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Liquid Crystals

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Liquid-crystalline properties of chiral malolactonate monomers and their comb-shaped polymers

by KOICHI FUJISHIRO† and ROBERT W. LENZ*

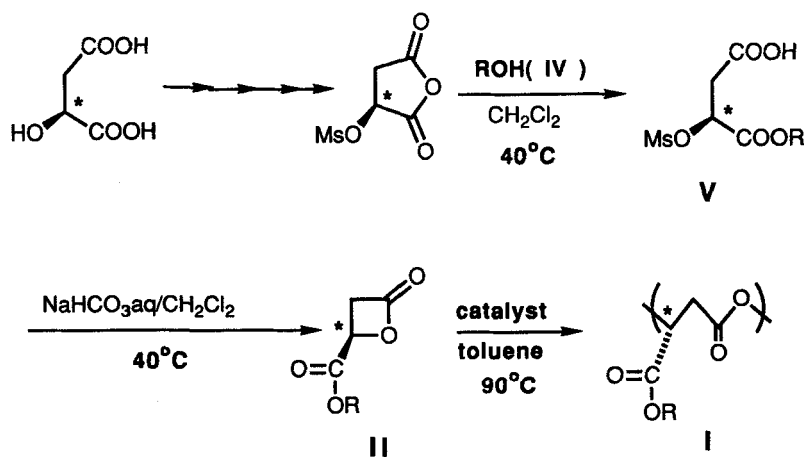
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A series of optically pure mesogenic ester precursors, and the malolactonate monomers containing mesogenic alcohols obtained from them were prepared and polymerized to homopolymers and copolymers. The liquid-crystalline properties of the precursors, monomers and polymers were investigated by differential scanning calorimetry, polarized light microscopy and wide angle X-ray diffraction. The liquid-crystalline properties of the chiral mesogenic precursors and monomers were only slightly influenced by the chemical structure, configuration and the alkyl spacer length of the mesogenic alcohol substituent of the ester. The precursor, 1-[6-(4'-hexyloxy-4-biphenyl)oxyhexyl] hydrogen (*S*)-*O*-mesylmalate (**V**-(*S*)-6) formed smectic E and smectic A phases on melting, while the monomer, 6-(4'-hexyloxy-4-biphenyl)oxyhexyl (*R*)-malolactonate (**II**-(*R*)-6) showed only a crystal-isotropic phase transition. In contrast, the homopolymer of the latter exhibited a chiral smectic C phase. Copolymers from 2-(4'-hexyloxy-4-biphenyl)oxyethyl (*R*)-malolactonate (**II**-(*R*)-2) also formed chiral smectic C phases.

1. Introduction

A previous report from this laboratory described the synthesis of a new structural type of chiral side chain liquid-crystalline polymers, **I**, by the ring opening polymerization reactions of optically active malolactonate monomers, **II**, which contained

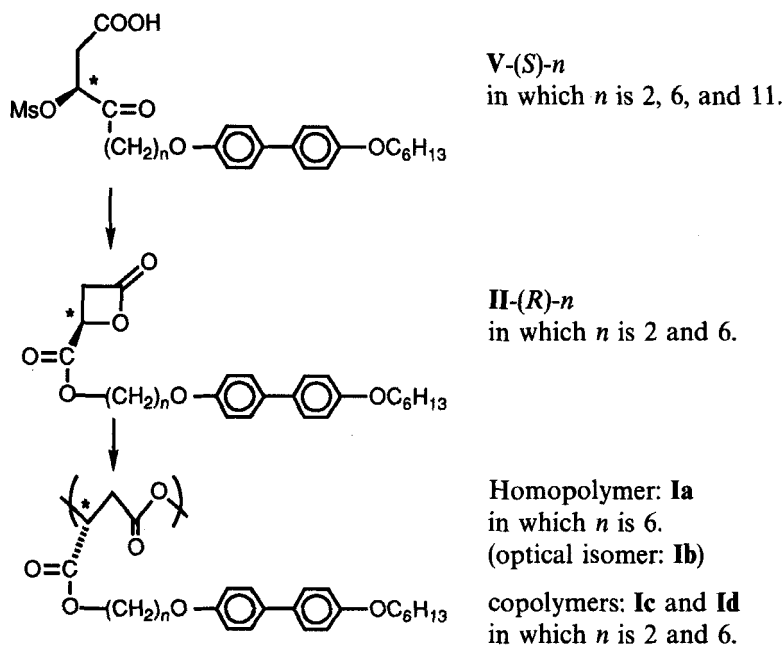


Scheme 1.

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mesogenic units as shown in scheme 1 in which R is a mesogenic group with an alkyl spacer, and Ms is $-\text{OSO}_2\text{CH}_3$ [1]. These polymers, **I**, have chiral centres in their backbones and mesogenic groups linked to the chiral centres through spacers. This structural type of chiral liquid-crystalline polymers should exhibit a large spontaneous polarization if it forms a chiral smectic C (S_C^*) phase [2–4]. In scheme 2, several new chiral mesogenic precursor compounds, V -(S)- n , monomers, **II**-(R)- n , homopolymers, **Ia** and **Ib**, and two copolymers with different spacer lengths, **Ic** and **Id**, were prepared and characterized for their liquid-crystalline properties.



Scheme 2.

The liquid-crystalline phases formed by these mesogenic precursors, monomers and their polymers were found to vary considerably depending on the chemical structure, alkyl spacer length (n) in the alcohol substituent and the configuration (R or S) in the polymer main chain.

