# Suppression of side chain crystallization and transformation of monotropic mesophases into enantiotropic mesophases by copolymerization of the parent polymers' monomer pairs containing constitutional isomeric mesogenic side groups

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The synthesis and characterization of several copolymers based on the monomer pairs of 11-[4-methoxy-(4′-oxy)-α-methylstilbene]undecanyl methacrylate (4-11-MA) and 11-[4-oxy-4′-methoxy)-α-methylstilbene]undecanyl methacrylate (4′-11-MA), 11-[4-methoxy-(4′-oxy)-α-methylstilbene]undecanyl acrylate (4-11-AC) and 11-[4-oxy-(4′-methoxy)-α-methylstilbene]undecanyl acrylate (4′-11-AC), and 8-[4-methoxy-(4′-oxy)-α-methylstilbene]octyl acrylate (4-8-AC) and 8-[4-oxy-(4′-methoxy)-α-methylstilbene] octyl acrylate (4′-8-AC) are described In the case of polymers with polymethacrylate backbones, the copolymerization of the two constitutional isomeric mesogenic monomers cancels the side chain crystallization tendency characteristic of their parent homopolymers. Subsequently, the copolymer presents a broader mesophase temperature range than any of the two parent homopolymers. In the case of polymers with polyacrylate backbones, copolymerization suppresses the tendency towards side chain crystallization and subsequently, transforms one or even two monotropic mesophases into enantiotropic mesophases.

**(Keywords: polymethacrylate; polyacrylate; constitutional isomeric mesogens; monotropic; enantiotropic)**

## INTRODUCTION

In a series of publications from our laboratory[1–3], we have suggested that copolymerization of monomer pairs containing mesogenic units which are constitutional isomers should depress the tendency toward side chain crystallization of polymers containing long flexible spacers, and simultaneously provide qualitative information about the degree of decoupling. The previous experiments were performed with side groups based on 4-methoxy-4′-hydroxy-α-methylstilbene (4-MHMS) and 4-hydroxy-4′-methoxy-α-methylstilbene (4′-MHMS) constitutional isomers. Although the molar ratio between the two constitutional isomeric side groups was determined by spectroscopic methods, no information about the behaviour of each of the two homopolymers based on only one individual constitutional isomer was available. Meanwhile, we have synthesized and characterized the phase behaviour of the homopolymers based on 4-MHMS[4] and 4′-MHMS[5] individual isomers. In a recent communication[6], we have presented the first quantitative results on this subject. These first results have demonstrated that copolymerization of the parent polymer's monomer pair containing constitutional isomeric mesogenic side groups can lead to the transformation of a monotropic nematic mesophase into an enantiotropic mesophase. This experiment was performed with side chain liquid crystalline polymers containing a polymethylsiloxane backbone.

The goal of this paper is to quantitatively discuss a final series of polymers based on polymethacrylate and polyacrylate backbones. These results will present the influence of constitutional isomeric mesogenic monomer units on the phase behaviour of the resulting copolymers and compare it with the phase behaviour of the parent homopolymers.

## EXPERIMENTAL

### *Materials*

All reagents and intermediate compounds were used as received or synthesized and purified as previously described[3–5]. 2,2′-Azoisobutyronitrile (AIBN) (Fluka) was freshly recrystallized from methanol below 40°C. Toluene used as a polymerization solvent was first washed with concentrated sulphuric acid and then water, dried over anhydrous $CaCl_2$, refluxed over $CaH_2$, distilled, refluxed over sodium and then distilled under argon.

### *Techniques*

200 MHz $^1$H-n.m.r. spectra were recorded on a Varian XL-200 spectrometer. All spectra were recorded in $CDCl_3$ with TMS as an internal standard.

