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Phase characterization of two homologous series of LC methacrylic monomers based on ω -hexyl- and ω -butyl-oxysalicylaldimine groups with different alkoxy tail substitutions

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The phase characterization of two homologous series of liquid crystalline methacrylic monomers based on ω -hexyl- and ω -butyloxysalicylaldimine groups, with different alkoxy tails, is presented. The liquid crystalline materials were characterized by polarising optical microscopy, differential scanning calorimetry, differential thermal analysis, and X-ray diffraction. All the monomers exhibit the simultaneous occurrence of smectic A and C phases. When the alkyl chain is short, a narrow nematic phase is observed, leading to an I–N–SmA–SmC phase sequence.

1. Introduction

Liquid crystals, and especially ferroelectric liquid crystal materials, have a great potential as sensors and displays, among other applications. Their advantage over other systems is related to their special physical and chemical properties [1, 2]. Their behaviour is in general attributed to the existence of an asymmetric centre. Among these ferroelectric liquid crystals are included polymeric liquid crystalline materials [3], having the potential to freeze the polar order in the glassy state. Since 1995 we have been interested in a system consisting of side chain liquid crystalline polymer–monomer mixtures [4]. A hydroxy group imparts a lateral dipole and is stabilized via hydrogen bridges that are crucial in the appearance of polarization [5]. The type of mesophase in the mixture also plays a decisive role in the observed antiferroelectric nature of samples [6]. The structure of the materials consists of a salicylaldimine group rigid core, linked to a methacrylic group via an aliphatic ‘spacer’ of usually six methylenic groups.

In a separate communication, the mesomorphic properties of some side chain liquid crystalline polymeric materials, prepared by the polymerization of monomers, has been reported [7]. Concerning the

polymer structural features, the existence of bilayered smectic C_2 phases and interdigitated smectic A_d phases was described [6, 7]. In highly concentrated mixtures of monomer in polymer, a segregation of the excess of monomer from the optimized ratio (33%) takes place [8].

The acronym used M_nR_m is in accordance with previous work [4–8], where M_n indicate the presence of a methacrylate group with four ($n = 4$, M4 series) and six ($n = 6$, M6 series) methylene units as spacer, and bonded to the aromatic phenylimine rigid core (R). This group possesses, in its *para*-position, an alkoxy flying tail (R $_m$) with m methylene units (see figure 1).

In previous communications, some detail concerning the identification of liquid crystalline phases was described. M6R6 and M6R8 display, in the smectic phase, interlayer spacings that are very close to their molecular length. This fact, together with a monotonic behaviour of the

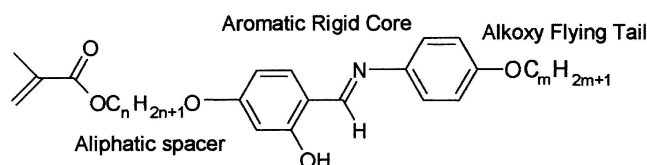


Figure 1. Structures of the investigated series: series M4, $n = 4$, $m = 4$ –12; series M6, $n = 6$, $m = 6$ –12.

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temperature dependence of the interlayer distance, led us to postulate for these samples the existence of just a smectic A layering in the whole temperature range [6]. Furthermore, a detailed description of the observed texture for M6R8 was described as a schlieren texture accompanied by sharper dark lines and a fan-shaped texture, more representative of a smectic C phase [9].

In a continuing program on the synthesis of achiral antiferroelectric polymer mixtures with high macroscopic polarization, we have synthesized two homologous series of methacrylic monomers. The detailed phase characterization of these are presented in this paper, allowing us to answer whether only the smectic A phase is present. This structural change in the aliphatic character of the lateral group in the respective side chain polymers influences the electrical behaviour of our systems. First, however, the mesomorphic character of the synthesized monomers require further clarification.

2. Experimental

The syntheses of all the monomers were carried out using a convergent synthetic pathway already described [9, 10]. The compounds investigated were characterized by $^1\text{H-NMR}$ spectroscopy using a 300 MHz spectrometer (Bruker, WM 300), elemental analysis (Perkin Elmer, 240 B), infrared spectroscopy (FTIR Paragon Spectrometer, 100PC) and HPLC-mass spectrometry (Fisons Platform). As an example, the analytical data for 4-[4-(4-pentyloxyphenyliminomethyl)-3-hydroxyphenoxy]butyl methacrylate (M4R5) are presented.