2. Experimental

All mesogenic precursor compounds, monomers and polymers were prepared and characterized for specific rotations, optical purities and molecular weights as previously described [1]. In this paper, thermal transitions and crystalline and liquid-crystalline morphologies of these compounds were characterized by differential scanning calorimetry (DSC), polarized light microscopy and wide angle X-ray diffraction. Thermal analyses of the compounds were obtained on a Perkin-Elmer DSC-2 at a scanning rate of $20^\circ\text{C min}^{-1}$. The peak maxima of the phase transitions were recorded from the second heating and cooling scans for each sample. All samples were scanned 5 to 10 times on the DSC instrument to determine their thermal stabilities. Liquid-crystalline textures were observed with a Leitz Ortholus optical microscope equipped with a Metler FP2 hot stage. Wide angle X-ray diffraction patterns of **V** and Polymer **I** were obtained with a Laue camera using Ni filtered Cu

radiation on unoriented samples in glass capillaries with a hot stage at different temperatures on the second heating cycle, after annealing for 30 min and 2 h for **V** and polymer **I**, respectively, at the measured temperatures.

3. Results and discussion

The second heating cycles of the DSC thermograms of a series of mesogenic compounds having a hexamethylene spacer, which were prepared from (*S*)-malic acid, are shown in figure 1. Only a single endothermic peak was present in the second heating cycle thermogram, as shown in figure 1(a), for the mesogenic alcohol, 4-(6-hydroxyhexyloxy)-4'-hexyloxybiphenyl (**IV-6**), and this transition was observed by polarized light microscopy to be a crystal-isotropic transition. However, the thermogram of the ester of this alcohol, 1-[6-(4'-hexyloxy-4-biphenyl)oxyhexyl] hydrogen (*S*)-*O*-mesylmalate (**V-(S)-6**) contained three endotherms in the second heating cycle as shown in figure 1(b) and it appears from polarized light microscopy that **V-(S)-6** formed at least two different types of liquid-crystalline phases. After lactonization of **V-(S)-6**, the monomer, 6-(4'-hexyloxy-4-biphenyl)oxyhexyl (*R*)-malolactonate, **II-(R)-6**, exhibited only one endotherm in the second heating cycle, as seen in figure 1(c). In contrast, the thermogram of homopolymer, **Ia**, obtained from monomer, **II-(R)-6**, contained both a small and a broad endotherm at 98°C and 157°C, respectively, in the heating cycle.

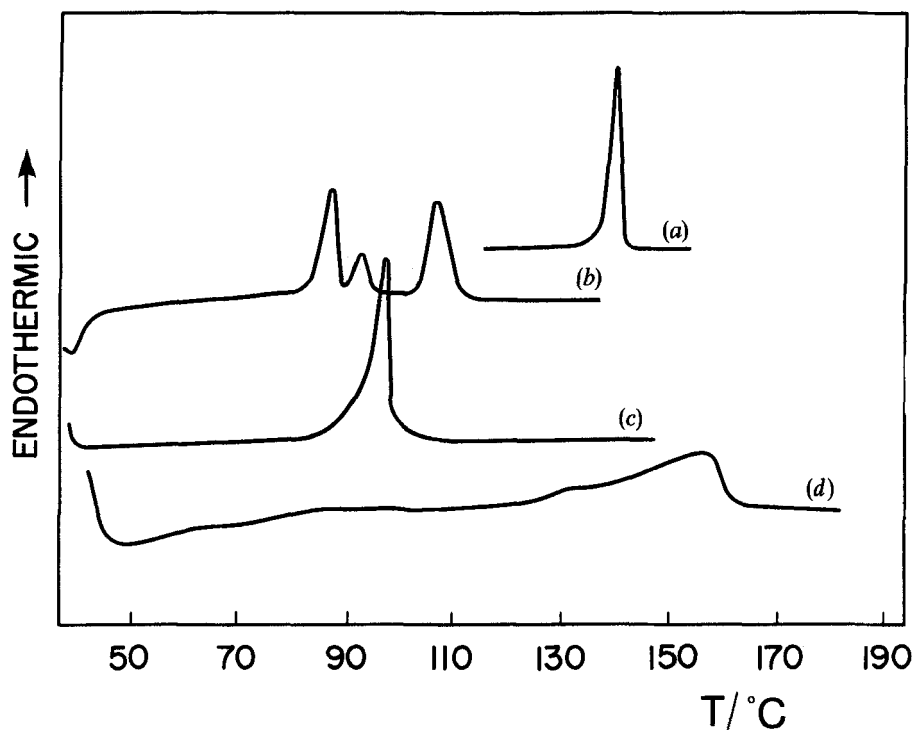


Figure 1. DSC thermograms for the second heating cycles of a series of chiral precursor compounds having hexamethylene spacers: (a) **IV-6** (4.0 mg), (b) **V-(S)-6** (9.2 mg), (c) **II-(R)-6** (4.3 mg), (d) polymer **Ia** (11.2 mg).

In this series of mesogenic compounds, the phase behaviours varied extraordinarily with the functional groups located at the terminal position of the alkyl chain. These phase behaviours were also influenced by the length of the alkyl spacer, n , and by the configuration of the compound. More detailed results and the identification of liquid-crystalline phases formed are discussed later.