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A Perkin–Elmer DSC-4 differential scanning calorimeter equipped with a TADS 3600 data station was used to determine the thermal transitions, which were read at the maximum of the endothermic or exothermic peaks. Unless specified otherwise, all heating and cooling scans were 20°C/min. Glass transition temperatures ($T_g$) were read as the middle of the change in the heat capacity. Most thermal transitions were read from second or later heating scans, and first or later cooling scans. Second and subsequent heating scans, and first and subsequent cooling scans were perfectly reproducible unless stated otherwise. When the second d.s.c. heating scan differed from the first heating scan, the difference will be mentioned and attempts made to explain it. Both enthalpy changes and transition temperatures were determined using indium as a calibration standard.

A Carl Zeiss optical polarized microscope (magnification 100 × ) equipped with a Mettler FP 82 hot stage and a Mettler FP 800 central processor was used to observe the thermal transitions and to analyse the anisotropic textures[7,8].

Molecular weights were determined by gel permeation chromatography (g.p.c.) with a Perkin–Elmer Series 10 LC instrument equipped with an LC-100 column oven, an LC-600 autosampler, and a Sigma 15 data station. High pressure liquid chromatography (h.p.l.c.) purity determinations were performed with the same instrument. The measurements were made using a u.v. detector, THF as solvent (1 ml/min, 40°C), a set of PL gel columns of $10^2$, $5 \times 10^2$, $10^3$, $10^4$ and $10^5$Å, and a calibration plot constructed from polystyrene standards.

### *Synthesis of monomers*

11-[4-Methoxy-(4′-oxy)-α-methylstilbene]undecanyl methacrylate (4-11-MA)[4], 11-[4-methoxy-(4′-oxy)-α-methylstilbene]undecanyl acrylate (4-11-AC)[4], 8-[4-methoxy-(4′-oxy)-α-methylstilbene]octyl acrylate (4-8-AC)[4], 11-[4-oxy-(4′-methoxy)-α-methylstilbene]undecanyl methacrylate (4′-11-MA)[5], 11-[4-oxy-(4′-methoxy)-α-methylstilbene]undecanyl acrylate (4′-11-AC)[5], and 8-[4-oxy-(4′-methoxy)-α-methylstilbene]octyl acrylate (4′-8-AC)[5] were synthesized as previously described. Their purity was higher than 99.9% in all cases (h.p.l.c.).

### *Radical polymerization and copolymerization of monomers*

Polymers and copolymers were synthesized by radical polymerization or copolymerization of the monomers in dry toluene and using AIBN as initiator at 60°C for 20 h. Polymerizations were carried out in Schlenk tubes under an argon atmosphere after the monomer solutions were degassed by several freeze–pump–thaw cycles under vacuum. The monomer and initiator concentrations for the polymerization of methacrylates were 20% (w/v) and 0.5% (w/w) of monomer, respectively, while those for the polymerization of acrylates were 20% (w/v) and 0.25% (w/w) of monomer, respectively. After polymerization, the reaction mixture was diluted with chloroform and precipitated into methanol. The filtered polymers were dried under vacuum and then purified by successive precipitations from THF into acetone/methanol mixtures and methanol, until g.p.c. chromatograms showed no traces of unreacted monomer and oligomers. After the final purification, conversions were higher than 90% in all cases. The molecular weights of the purified polymers and their phase transitions are reported in *Table 1*.

Throughout this paper, the homopolymers such as poly(4-11-MA) will be designated as 4-11-(PMA. Similarly, copolymers will be designated, for example, as 4,4′-(1/1)-11-coPMA which represents the copolymer containing a 1/1 molar ratio of 4-11-MA and 4′-11-MA (*Scheme 1*).