$^1\text{H-NMR}$, δ ppm, CDCl_3 : 13.95 (s, 1H, OH-Ar); 8.52 (s, 1H, -CH=N-); 7.26 (m, 3H, H-Ar-OH y H-Ar-N=C-); 6.93 (d, 2H, H-Ar); 6.43 (d, 2H, H-Ar-OH); (s, 1H, *trans* $\text{CH}_2=\text{CR}$ -); 5.58 (s, 1H, *cis* $\text{CH}_2=\text{CR}$ -); 4.25 (t, 2H, $\alpha\text{CH}_2\text{-O}$ -); 4.06 (t, 2H, $\alpha\text{CH}_2\text{-O}$ -); 4.00 (t, 2H, $\alpha\text{CH}_2\text{-O}$ -); 1.97 (t, 3H, $\text{CH}_3\text{-CR}=\text{CH}_2$); 1.92 (m, 4H, $\beta\text{CH}_2\text{-O}$ -); 1.82 (m, 2H, $\beta\text{CH}_2\text{-O}$ -); 1.45 (m, 4H, - CH_2 -); 0.96 (t, 3H, $\text{CH}_3\text{-R}$). MS (70 eV) m/z 438 (M^+ , 100%). IR data (KBr), cm^{-1} : 1700 s (ν C=O), 1628 m (ν C=N), 1287 m, 1248 m, 1185 w, 1160 w, 1138 m (ν C-O), 646 m, 583 m, 532 m, 508 w, 468 w, 436 w. $\text{C}_{26}\text{H}_{33}\text{NO}_5$; $M = 439.5$. Calc. C 71.05, H 7.53, N 3.19; found C 71.56, H 7.65, N 3.37%.

The phase transition temperatures for the investigated compounds were determined using a differential scanning calorimeter (Perkin Elmer, DSC-7) with an accuracy of ± 0.1 K, and a differential thermal analyser (Mettler, FP90 DTA), accuracy ± 0.1 K. A polarizing microscope (Leica, DLMP), equipped with a heating stage (HS-1, Instec) was used for temperature dependent investigations of liquid crystal textures. A video camera (Panasonic WVCP414P), installed on the polarizing microscope, was coupled with a video capture card (Miro DC-30),

allowing real time video capture and image saving. The samples were supported between glass plates or suspended in an aluminium plate with a 2 mm diameter hole.

X-ray measurements were carried out using CuK_α radiation. The samples were contained in 1.0 mm glass capillaries (Lindemann) and held in a copper block. Data for aligned samples in the small angle region were obtained using a focusing horizontal two-circle X-ray diffractometer (STOE, STADI 2) with a linear position-sensitive detector [11, 12]. The temperature was stabilized within the range 30 to 200°C at ± 0.5 K during the measurements.

3. Results

3.1. Texture identification

By using polarizing optical microscopy (POM) for M4R4, M4R5 and M4R6, the presence of a nematic phase on cooling from the isotropic state, in a narrow temperature range, can be seen. Figure 2(a) shows the typical schlieren texture for this phase with disclination points showing 2-brush singularities ($s = +/ - 1/2$). In the case of M4R4 and M4R5, this phase was also detected by DSC studies. M4R6 shows two poorly resolved peaks, indicative of the presence of two different phase transitions to the isotropic.

The next phase shown on cooling in free-standing films, was a homeotropic-like texture where layers of material possessing different thickness travel in a parallel fashion and converge to the centre of the hole creating different edge dislocations, see figure 2(b). Such behaviour is indicative of a low viscosity medium and therefore a less ordered smectic phase. This texture is different from the nematic phase due to the type of layer formation and the homeotropic orientation regions. This evidence is quite conclusive for the existence of a smectic A phase.

The compounds in the M4 series show another phase that also possesses low viscosity on cooling. The difference from the smectic A phase is observed in the phase transition, where the region of homeotropic orientation of the orthogonal smectic A phase becomes birefringent, forming a schlieren texture, with disclination points showing 4-brush singularities ($s = +/ - 1$), see figure 2(c). Therefore, this birefringence must be associated with a biaxial smectic C phase.