3.1. Phase behaviour of monoesters V

The DSC thermograms of V-(S)-6 in the second heating (a) and cooling (b) cycles are shown in figure 2. Both thermograms contained three peaks, and both did not change over ten successive DSC scans. The appearance of this compound was observed on a hot stage of a polarizing microscope. The sample observed formed a viscous fluid above the first endothermic peak temperature, T_m , and the texture of the crystalline state changed into that of a homeotropic texture. When the sample was sheared in the homeotropic state, disclination lines appeared, but the sample did not show any colours. At the second endotherm in figure 2(a), the melt viscosity decreased, but the texture was still homeotropic, although the disclination lines in the texture became coloured and contained retardation lines. After the last endotherm, the sample became black in appearance and very fluid. These observations revealed that the first endotherm was a melting transition, T_m , and the last one was an isotropization transition, T_i .

In order to identify the types of liquid-crystalline phases formed, the textures of the homogeneously aligned sample on a polarized light microscope were observed, and

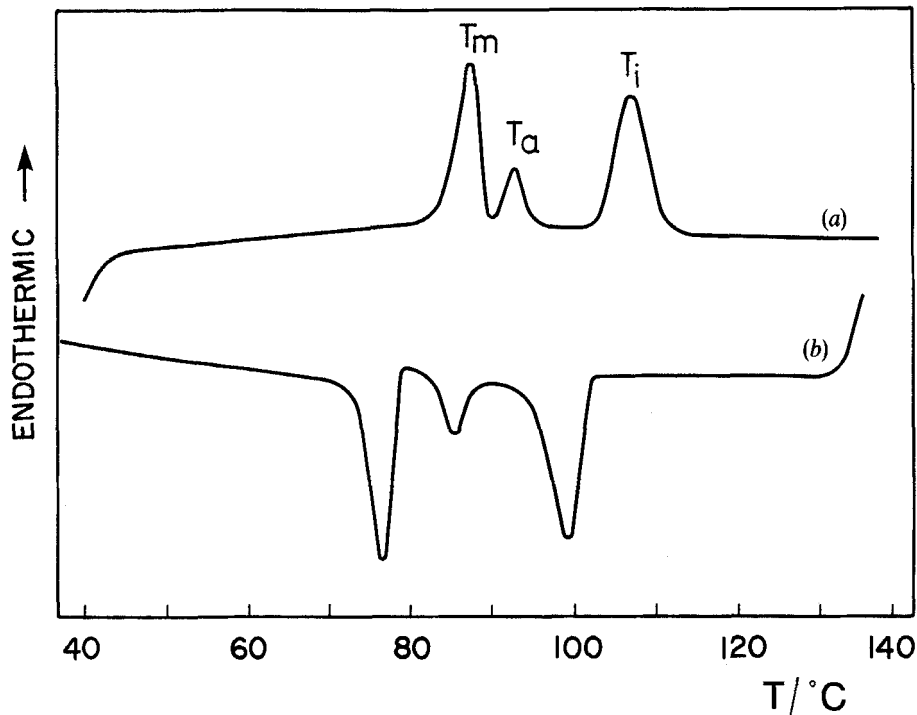


Figure 2. DSC thermograms of V-(S)-6 (9.2 mg): (a) second heating cycle, (b) second cooling cycle.

wide angle X-ray diffraction patterns were taken for each phase of V-(S)-6. The sample was put between rubbed polyimide films coated on glass plates to align the sample in a homogeneous state. Microphotographs of the textures observed in the second cooling cycle from the isotropic state are shown in figure 3. Firstly, a fan-shaped texture was observed below T_i as seen in figure 3 (a), after which the striations appeared in the fans below T_a as shown in figure 3 (b). In the X-ray patterns, the crystalline state contained many sharp rings and one diffuse ring as shown in figure 4 (a), while the pattern for the lower temperature liquid-crystalline state showed three sharp inner rings and three sharp outer rings, as seen in figure 4 (b). Two of the inner rings at 38.5 Å and 19.5 Å corresponded to the first and the second diffraction lines expected for a smectic layer structure, respectively. The inner ring at 16.7 Å presumably came from the coexistent crystalline phase because of heterogeneity of the temperature in the sample. From the presence of a strong outer ring at 4.41 Å and two weak outer rings equivalent to 4.66 Å and 4.07 Å, a high order smectic phase was deduced. In contrast, above T_a , the diffraction pattern contained two sharp inner rings and a diffuse outer ring. The inner rings equivalent to 38.5 Å and 19.3 Å corresponded to the first and second order spacings of a smectic layer structure. The results from microscopy observations and from wide angle X-ray diffraction patterns revealed that V-(S)-6 formed a smectic E phase between T_m and T_a , and a smectic A phase between T_a and T_i [5–7].

The opposite optical isomer, V-(R)-6, was also prepared and characterized by the same methods. The thermal transitions and thermodynamic data obtained are collected in table 1 for a comparison of the isomers. V-(R)-6 exhibited the similar phase transitions and textures to V-(S)-6, but the former had slightly higher transition temperatures than the latter.