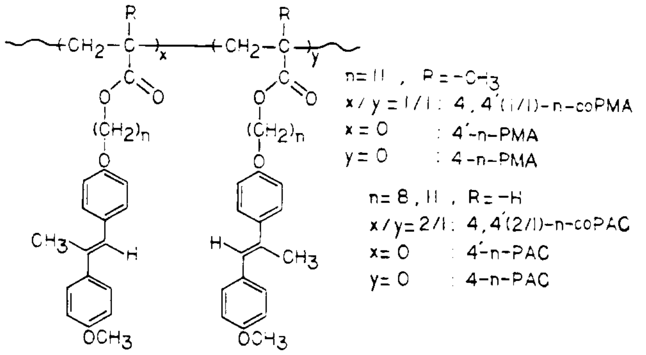
## RESULTS AND DISCUSSION

The nature of the mesomorphic phases exhibited by side chain liquid crystalline polymers with degrees of

**Table 1** Thermal transitions and thermodynamic parameters of polymers and copolymers

| | $\bar{M}_n$ | $\bar{M}_w/\bar{M}_n$ | Phase transitions (°C) and corresponding enthalpy changes (kcal/mru) | |
|---|---|---|---|---|
| Polymer | g.p.c. | | Heating$^{e}$ | Cooling$^{e}$ |
| 4-11-PMA$^{a}$ | 30.1 | 2.1 | g 14 k 59(0.26) s 119(0.93) i | i 106(0.98) s 6 g |
| 4-11 PMA | 30.1 | 2.1 | g 14 s 114(1.03) i | i 106(0.98) s 6 g |
| 4′-11-PMA$^{a}$ | 23.4 | 2.0 | g 15 k 55(0.55) k 83(0.39) s 119(0.99) i | i 105(1.13) s 4 g |
| 4′-11-PMA | 23.4 | 2.0 | g 12 s 116(1.25) i | i 105(1.13) s 4 g |
| 4,4′(1/1)-11-PMA$^{a}$ | 86.3 | 2.1 | g 18 s 124(1.20) i | i 113(1.07) s 8 g |
| 4,4′(1/1)-11-PMA | 86.3 | 2.1 | g 13 s 129(1.10) i | i 113(1.07) s 8 g |
| 4-11-PAC | 5.5 | 1.2 | g 6 k 104(4.15) i | i 88(0.95) s 68(2.64) k 1 g |
| 4′-11-PAC | 15.9 | 2.0 | g 12 k 106(2.86) s 115$^{b}$(0.80) i | i 107(0.72) s 35(1.08) k 3 g |
| 4,4′(2/1)-11-PAC$^{a}$ | 6.7 | 1.3 | k 51, 65, 73(2.57)$^{b}$ s 98(0.70) i | i 88(0.65) s 5 g |
| 4,4′(2/1)-11-PAC | 6.7 | 1.3 | g 10 k 65(0.25) s 90(0.68) i | |
| 4,4′(2/1)-11-PAC$^{d}$ | 6.7 | 1.3 | g 11 k 56, 68, 74(1.25)$^{b}$ s 90(0.21)$^{b}$ i | |
| 4-8-PAC | 3.4 | 1.2 | g 4 k 46$^{c}$ k 97(3.18) i | i 85(0.21) n 53(0.04) s −1 g |
| 4′-8-PAC | 12.2 | 1.8 | g 11 s 66(0.03) n 83$^{c}$(0.39) k 99(0.55) n 104(0.07) i | i 99(0.23) n 62(0.03) s 6 g |
| 4,4′(2/1)-8-PAC$^{a}$ | 6.6 | 1.4 | g 10 k 53(1.36) s 67(0.01) n 96(0.19) i | i 88(0.17) n 54(0.02) s 7 g |
| 4,4′(2/1)-8-PAC | 6.6 | 1.4 | g 10 s 58(0.01) n 92(0.19) i | |

[a] First heating scan
[b] Overlapped transitions
[c] Crystallization exotherm
[d] Heating scan after sample was annealed at 35°C for 1h
[e] g = glassy, i = isotropic, k = crystalline, n = nematic, s = smectic



