Synthesis of ferroelectric liquid-crystalline polymethacrylates containing 1,2-diphenylethane based mesogens

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SUMMARY:
   The synthesis of side-chain liquid-crystalline polymethacrylates containing (2*S*)-2-chloro-4-methylvaleric acid end groups and 1,2-diphenylethane based mesogenic units is presented. Differential scanning calorimetry, optical polarizing microscopy and X-ray diffraction were used to determine the thermal transitions and to analyze the anisotropic phases. Among the methacrylate monomers prepared in this study, those without lateral chloro substituent show only a smetic A phase while those with a lateral chloro substituent display a cholesteric phase. All polymers exhibit smectic mesomorphism and do not undergo side-chain crystallization. All four polymethacrylates without lateral chloro substituents reveal enantiotropic smectic A and smectic B phases while the other four polymethacrylates with lateral chloro substituents reveal enantiotropic smectic A and chiral smectic C phases. The results seem to demonstrate that incorporating a lateral chloro substituent into the mesogenic core enhances the formation of a tilted chiral smectic C phase.

Introduction

   The potential application of ferroelectric liquid crystals (FLCs) in fast-switching, high-resolution electrooptical devices is well documented[1-3]. Besides low-molar-mass FLCs, a number of ferroelectric liquid-crystalline side-chain polymers have been successfully prepared during the past few years[4-30]. These polymers are interesting because of their ferroelectric properties[17-26]. This field has been reviewed by Le Barny and Dubois[28]. However, the detailed structure-property relationship of ferroelectric liquid-crystalline polymers (LCPs) has not been very clear until now. It seems necessary to introduce additional functional groups into the mesogenic units, spacers, and polymer backbone of side-chain liquid-crystalline polymers to create some new property combinations, in order to achieve these goals.

   Investigations of the effect of lateral substituents on liquid-crystalline behavior may have several objectives, such as the desire to determine to what extent clearing points and the relative stabilities of different mesophases are affected by the size and type of lateral substituents or to find out how physical properties, e.g., dielectric anisotropy, elastic constants and viscosity are modified. The effect of molecular structure on the occurrence of tilted smectic C phases is very different to that on nematic or orthogonal smectic phases. The molecules should possess some degree of steric asymmetry, so that they can arrange themselves in a tilted layer when they are packed together. The influence of lateral substituents on the formation of a chiral

smectic C phase for low-molar-mass liquid crystals has been studied by Coates et al.[31]. Their experimental results demonstrate that the incorporation of a lateral substituent into the mesogenic core of a molecule, reduces the occurrence of higher-ordered smectic phases and also decreases their melting point in most cases. According to some other reports on low-molar-mass liquid crystals the literature[32–35] also shows that introducing a suitable lateral substituent, e. g., a fluoro group, into their mesogenic cores enhances the formation of a tilted smectic C phase.

In some previous papers[36–38], we have presented the synthesis and characterization of side-chain liquid-crystalline polysiloxanes, polymethacrylates and polyacrylates containing benzyl ether and 1,2-diphenylethane based mesogens. Because of the free rotation around a flexible "oxymethylene" or "ethylene" linkage, these polymers represent the simplest class of liquid-crystalline polymers containing mesogenic groups that present conformational isomerism. The phase behavior of the obtained polymers showed that these kinds of mesogenic groups depress the tendency toward side-chain crystallization of the side-chain liquid-crystalline polymers. Recently Seto et al.[39] reported the synthesis of new ferroelectric liquid crystals having a 1,2-diphenylethane structure.

The goal of this paper is to present the synthesis of two series of side-chain liquid-crystalline polymethacrylate containing (2S)-2-chloro-4-methylvaleric acid end groups and 1,2-diphenylethane based mesogens. Their characterizations by means of differential scanning calorimetry, optical polarizing microscopy, and X-ray diffraction have been presented. The effects of the 1,2-diphenylethane based mesogen and the lateral chloro substituent on the mesomorphic properties of the obtained monomers and polymers are discussed.

Experimental part

Materials

L-Leucine (specific optical rotatory power[a] $[a]_D^{23}$ = +15.0 deg $\cdot$ dm^{-1} $\cdot$ g^{-1} $\cdot$ cm^3 (concentration c = 2 g $\cdot$ cm^{-3}, 5M HCl)), 4-hydroxybenzoic acid, 3-chloro-4-hydroxybenzoic acid and methacryloyl chloride and all other reagents were obtained from Aldrich, Milwaukee, USA and used as received. 1,4-Dioxane was first refluxed over sodium and then distilled under nitrogen. 2,2′-Azoisobutyronitrile (AIBN; from Fluka, Switzerland) was freshly recrystallized from methanol. 4,4′-Ethylenediphenol was prepared according to a similar synthetic procedure reported in the literature[37,40].