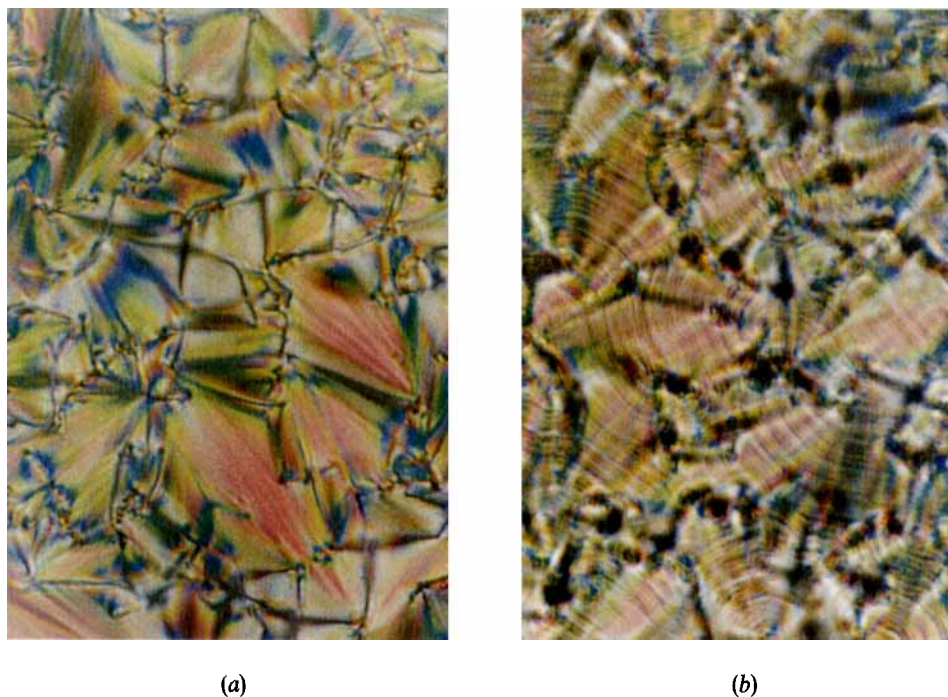


Figure 3. Photomicrographs of textures for V-(S)-6 in the homogeneously aligned state at: (a) 105°C, (b) 90°C in the second cooling cycle.

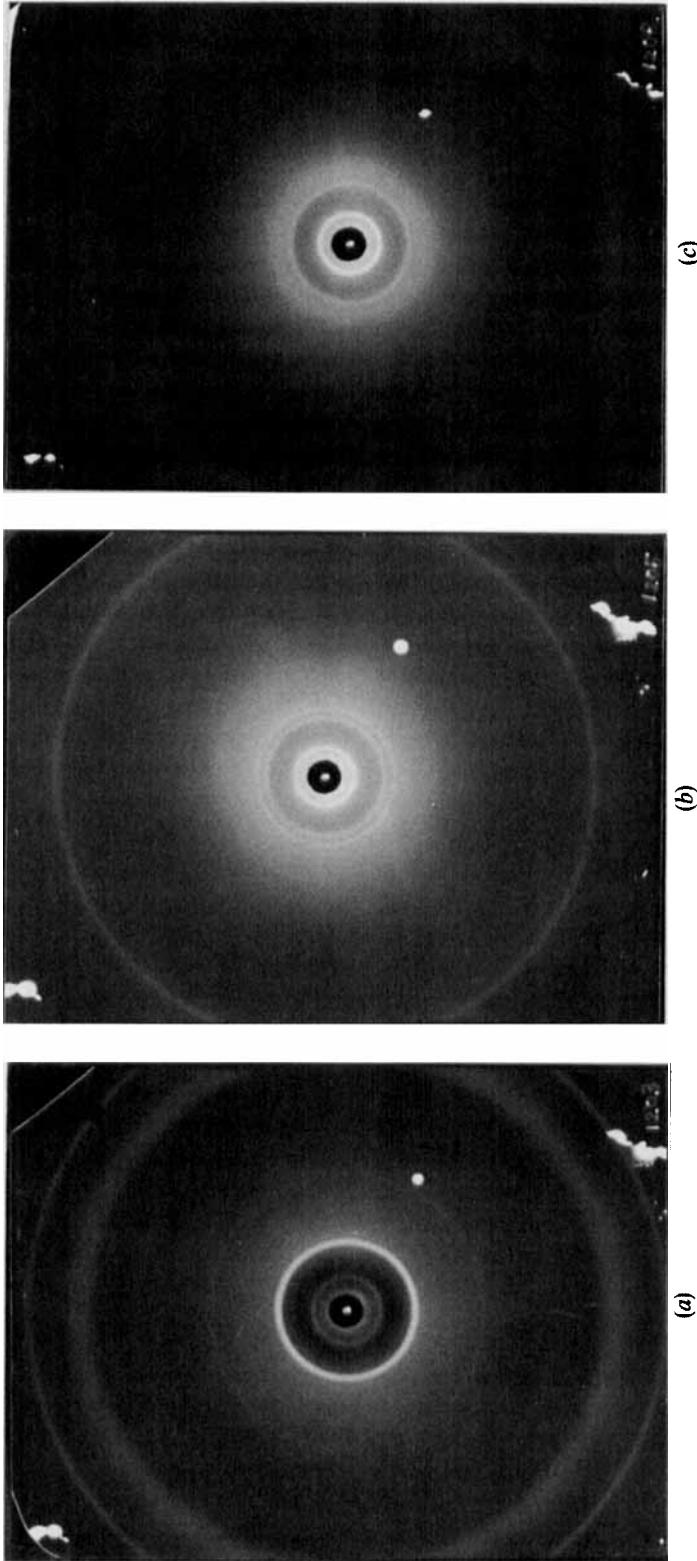


Figure 4. Wide angle X-ray diffraction patterns for V-(S)-6 at: (a) 50°C, (b) 90°C, (c) 100°C on the second heating cycle.

Table 1. Thermal transitions and enthalpies for optical isomers, V-(S)-6 and V-(R)-6†.