**Scheme 1** Polymers and copolymers containing 4-MHMS and 4'-MHMS based mesogenic side groups and different spacer lengths

polymerization higher than twelve are usually controlled by the spacer length and the nature of the mesogenic group[3–5,9–11]. However, for the same spacer length and degree of polymerization, the degree of decoupling seems to be strongly dependent on the nature of the polymer backbone. The degree of decoupling increases with decreasing polymer backbone flexibility. Therefore, a more flexible polymer backbone enhances the tendency toward side chain crystallization. Subsequently, upon going from a rigid polymer backbone toward more flexible polymer backbones, an enantiotropic mesophase is often transformed into a monotropic or even virtual mesophase[4,5]. Since the flexibility of the polymer backbone is molecular weight dependent, effects similar to those observed when varying the backbone flexibility should be detected by decreasing the degree of polymerization of a certain polymer. The influence of molecular weight on polymer phase transitions is the result of a combination of thermodynamic and kinetic effects which were already discussed in a previous publication[12]. This influence is strongly dependent on the intrinsic flexibility of the polymer backbone. Upon increasing the degree of polymerization of a flexible backbone, thermal transition temperatures increase while the rate of side chain crystallization decreases[13,14]. As a result, the temperature range of the mesomorphic phase increases. However, upon going to more rigid polymer backbones, particularly when the polymer displays a second mesophase near the glass transition temperature of the polymer, the kinetic effect which controls the rate of crystallization of flexible side chain liquid crystal polymers, may also influence the rate of formation of this second mesomorphic phase. Consequently, observation of this second mesomorphic phase depends on polymer molecular weight, and it may therefore be enantiotropic, monotropic or even virtual[12].

Presently, there is no synthetic methodology which can be used to manipulate the ratio between the rates of side chain crystallization and mesomorphic phase formation in a side chain liquid crystalline polymer based on a specific flexible backbone, spacer length and mesogenic unit. Our approach to this problem is based on the use of copolymers of monomer pairs containing constitutional isomeric mesogenic side groups. As expected[4,5], the mesomorphic phase of two homopolymers which have either 4-MHMS or 4'-MHMS side groups are not different.

Following the rules of miscibility derived by Arnold, Sackman and Demus for low molar mass liquid crystals[15–17], isomorphic mesophases exhibited by different structural units of a side chain liquid crystalline polymer should also be miscible, and therefore similar phase diagrams as a function of copolymer composition should be observed. Based on miscibility rules and the fact that co-crystallization of two compounds is strongly suppressed while the phase transition temperatures of their miscible mesomorphic mixtures display a weight averaged dependence of composition, isomorphic mixtures of low molar mass liquid crystals are frequently used to determine virtual mesomorphic transitions[18,19]. This concept was already extended to the field of main chain liquid crystalline copolymers and provides a very reliable method for determining virtual liquid crystalline transitions and their enthalpy changes, as well as for engineering copolymer phase transitions[20]. Although the extension of this concept to the field of side chain liquid crystalline copolymers may not be as straightforward as with main chain liquid crystalline copolymers, it should at least provide a tool for designing mesomorphic phase transitions[5,9–11]. Alternatively, the independent crystallization of each constitutional isomer may occur in highly decoupled systems providing at least qualitative information on the degree of decoupling.

All copolymers discussed in this manuscript are based on monomer pairs containing the same methacrylate or acrylate polymerizable group, identical spacer length, and either 4-MHMS or 4'-MHMS constitutional mesogenic groups (*Scheme 1*). We can safely assume that all these systems copolymerize azeotropically and that the copolymer composition is therefore identical to that of the comonomer feed at any conversion. This assumption is based on the fact that the reactivity of the two monomers of any monomer pair used in these copolymerization experiments should be identical. This is due to the fact that each monomer pair used in these experiments consists of an identical polymerizable group and spacer length, with only the constitutional isomeric mesogens being different. Therefore $r_1 = r_2 = 1.0$. This also assumes that the sequence distribution of the two structural units is random.

