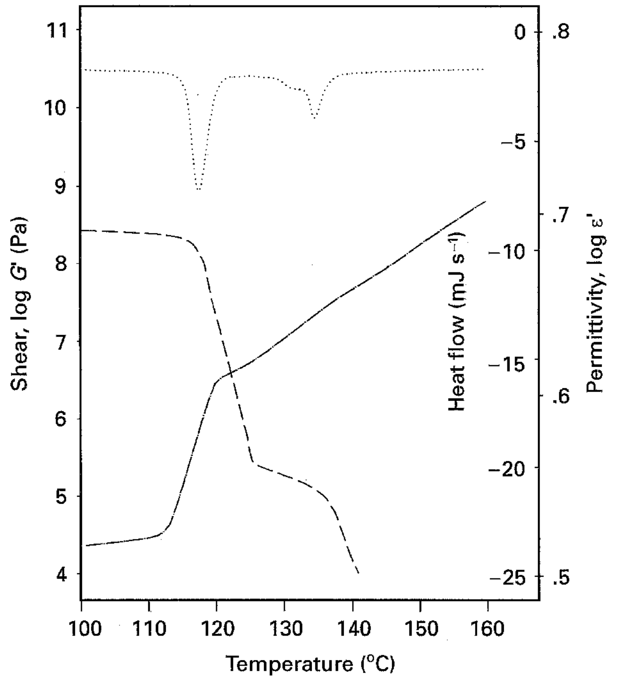

Figure 4 DMTA, DETA (measured at 1 kHz) and DSC traces for 6-OMe. Shear (– – –); permittivity (–·–·); heat flow (···).

transition. Finally, the DMTA trace contains a second broad, weak transition at ca. − 30 °C and the origin of this will be discussed later.

5-OMe, 6-OMe and 7-OMe exhibit the phase sequence glass (g)–E–S_A–I and each of these transitions is evident in the DSC trace (see Fig. 4). (The glass transition is, in fact, too weak to be observed on the scale used.) For 5-OMe, the E–S_A and S_A–I transitions are detected using both DMTA and DETA: the dielectric relaxation associated with the E–S_A transition is considerably larger than that associated with the S_A–I transition. There is an observed softening of the material prior to the E–S_A transition with an onset at ca. 130 °C. In addition, 5-OMe, 6-OMe and 7-OMe exhibit a weak transition in the range − 20 to − 30 °C. The thermal behaviour of 6-OMe is very similar to that described for 5-OMe. The clearing peak in the DSC has a reproducible shoulder (see Fig. 4), which has been interpreted by Hahn *et al.* [13] in terms of an S_A–N–I sequence. The DETA traces offer some support for this view (see Fig. 4), in which the most rapid increase in permittivity corresponds more closely to the shoulder than the clearing peak. This is in agreement with the observation for 4-OMe which revealed the S_A–N transition to be dielectrically more active than the N–I transition. Furthermore, the 6-OMe DETA traces are the only examples in which the apparent clearing transition is significantly below the DSC clearing temperature suggesting that in the DETA trace the S_A–N transition is obscuring the N–I transition. Rather surprisingly, the DMTA trace shows two transitions corresponding to the E–S_A transition while there is no evidence for the glass transition detected using DSC. Similar behaviour is observed for 7-OMe.

8-OMe, 9-OMe and 10-OMe have been tentatively assigned the same phase sequence, g-crystal B (B) or smectic B (S_B)–S_A–I, and each of these transitions

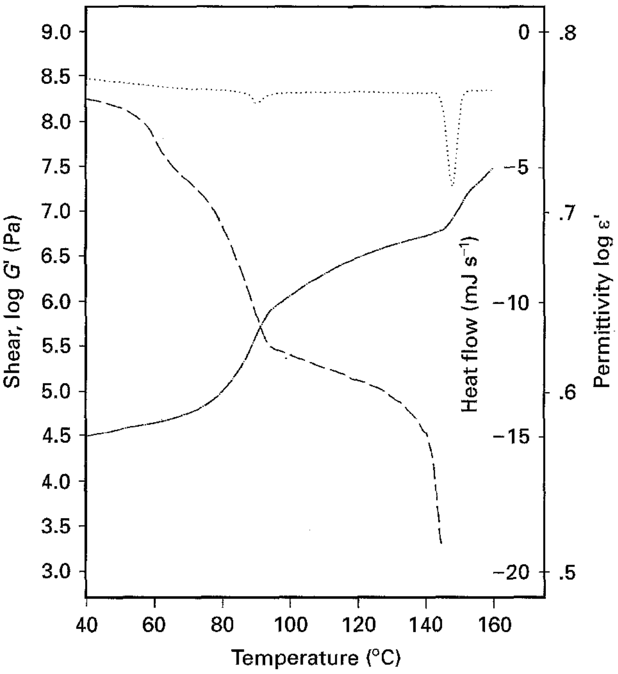

Figure 5 DMTA, DETA (measured at 1 kHz) and DSC traces for 9-OMe. Shear (– – –); permittivity (–·–·); heat flow (···).