Precursor compound	$T_m/^\circ\text{C}$	$T_a/^\circ\text{C}$	$T_i/^\circ\text{C}$	$\Delta H_m/\text{kJ mol}^{-1}$	$\Delta H_a/\text{kJ mol}^{-1}$	$\Delta H_i/\text{kJ mol}^{-1}$
V-(S)-6	87	93	107	6.3	2.6	8.8
V-(R)-6	89	97	111	7.1	2.9	8.8

† All data were taken from the DSC thermogram in the second heating cycle.

The phase transitions in this series of compounds were also influenced by the alkyl spacer length, n . The DSC thermograms of 1-[2-(4'-hexyloxy-4-biphenyl)oxyethyl] hydrogen (S)-O-mesylmalate, V-(S)-2, in the first cooling and second heating cycles are shown in figure 5. Three exotherms were observed in the first cooling cycle thermogram, while a broad endotherm and an exotherm are seen in the second heating cycle thermogram. These thermograms indicate that different phase behaviours occurred in the heating and cooling cycles. Polarizing light microscopy observations of the sample placed between polyimide films in the first cooling cycle revealed that battonets appeared in the isotropic liquid and a fan-shaped texture was formed as shown in figure 6(a). On further cooling, striations appeared in the fans, as seen in figure 6(b), then changed to a paramorphic texture, as shown in figure 6(c). In the second heating cycle, the texture which was formed at room temperature after the first cooling scan changed to a black appearance at 130°C. Unfortunately, wide angle X-ray

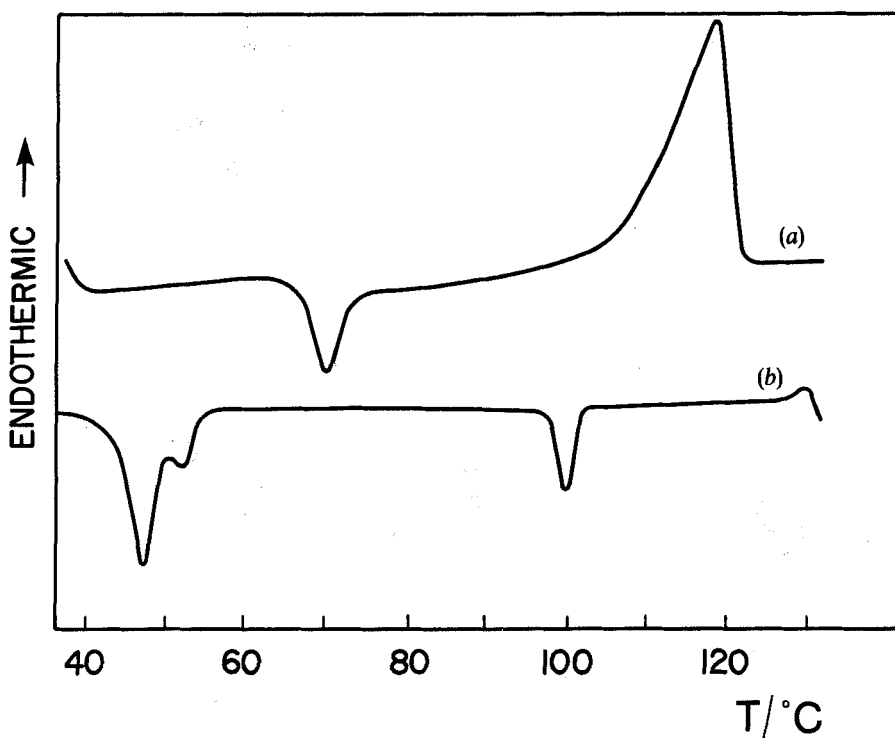
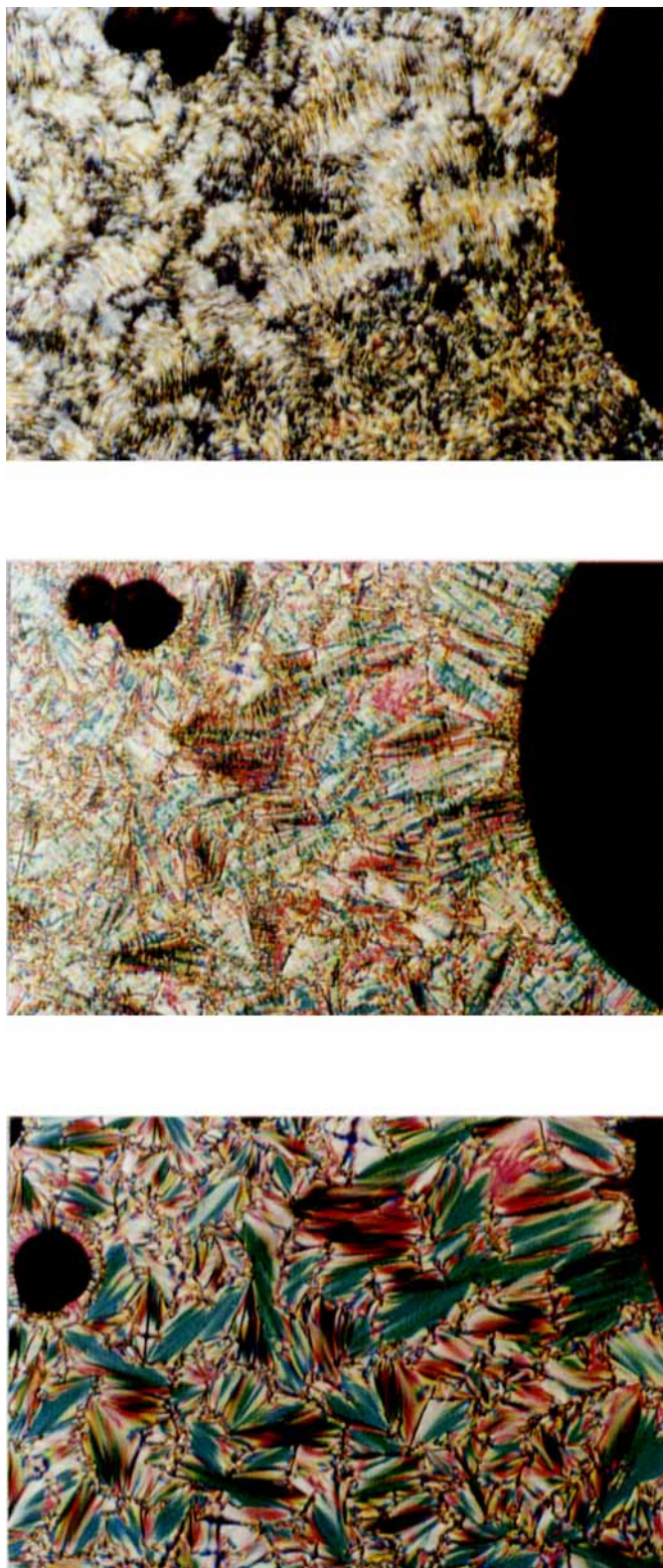