Let us begin our discussion by inspecting the phase behaviour of 4-11-MA, 4'-11-MA and of the corresponding copolymer containing a 1/1 molar ratio of the two structural units (*Scheme 1, Figure 1*). The molecular weights of all the polymers in *Table 1* are high enough to exhibit phase transition temperatures which are almost independent of molecular weight[9–14]. The first d.s.c. heating scans of 4-11-PMA (*Figure 1, curve A*) and 4'-11-PMA (*Figure 1, curve D*) exhibit one or two crystalline melting transitions followed by a smectic mesophase which undergoes isotropization at 119°C in both cases. The corresponding cooling scans display only an isotropic–smectic transition. Side chain crystallization does not appear on cooling or on the second or any subsequent heating scans. However, extensive annealing at temperatures above the polymer glass transition temperature and below the first melting transition reinduces the crystalline phases observed in the first heating scans. Therefore, the side chain crystallization process is very slow both in the case of 4-11-PMA and in the case of 4'-11-PMA. The first d.s.c. heating scan of 4,4'-(1/1)-coPMA is presented as curve G in *Figure 1* and is quite similar to its second heating scan (*Figure 1, curve H*). Because the molecular weight of the copolymer is much higher than those of the two parent

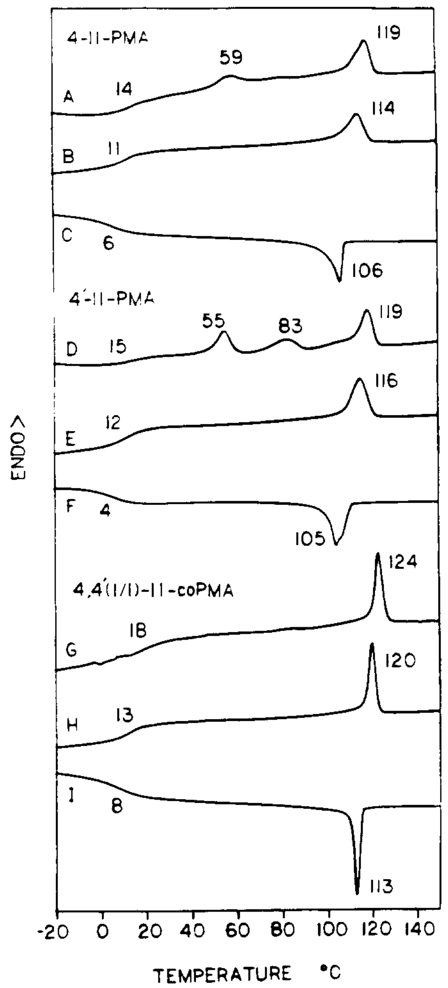


**Figure 1** Normalized d.s.c. traces (20°C/min) of: curve A, 4-11-PMA, first heating scan; curve B, 4-11-PMA, second and subsequent heating scans; curve C, 4-11-PMA, first and subsequent cooling scans; curve D, 4'-11-PMA, first heating scan; curve E, 4'-11-PMA, second and subsequent heating scans; curve F, 4'-11-PMA, first and subsequent cooling scans; curve G, 4,4'(1/1)-11-coPMA, first heating scan; curve H, 4,4'(1/1)-11-coPMA, second and subsequent heating scans; curve I, 4,4'(1/1)-11-coPMA, first and subsequent cooling scans

homopolymers, the isotropization transition of the copolymer appears at a temperature 5°C higher than those of the parent homopolymers. Independent of the thermal treatment of 4,4'-(1/1)-11-coPMA, no side chain crystallization could be detected. That is, copolymerization of two methacrylates containing constitutional isomeric side groups led to the complete loss of the ability of the resulting copolymer to undergo side chain crystallization. Both the homopolymers and the copolymer present a smectic mesophase which is characterized by a focal conic fan shape texture. An interesting observation is that, in all cases, the isotropization transition occurs at slightly higher temperatures on the first heating scans (*Figure 1*). All phase transitions discussed so far are summarized in *Table 1*.