For the M6 series, as for M4R6, a narrow nematic phase was clearly seen by POM for compound M6R6 before reaching the isotropic state. For the remaining compounds in the series the simultaneous occurrence of smectic A and C phases was seen. Texture features were the same as described for the M4 series and will be not discussed.

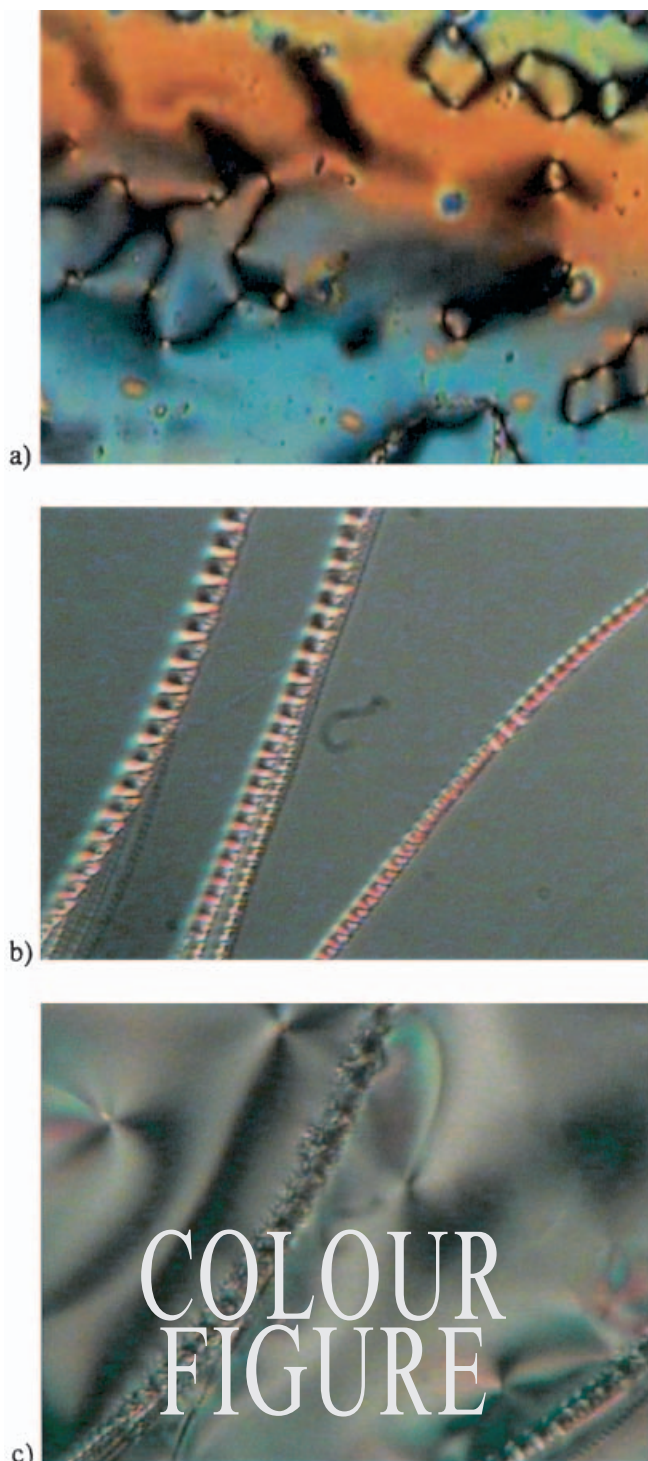


Figure 2. Observed texture: (a) nematic phase (M4R5, $T = 88.1^\circ\text{C}$); (b) smectic A phase (M4R6, $T = 72.5^\circ\text{C}$), (c) smectic C phase (M4R6, $T = 66.5^\circ\text{C}$).

3.2. Thermodynamic results

The phase transition temperatures and enthalpies obtained by DSC under cooling are summarized in table 1. The transition temperatures were confirmed by

DTA and POM. In the case of M4R4 and M4R5, the enthalpy values given correspond sequentially to the transitions Cr–SmC; SmA–N and N–I. The remaining compounds have enthalpies corresponding to Cr–SmC and SmA–I phase transitions. In both cases, the SmC–SmA enthalpy was not determined. This fact is related to the second order character observed for this phase transition, whose temperature was obtained by POM and in most of cases corroborated by DSC.