Figure 5. DSC thermograms for V-(S)-2 (4.8 mg): (a) second heating cycle, (b) the first cooling cycle.



(a)

(b)

(c)

Figure 6. Photomicrographs for V-(S)-2 in the first cooling at: (a) 102°C, (b) 73°C, (c) 53°C.

diffraction patterns could not be obtained because of decomposition, which was observed in the DSC thermograms and which gradually increased during several scans. From these results, however, it can be concluded that V-(S)-2 was a monotropic liquid crystal, which showed only a crystal-isotropic transition in the heating cycle and two different liquid-crystalline phases in the cooling cycle, although it was not thermally stable. The liquid-crystalline phases observed in the cooling cycle were presumably a smectic A and smectic E because both textures were very similar to those of V-(S)-6, respectively. In contrast, the monoester with a dodecamethylene spacer, V-(S)-11, decomposed at 130°C after just the first melting.

3.2. Phase behaviour of monomers II

The optically pure malolactonates with a hexamethylene spacer, II-(R)-6, II-(S)-6, and an ethylene spacer, II-(R)-2, II-(S)-2, were prepared, but the malolactonate with a dodecamethylene spacer was not obtained as described before [1]. All malolactonate monomers had only crystal-isotropic phase transitions on both the cooling and heating cycles, as shown in figure 7 for II-(R)-6. The monomers having an ethylene spacer, II-(R)-2 and II-(S)-2, decomposed at their melting temperatures, 117–120°C, during DSC measurements, and no liquid-crystalline properties were observed.

3.3. Phase behaviour of polymers

The DSC thermograms of polymer Ia, which was obtained from II-(R)-6 with an isobutylaluminumoxane catalyst, are shown in figure 8. Two clear endotherms were

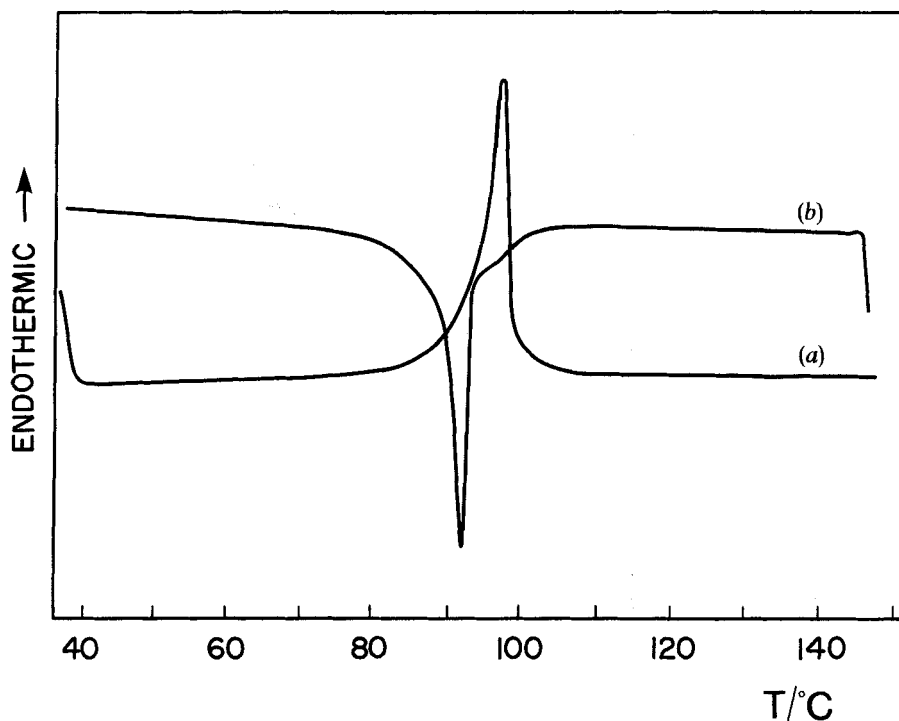


Figure 7. DSC thermograms for II-(R)-6 (4.3 mg): (a) second heating cycle, (b) second cooling cycle.