*Figure 2* presents the same experiment performed with a more flexible polyacrylate backbone. Both 4-11-PAC and 4'-11-PAC display melting transitions on first, second and subsequent heating scans (*Table 1*). 4-11-PAC displays a monotropic smectic mesophase (*Figure 2, curves A* and *B*) while 4'-11-PAC displays an enantiotropic smectic mesophase (*Figure 2, curves C* and *D* and *Table 1*). This mesophase overlaps the melting transition temperature on the heating scan (*Figure 2, curve C*). However, upon copolymerization, the crystallization process is strongly suppressed and subsequently, 4,4'-(2/1)-1-coPAC does not crystallize upon cooling (*Figure 2, curve G*). The crystallization and melting processes upon heating strongly depend on the thermal history of the sample (*Figure 2, curves E* and *F*). Nevertheless, independent of the copolymer's thermal history, the temperature range of smectic mesophase is broader than in 4'-11-PAC. It is interesting that upon annealing above the glass transition temperature, this copolymer displays three melting transitions (*Figure 2, curve F*), which, as previously suggested[3], may be associated with the meltings of each constitutional isomer and of their eutectic mixture. These multiple meltings were observed only in copolyacrylates and copolysiloxanes[6] containing eleven methylenic units in their flexible spacer. Although this does not necessarily mean that our assignment is correct, it strongly suggests that multiple meltings occur only for copolymers containing

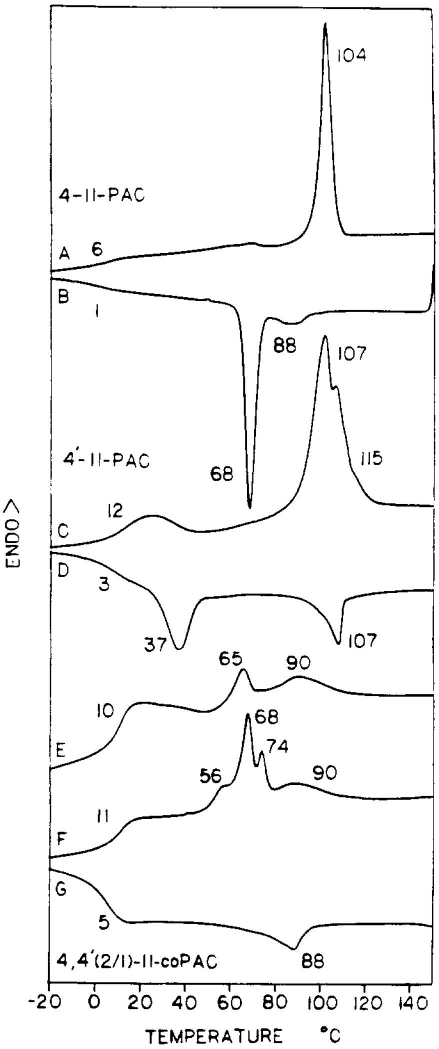


**Figure 2** Normalized d.s.c. traces (20°/min) of: curve A, 4-11-PAC, second and subsequent heating scans; curve B, 4-11-PAC, first and subsequent cooling scans; curve C, 4'-11-PAC, second and subsequent heating scans; curve D, 4'-11-PAC, first and subsequent cooling scans; curve E, 4,4'(2/1)-11-coPAC, second and subsequent heating scans; curve F, 4,4'(2/1)-11-coPAC, heating scan after sample was annealed at 35° for 1 h; curve G, 4,4'(2/1)-11-coPAC, first and subsequent cooling scans