In figure 3 the corresponding phase diagrams for both series under cooling are displayed. The temperature transition to the isotropic state increases slightly as the molecular weight increases in the M4 series, with a slight disturbance because of the presence of the nematic phase for M4R4 and M4R5; in the M6 series there is almost

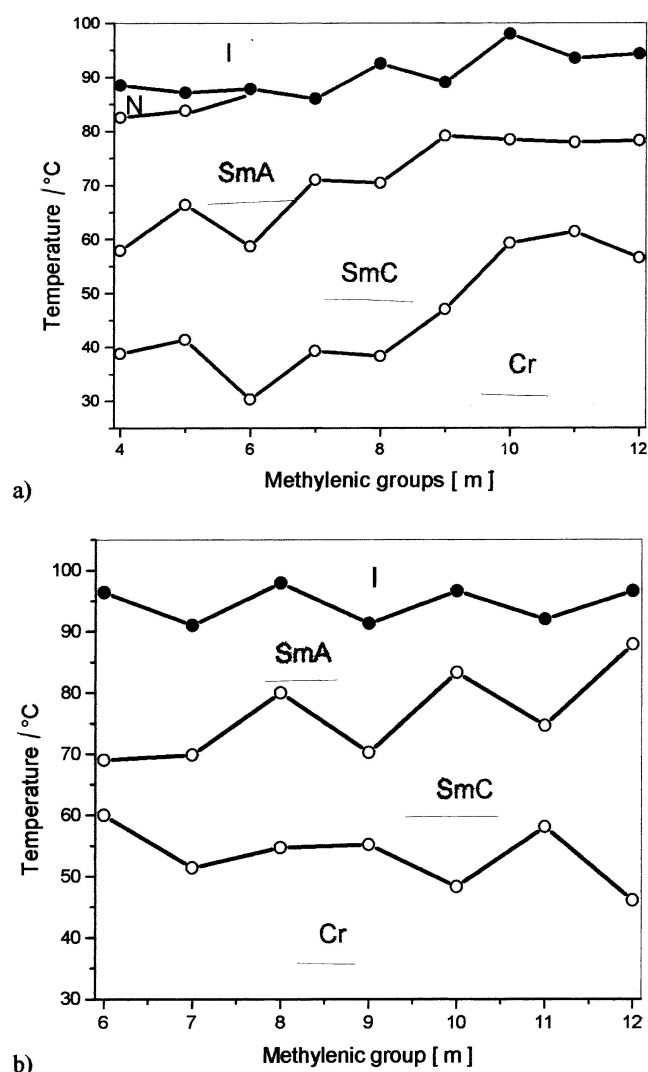


Figure 3. Phase diagram obtained under cooling. Full circles from DSC data and empty circles by polarizing microscopy: (a) series M4; (b) series M6.

Table 1. Phase transition temperature and enthalpy for the compounds under investigation.

| Compound | Mesophase | Enthalpy/kJ mol ⁻¹ (n.d. = not determined) |
|----------|------------------------------------|---|
| M4R4 | Cr–38.8–SmC–57.9–SmA–82.5–N–88.5–I | 30.25–n.d.–2.08–4.76 |
| M4R5 | Cr–41.4–SmC–66.4–SmA–83.8–N–87.1–I | 45.00–n.d.–2.50–1.54 |
| M4R6 | Cr–30.3–SmC–58.7–SmA–87.8–I | 45.66–n.d.–5.12 |
| M4R7 | Cr–39.3–SmC–71.0–SmA–86.0–I | 48.52–n.d.–6.63 |
| M4R8 | Cr–38.3–SmC–70.4–SmA–92.5–I | 50.26–n.d.–6.83 |
| M4R9 | Cr–47.0–SmC–79.1–SmA–89.0–I | 50.84–n.d.–7.03 |
| M4R10 | Cr–59.3–SmC–78.4–SmA–98.0–I | 56.09–n.d.–7.23 |
| M4R11 | Cr–61.4–SmC–77.9–SmA–93.5–I | 60.25–n.d.–6.90 |
| M4R12 | Cr–56.5–SmC–78.2–SmA–94.3–I | 59.12–n.d.–7.95 |
| M6R6 | Cr–60.0–SmC–69.0–SmA–96.4–I | 38.72–n.d.–5.53 |
| M6R7 | Cr–51.4–SmC–69.8–SmA–91.4–I | 27.72–n.d.–5.00 |
| M6R8 | Cr–54.7–SmC–80.0–SmA–97.9–I | 39.38–n.d.–5.80 |
| M6R9 | Cr–55.2–SmC–70.2–SmA–91.3–I | 29.29–n.d.–6.01 |
| M6R10 | Cr–48.3–SmC–83.3–SmA–96.6–I | 30.02–n.d.–6.82 |
| M6R11 | Cr–58.1–SmC–74.6–SmA–92.0–I | 41.99–n.d.–7.27 |
| M6R12 | Cr–46.1–SmC–87.9–SmA–96.6–I | 33.28–n.d.–7.12 |