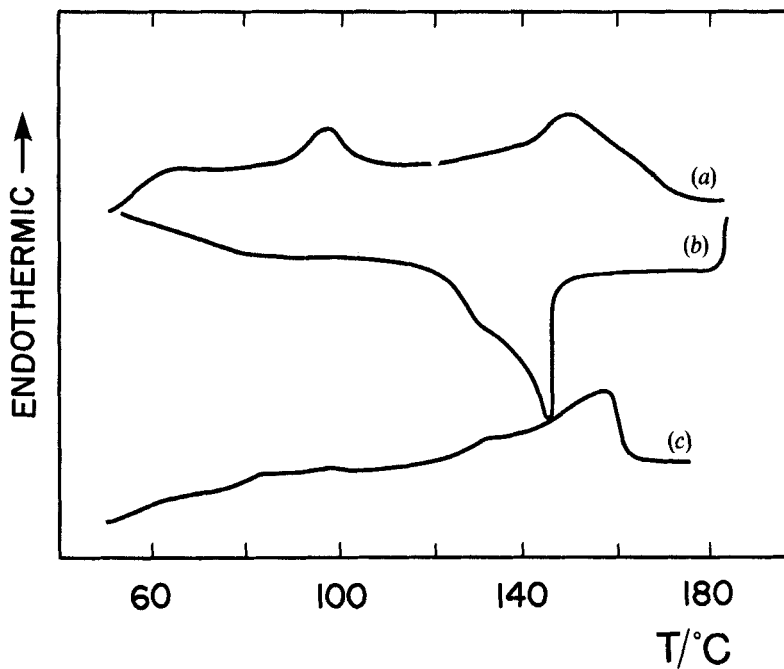


Figure 8. DSC thermograms for polymer Ia (11.2 mg): (a) first heating cycle, (b) first cooling cycle, (c) second heating cycle.

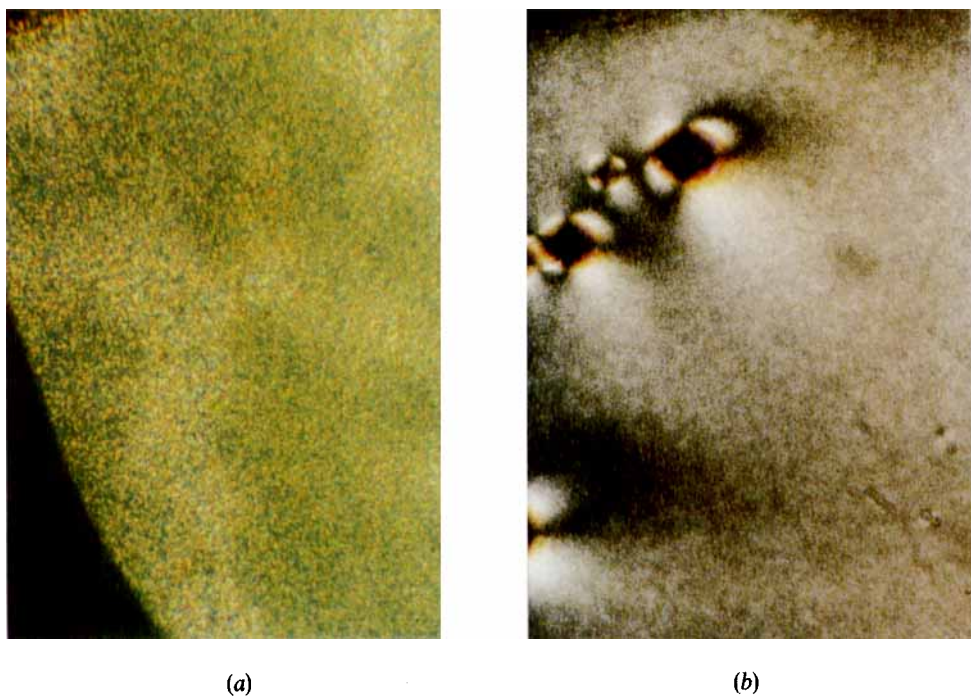


Figure 9. Photomicrographs of polymer Ia at 144°C in the second heating cycle: (a) sample placed between non-treated glass plates, (b) sample placed between glass plates coated with hexadecyltrimethylammonium bromide.

observed at 101°C and 147°C in the first heating cycle in figure 8 (a), but only a broad exotherm was observed at 140°C in the first cooling cycle, as shown in figure 8 (b). In the second heating cycle thermogram, shown in figure 8 (c), the first endotherm at 98°C became very small, and the second endotherm shifted to 157°C with an additional shoulder at 130°C. Observations with a polarizing microscope revealed that the polymer melted at the first endotherm, T_m , to form a viscous anisotropic liquid, and isotropization occurred above the second endotherm, T_i . A schlieren texture was observed below T_i , as seen in figure 9 (a), and no change in the texture occurred, as it was then quickly frozen below T_m . When the sample was put between two glass plates on which hexadecyltrimethylammonium bromide was coated and annealed at 144°C after cooling from the isotropic state, the texture was composed of very fine fingerprints as seen in figure 9 (b).