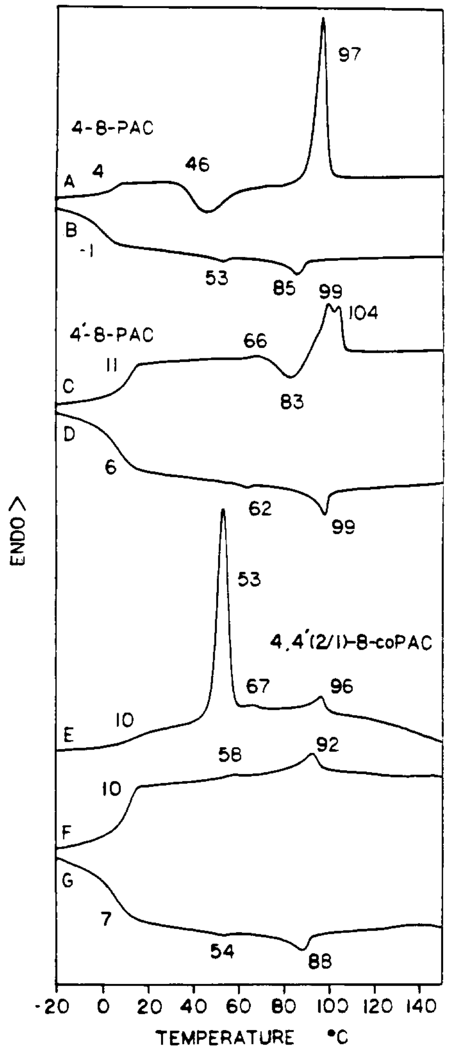


**Figure 3** Normalized d.s.c. traces (20°C/min) of: curve A, 4-8-PAC, second and subsequent heating scans; curve B, 4-8-PAC, first and subsequent cooling scans; curve C, 4'-8-PAC, second and subsequent heating scans; curve D, 4'-8-PAC, first and subsequent cooling scans; curve E, 4,4'(2/1)-8-coPAC, first heating scan; curve F, 4,4'(2/1)-8-coPAC, second and subsequent heating scans; curve G, 4,4'(2/1)-8-coPAC, first and subsequent cooling scans

flexible backbones and long flexible spacers. Nevertheless, additional research is required to substantiate this statement.

The most interesting experiment is illustrated in *Figure 3*. 4-8-PAC displays a monotropic nematic and a monotropic smectic mesophase (*Figure 3, curves A* and *B*). This is due to the interesting kinetics of crystallization and melting processes. Crystallization occurs only in the heating scan and eventually overlaps the temperature range where the smectic–nematic transition should occur. Simultaneously, the melting transition temperature overlaps the nematic–isotropic transition temperature. 4'-8-PAC displays both an enantiotropic nematic and an enantiotropic smectic mesophase (*Figure 3, curves C* and *D*). This behaviour results from a crystallization process which takes place on the heating scan at a temperature just above the smectic–nematic transition at 66°C. Interestingly, melting occurs at 99°C. This temperature is just below the nematic–isotropic transition at 104°C. Copolymerization of a 2/1 molar ratio of 4-8-AC and 4'-8-AC leads to the copolymer 4,4'(2/1)-8-coPAC which displays enantiotropic nematic and smectic mesophases (*Figure 3, curves E, F, G* and *Table 1*). In the first heating scan and the scan after annealing above the glass transition temperature, this copolymer presents a melting transition at 53°C, followed by a smectic–nematic transition at 67°C and a nematic–isotropic transition at 96°C. Second and subsequent heating and cooling scans display only the smectic and the nematic mesophases.