no appreciable variation of the transition temperature (apart from the odd–even fluctuation).

The only difference between the series, beside the smooth change of transition temperature to the isotropic state in the M4 series, is the presence of a well defined nematic phase for compounds M4R4 and M4R5.

3.3. X-ray studies

X-ray studies were carried out on six representative compounds: M4R5, M4R6, M4R8, M6R6, M6R8 and M6R9. In the M4 series, the narrow temperature range nematic phase was not investigated by X-ray diffraction (XRD). For this series the diffractograms below the isotropic transition point showed sharp small angle peaks that are associated with the smectic character of the mesophases, see figure 4(a). The diffuse wide angle peaks shown in figure 4(b) for the same compounds are related to the degree of disorder within the smectic layers, showing liquid-like-in-plane order.

The molecular length L , calculated using MOPAC93 molecular approximation software, for the monomers previously studied by XRD are given in table 2. L is the distance in the stretched molecular conformation, between the last carbon atom in the aliphatic flying tail

Table 2. Calculated length of molecules L , average molecular distance in the layers D , experimental interlayer distance d and tilt angle θ in the smectic C phase at the indicated temperature.

| Monomer | $L/\text{Å}$ | $D/\text{Å}$ | $d/\text{Å}$ | $\theta/^\circ$ | Temp/ $^\circ\text{C}$ |
|---------|--------------|--------------|--------------|-----------------|------------------------|
| M4R5 | 28.92 | 4.38 | 27.08 | 20.55 | 30.1 |
| M4R6 | 30.15 | 4.36 | 28.95 | 16.22 | 30.5 |
| M4R8 | 32.65 | 4.37 | 32.37 | 7.51 | 40.0 |
| M6R7 | 33.71 | 4.32 | 31.22 | 22.16 | 64.8 |
| M6R8 | 34.89 | 4.35 | 34.06 | 12.53 | 55.5 |

and the first ethylenic carbon atom of the methacrylic group. In this table the average molecular distance in the layers D , the experimental interlayer distance d and tilt angle θ of the mesophases at the indicated temperature are also included. In table 2, the reported values were estimated at the smectic C phase transition temperature. In case of M4R5, at 30.1 $^\circ\text{C}$, a supercooled structure of the smectic C phase inside the capillary where the measurements were carried out, was formed.

The temperature dependence of the experimental interlayer distance d for some of the monomers studied, are displayed in figure 5. The temperature variation of the first order reflux shows the existence of two different regions in the mesophase. The observed isotropic to smectic A change in the case of the M4 series correlates reasonably well with the transition temperatures obtained by DSC and DTA. For M6R8, belonging to the M6 series, a similar behaviour is observed. The behaviour of the observed d -values in the liquid crystalline phase for the monomers studied reflects the existence of monolayer structures.

4. Discussion

For both series of monomers the existence of layered mesophases has been observed. The SmA–SmC phase transition, with a corresponding wide transition enthalpy, was difficult to recognize using DSC; see, for example, figure 6, for compound M4R5. To clarify the situation, investigations by POM were carried out. The SmA to SmC phase transition was indicated by the formation of focal-conic textures (not shown here), observed between glass plates as a smooth visual transition to black stripes. This can be interpreted as the change from a homeotropic layering order to tilted layers that cause birefringent zones in the freely suspended film observations; see, for example, figures 2(b) and 2(c) for M4R5.