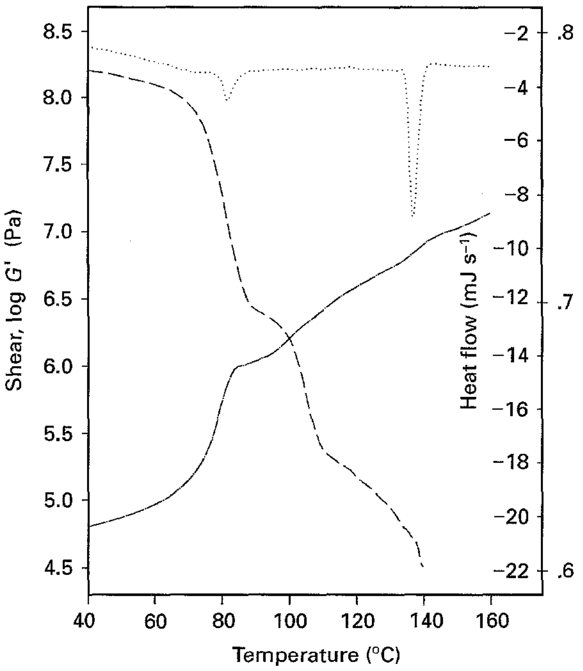

Figure 6 DMTA, DETA (measured at 1 kHz) and DSC traces for 12-OMe. Shear (– – –); permittivity (–·–·); heat flow (···).

are observed using DSC. For 8-OMe, the DETA and DMTA traces contain two transitions (see Fig. 1), corresponding to the B (S_B)–S_A and clearing temperatures. In addition, DMTA revealed a weak transition at ca. − 30 °C. The DETA traces for this polymer are unique for this series in that the clearing transition is the stronger dielectric transition. For 9-OMe, the weak subambient transition is not observed using DMTA but a mechanical transition at 65 °C is revealed (see Fig. 5). This is presumably associated with the glass transition. The thermal behaviour of 10-OMe is similar to that of 9-OMe.

11-OMe and 12-OMe have been tentatively assigned the phase sequence g–(B or S_B)–S_A–I on the basis of their DSC traces and optical textures. However, both DETA and DMTA reveal the presence of an additional transition in the S_A range (see Fig. 6). For 12-OMe the transition gives rise to a more pronounced change in the shear modulus than the permittivity while the reverse is true for 11-OMe. A focal conic fan texture in coexistence with homeotropic regions was obtained on cooling both 11-OMe and 12-OMe from the isotropic phase and no change in this was observed on further cooling to temperatures below that of the transition detected using DMTA and DETA. Thus this is not a second order S_C–S_A transition in which the directors tilt. We propose that it is a monolayer–bilayer smectic A transition although further speculation must now await the results of structural studies using X-ray diffraction. The DMTA trace for 11-OMe contains a transition corresponding to the glass transition temperature while the glass transition is not detected for 12-OMe.

DSC detected second order transitions, assigned as glass transitions, in seven members of the n-OMe series, $n = 5$–7 and 9–12. A surprising feature of the DMTA and DETA studies was the absence of data supporting these assignments for $n = 5$–7 and 12. Both techniques, in principle, exhibit enhanced sensitivity over DSC towards second order transitions although T_g would be shifted to higher temperatures. Thus a possible explanation for the absence of these transitions for $n = 5$–7 and 12 is that the temperature shift results in their overlap with the smectic–smectic transition. This would account also for the observation that for 6-OMe and 7-OMe, DMTA reveals that the smectic–smectic transition appears to have two components. Alternatively, the nature of the transition that gives rise to the change in specific heat capacity is such that the mechanical and dielectric properties of the sample are unchanged and hence, only DSC would detect the transition.

In general, and with the exception of T_g, the transition temperatures obtained using the three techniques exhibit very good agreement and this reflects the first order character of the transitions. The notable exception to this is the low temperature smectic–smectic transition observed for $n = 9$–12 for which DETA reveals a small but definite frequency dependence. This surprising result may imply that this transition is in fact two or more overlapping events.

The broad, weak transition at ca. − 30 °C observed for $n = 4$–8 may reflect the presence of a small amount of water. Poly(methyl methacrylate) on which these polymers are based absorbs up to 2% by weight water resulting in a mechanical relaxation between − 100 and 0 °C [14]. The detection of absorbed water is an important result because the presence of water has serious implications for the processing of these materials using high electric field strengths as proposed for a variety of applications [1–3]. However, the temperature associated with this transition exhibits a small odd–even effect as n is varied implying that the relaxation may involve the spacer.

4. Conclusions

The thermal characterization of the *n*-OMe series by DMTA and DETA has revealed much new information including: (i) the resolution of overlapping phase transitions in the DSC traces; (ii) the detection of a weak subambient relaxation which may correlate with the absorption of water; (iii) the unexpected detection of a smectic–smectic phase transition overlooked previously using DSC and optical microscopy. It is clear that these techniques, and in particular DMTA, have an important role to play in the characterization of SCLCPs and their use will enhance our understanding of structure-property relationships in this important class of new materials.

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