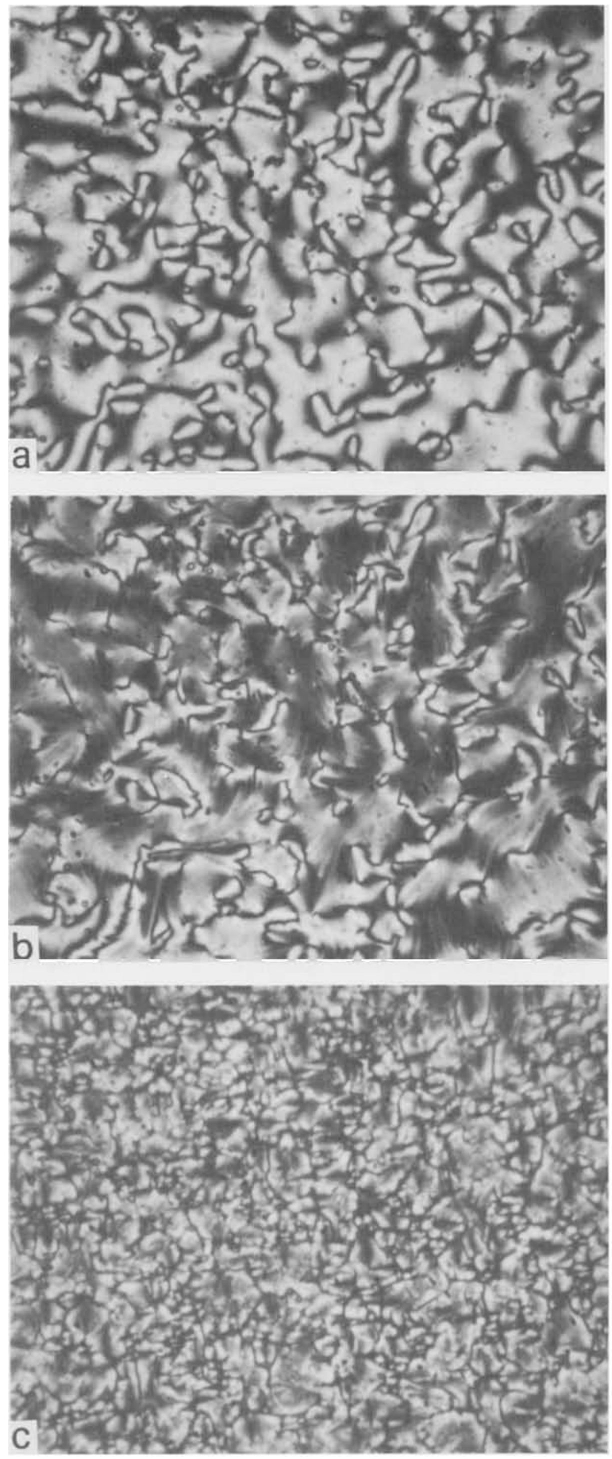


**Figure 4** Representative optical polarization micrographs (magnification 70×) exhibited by 4,4'(2/1)-8-coPAC. (a) Schliering nematic texture obtained after 30 min of annealing at 81°C; (b) the transition from the nematic to the smectic mesophase observed after 5 min of annealing at 55°C on cooling; (c) the smectic texture obtained after 20 h of annealing at 54°C (small fan shape focal conic texture)

This experiment demonstrates that copolymerization of two acrylates whose parent homopolymers exhibit respective monotropic and enantiotropic mesophases which are either metastable or overlap the crystalline phases led to a copolymer displaying two enantiotropic mesophases. Additional evidence for this statement is provided by the optical polarization micrographs shown in *Figure 4* which demonstrate the presence of the nematic and smectic mesophases.

The results of these experiments are rewarding. This is so because the constitutional isomeric monomers based on similar polymerizable groups, spacer lengths, and 4-MHMS or 4′-MHMS give rise to homopolymers with identical types of mesophases. The suppression of side chain crystallization upon copolymerization of these monomer pairs which differ only in their mesogenic unit can transform depending on the polymer backbone flexibility, crystallizable polymers into noncrystallizable copolymers and monotropic or virtual mesophases into enantiotropic mesophases. These copolymerization experiments provide an important synthetic tool which can be used to transform metastable, i.e., monotropic or virtual mesophases into thermodynamically stable enantiotropic mesophases.

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