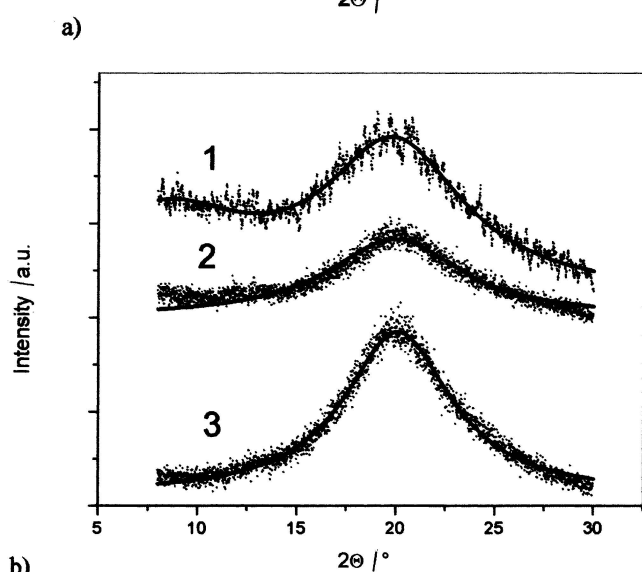
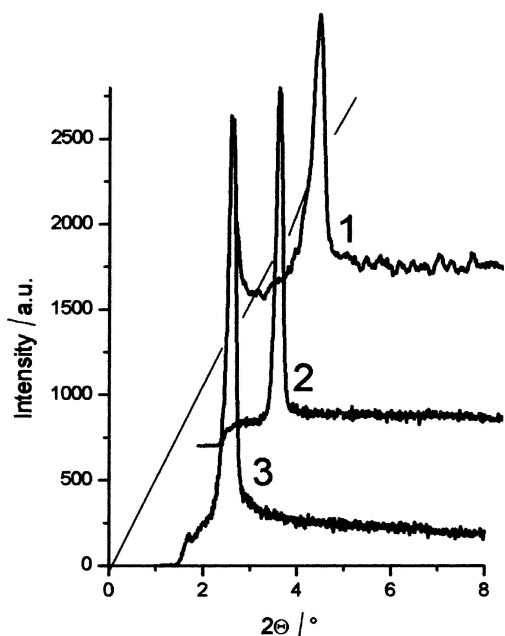


Figure 4. (a) X-ray diffraction pattern in the small angle scattering region at 80°C: (1) M4R5, (2) M4R6, (3) M4R8 in the smectic A phase; (b) diffuse wide angle halos. The solid lines correspond to the Lorentzian fit of the data.

From the structural point of view, XRD measurements were carried out in order to clarify the identification of the phases described. Figure 4(a) shows the small angle region at different temperatures for compounds of the M4 series (i.e. M4R5, M4R6 and M4R8). Only the first Bragg peak is observed, whose position is in good agreement with a monolayer structure. On cooling, there is a decrease in the interlayer distances beginning at a certain temperature for each monomer, related to the SmA–SmC phase transition; (see, for example, M4R5, M4R6 and M6R8, figure 5). This decrease on cooling

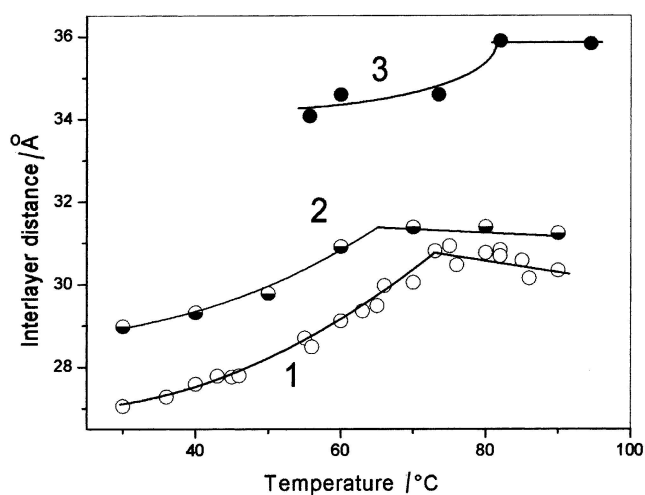


Figure 5. Temperature dependence of the interlayer distance under cooling: (1) M4R5, (2) M4R6, (3) M6R8.