Techniques

Proton nuclear magnetic resonance (^{1}H NMR) spectra (300 MHz) were recorded on a Varian VXR-300 spectrometer. Fourier-transform infrared (FTIR) spectra were measured on a Nicolet 520 FT-IR spectrometer. Polymer samples were film-cast onto a KBr tablet for the IR measurements. Thermal transitions and thermodynamic parameters were determined by using a Seiko SSC/5200 differential scanning calorimeter equipped with a liquid-nitrogen cooling accessory. Heating and cooling rates were 10°C/min. Thermal transitions reported were collected during the second heating and cooling scans. A Carl-Zeiss Axiophot optical polarizing microscope equipped with a Mettler FP 82 hot stage

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[a] Customarily called specific rotation.

and an FP 80 central processor was used to observe the thermal transitions and to analyze the anisotropic textures. Gel-permeation chromatography (GPC) was run on an Applied Biosystem 400 LC instrument equipped with a differential refractometer, an ultraviolet (UV) detector and a set of Polymer Laboratory gel columns of 10^2, 5×10^2, 10^3 and 10^4 Å. The molecular weight calibration curve was obtained by using standard polystyrenes. X-ray diffraction measurements were performed with nickel-filtered Cu-K_α radiation with a Rigaku powder diffractometer. Optical rotation values were measured at 23 °C on a Jasco DIP-140 polarimeter with chloroform as solvent for all compounds. Spontaneous polarization was evaluated by using a Displaytech (Boulder, Colorado, U.S.A.) APTII automated polarization tester.

Syntheses of monomers and polymers

The synthesis of monomers **1M−8M** is outlined in *Scheme 1:*
(−)-(2S)-2-Chloro-4-methylvaleric acid was prepared by the chlorination of diazonium salt of L-leucine according to a literature procedure[41]. Specific optical rotatory power $[\alpha]_D^{23} = -25.9$ deg $\cdot$ dm^{-1} $\cdot$ g^{-1} $\cdot$ cm^3 (neat liquid).

4-(ω-Hydroxyalkan-1-yloxy)benzoic acid (**1−4**) and 3-chloro-4-(ω-hydroxyalkan-1-yloxy)benzoic acid (**5−8**)

All compounds **1−8** were prepared by the etherification of ω-hydroxyalkyl bromide with 4-hydroxybenzoic acid or 3-chloro-4-hydroxybenzoic acid. The synthesis of compound **2** is described below:
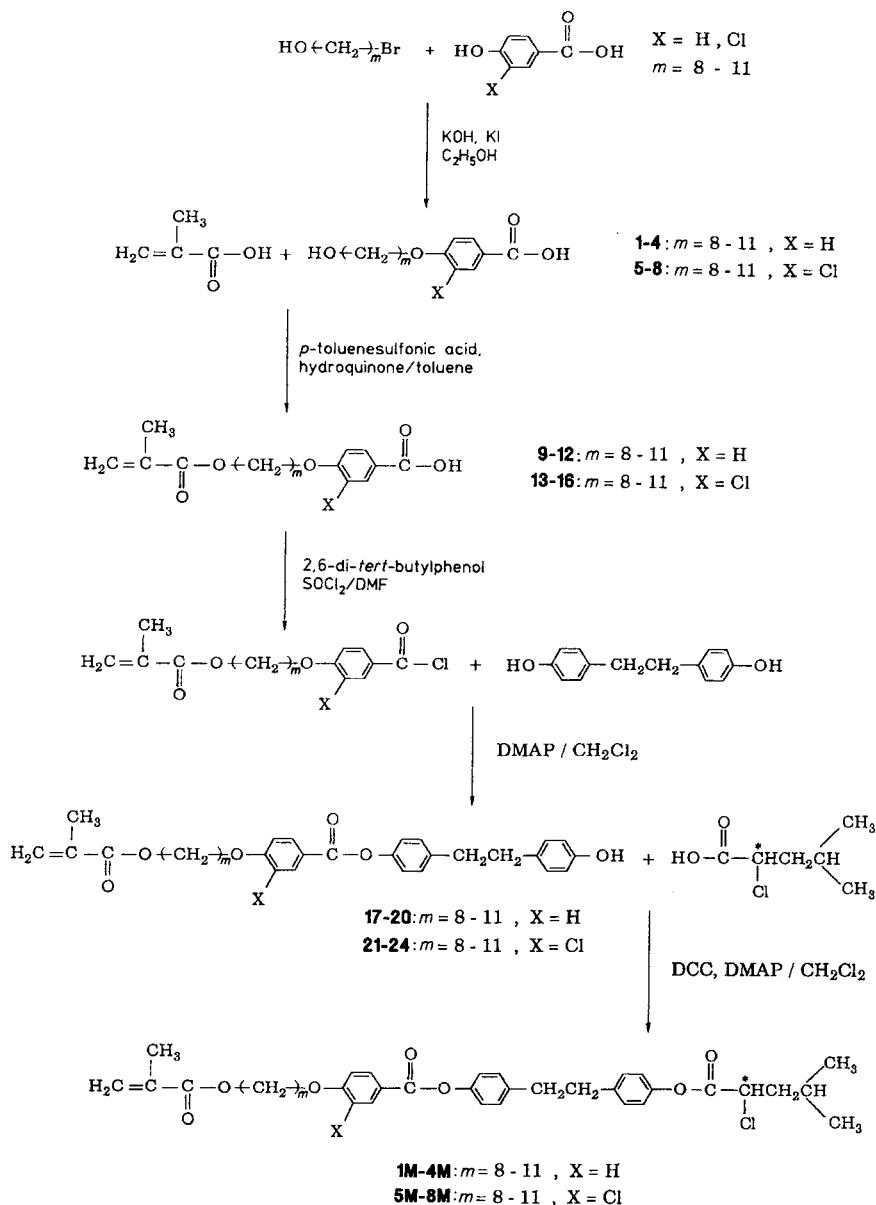4-Hydroxybenzoic acid (2.76 g, 20 mmol) was added to a stirred solution of KOH (2.70 g, 48 mmol) and KI (0.3 g) in 50 mL of 95 vol.-% ethanol. 8-Bromo-1-nonanol (4.46 g, 20 mmol) was added when dissolution was complete. The solution was refluxed overnight and cooled to room temperature. The solvent was then removed in a rotavap. The residue was acidified with dilute hydrochloric acid. The precipitate was filtered and recrystallized with a mixture of ethanol and water to yield 4.20 g (75%) of white crystals. mp = 116 °C; ^{1}H NMR (CDCl$_3$, δ, ppm): 1.30−1.91 (m, 14 H, −(CH$_2$)$_7$−), 3.50 (t, 2 H, HO−CH$_2$), 4.02 (t, 2 H, −CH$_2$−OPh−), 6.95 and 8.10 (2 d, 4 aromatic protons).