The wide angle X-ray diffraction pattern of this polymer taken at 144°C, is shown in figure 10; it contains two sharp inner rings equivalent to 59.6 Å and 19.7 Å spacings and a weak broad halo close to 4.6 Å. The two sharp rings probably corresponded to the first order and the third order spacings of smectic layers. From these results, it can be concluded that the polymer presumably formed a chiral smectic C phase. Assuming that the hexamethylene spacers and the *n*-hexyl tails in the side chains are fully extended in their *trans* conformations, the distance from the backbone and the methyl group in the side chain calculated from a computer drawn model of polymer **Ia** was approximately 32 Å. By comparing this calculation with the 59.6 Å spacing observed in the wide angle X-ray diffraction pattern, it can be concluded that the macromolecular chains formed a bilayer structure, in which the side chains were tilted at an angle of 20° to the layers without overlap of terminal alkyl groups between the different chains.

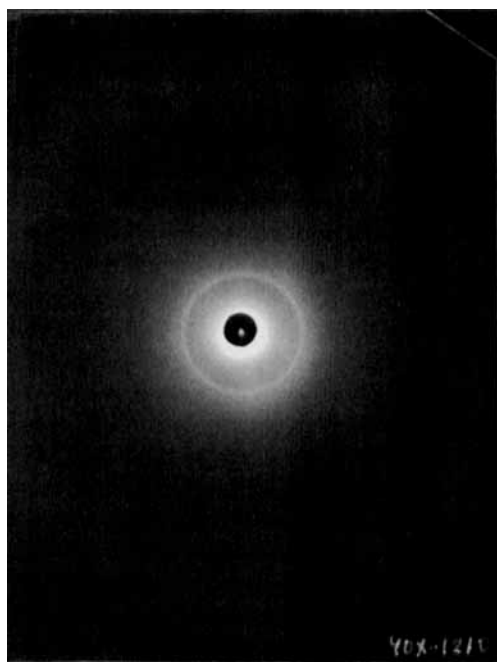


Figure 10. Wide angle X-ray diffraction pattern for polymer **Ia** at 144°C.

Table 2. Transition temperatures† and wide angle X-ray diffraction results for homopolymers and copolymers.

Polymer	Composition‡		$T_m/^\circ\text{C}$	$T_i/^\circ\text{C}$	$d/\text{\AA}\S$
	x	y			
Ia	100	0	98	157	59.6, 19.7 (at 144°C)
Ib	100¶	0	96	168	—¶
Ic	75	25	106	148	54.2, 27.0, 18.3 (at 140°C)
Id	25	75	115	155	51.6, 17.7 (at 140°C)

† Recorded as the peak maxima of the second heating cycle thermograms.

‡ Determined by ^1H NMR spectra for the polymers; x = content of **II-(R)-6**; y = content of **II-(R)-2**.

§ Sharp spacings of the inner rings are listed.

¶ Polymer **Ib** was prepared from monomer **II-(S)-6**.

¶¶ Wide angle X-ray diffraction data was not obtained.

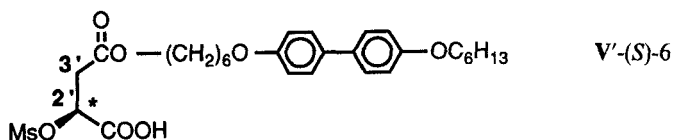
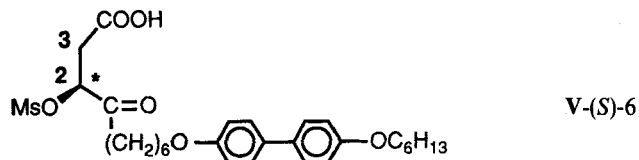
The opposite optical isomer of this polymer, polymer **Ib**, was also prepared from **II-(S)-6** and characterized with the results given in table 2. The thermodynamic behaviour of this polymer was essentially the same, but the isotropization transition appeared at a higher temperature than for polymer **Ia**. Two copolymers, **Ic** and **Id** were prepared from **II-(R)-6** and **II-(R)-2** and characterized with the results given in table 2. The melting transitions, T_m , slightly increased with increasing content of the mesogenic moiety containing the ethylene spacer (y), while the isotropization transition, T_i , changed by 10°C. The same textures as those in figure 9 were observed for samples on a polarizing microscope, and sharp inner rings were recorded in their wide angle X-ray diffraction patterns indicating that both copolymers also formed chiral smectic C phases. The separation distances of the smectic layers slightly decreased with increasing contents of **II-(R)-2** as shown in table 2.

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- [7] This liquid-crystalline behaviour was probably influenced by the isomer, *V'*-(*S*)-6, which was formed by the reaction of the mesogenic alcohol (IV) and the anhydride. The isomer was detected by ^{13}C NMR spectroscopy, but the content of the isomer, *V'*-(*S*)-6, in the product was estimated to be very low because of the ratios of the integration values, which were not exactly equal to the contents, corresponding to the following carbon signals in the ^{13}C NMR spectrum (100 MHz, in CDCl_3):



V-(*S*)-6: $\text{CH}_2(3)$ 36.5 ppm, $\text{CH}^*(2)$ 73.5 ppm, *V'*-(*S*)-6: $\text{CH}_2(3')$ 36.7 ppm, $\text{CH}^*(2')$ 73.3. The ratios of the integrated values; $\text{CH}_2(3)/\text{CH}_2(3')=99/1$, $\text{CH}^*(2)/\text{CH}^*(2')=98/2$.

In addition, the sharp phase transitions also implied the low content of *V'*-(*S*)-6. Therefore, *V'*-(*S*)-6 contained in the product presumably did not influence the formation of the smectic phases, though it changed the transition temperatures a little.