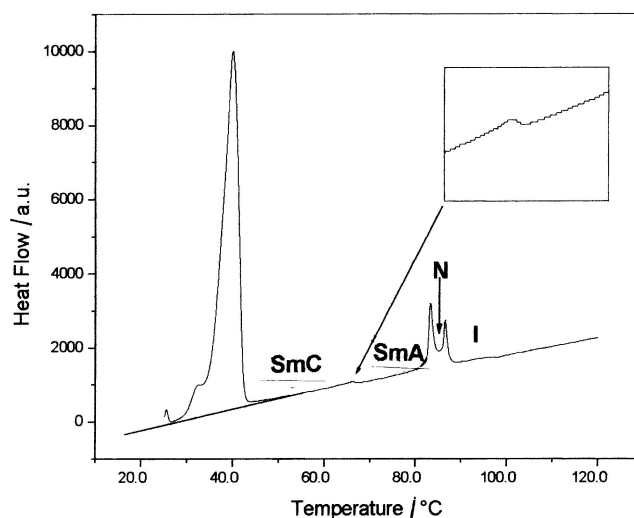


Figure 6. DSC trace for M4R5 at a heating rate of 10°C min⁻¹.

can be interpreted as due to the increase of the tilt angle θ within the layer, indicative of the existence of a SmC-type phase. Taking the interlayer distance and the full-length of the molecule (L values in table 2), we can calculate the tilt angle $\theta = \arccos(d/L)$. Table 2 summarizes this information for the investigated monomers at different temperatures within the smectic C phase. The increase of the interlayer distance from 27 Å for M4R5 to 32 Å for M4R8, at a fixed temperature of 75°C within the SmA phase, is attributed to the increase in the length of the molecules.

It would be expected, in a normal SmA phase of a low molar mass compound, to see a layered structure with a periodicity d slightly less than the molecular length L . In our case, the opposite occurs; that is, if we compare the data for L in table 2 with the experimental d values in figure 5 for the same compounds, it can be

seen that these values are actually larger than the calculated values. This can be attributed to molecular repulsion forces between the highly polar methacrylate group at the head of one molecule against the alkoxy flying tail (see figure 1) of another. This produces a shift of these groups outside the layers, thus increasing the experimental periodicity d . The dimension of whole polar group is approximately 4.5 Å, which should be the expected experimental variation in the d -value. But because of the averaged compression effect due to imperfections in both the molecular orientational order and the conformational disorder, this value is reduced to approximately 1.6 Å.

An interesting trend is also observed in the temperatures of transition to the isotropic state. This tendency, called 'even-odd' effect, is characterized by a linear plot in the clearing point trend of the monomer when m is odd or when m is even. In our case this tendency is also observed in the SmA to SmC phase transition observed by POM.

For all the compounds under study, the clearing point temperatures are more or less in the same range. The slight increase in the isotropic phase transition temperature for the M6 series (85–98°C) relative to the M4 one (92–98°C) is attributed to their higher molecular weight. This effect is diminished due to the different flexibility related to the longer aliphatic groups in the M6 spacer.

5. Conclusion

By the use of POM and XRD, it was possible to determine the existence of disordered lamellar phases confirming a monolayer structure for all the compounds of series M4 and M6. Short chain monomers also present a nematic phase before the isotropic state; this was not investigated by XRD. The nematic phase is clearly observed by DSC and M4R4 and M4R5. In case of M4R6 monomer, it was detected only by POM in a narrow temperature range at the phase transition to the isotropic.

An even-odd effect related to the alkoxy substitution length was observed in both series for the phase transition to the isotropic. In the case of short monomers belonging to the M4 series it was smoothly disrupted

by the presence of the nematic phase. This effect was also visible for both series in the phase transition from SmA to SmC under POM.

The slight increase in the interlayer periodicity relative to calculated values may be due to molecular repulsion forces between the highly polar methacrylate group and the aliphatic alkoxy group in neighbouring molecules.

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