4-(ω-Methacryloyloxyalkan-1-yloxy)benzoic acid (**9−12**) and 3-chloro-4-(ω-methacryloyloxyalkan-1-yloxy)benzoic acid (**13−16**)

Compounds **9−16** were prepared by esterification of methacrylic acid with the corresponding compounds **1−8**. The synthesis of compound **10** is given as follows:
4-(9-Hydroxynonan-1-yloxy)benzoic acid (4.20 g, 15 mmol), methacrylic acid (12.9 g, 150 mmol), p-toluenesulfonic acid (0.50 g) and hydroquinone (0.50 g) were dissolved in 50 mL of dried toluene. The reaction mixture was refluxed for 40 h, and water was collected on a Dean-Stark trap. After this reaction time, toluene and excess methacrylic acid were distilled off and the crude product was dissolved in diethyl ether. The diethyl ether solution was washed with water and dried over anhydrous MgSO$_4$, and the solvent was removed in a rotavap. The obtained solid was recrystallized with a mixture of ethanol and water to yield 3.03 g (58%) of white crystals.
mp = 115 °C; ^{1}H NMR (CDCl$_3$, δ, ppm): 1.30−1.91 (m, 14 H, −(CH$_2$)$_7$−), 1.92 (s, 3 H, =(C−)−CH$_3$), 4.02 (t, 2 H, −CH$_2$−O−Ph−), 4.12 (t, 2 H, −COO−CH$_2$−), 5.55 and 6.10 (2d, 2 H, =CH$_2$), 6.92 and 8.05 (2 d, 4 aromatic protons).

Scheme 1: Synthesis of monomers **1M-8M**

$$HO\!\leftarrow\!CH_2\!\xrightarrow{}_m\!Br \;+\; HO\!-\!\langle\!\bigcirc\!\rangle\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!OH \qquad \begin{array}{l} X = H, Cl \\ m = 8 - 11 \end{array}$$

KOH, KI
C_2H_5OH

$$H_2C\!=\!\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\parallel}}{C}}\!-\!C\!-\!OH \;+\; HO\!\leftarrow\!CH_2\!\xrightarrow{}_m\!O\!-\!\langle\!\bigcirc\!\rangle\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!OH \qquad \begin{array}{l} \textbf{1-4}: m = 8 - 11, \; X = H \\ \textbf{5-8}: m = 8 - 11, \; X = Cl \end{array}$$

p-toluenesulfonic acid,
hydroquinone/toluene

$$H_2C\!=\!\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\parallel}}{C}}\!-\!C\!-\!O\!\leftarrow\!CH_2\!\xrightarrow{}_m\!O\!-\!\langle\!\bigcirc\!\rangle\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!OH \qquad \begin{array}{l} \textbf{9-12}: m = 8 - 11, \; X = H \\ \textbf{13-16}: m = 8 - 11, \; X = Cl \end{array}$$

2,6-di-*tert*-butylphenol
$SOCl_2/DMF$

$$H_2C\!=\!\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\parallel}}{C}}\!-\!C\!-\!O\!\leftarrow\!CH_2\!\xrightarrow{}_m\!O\!-\!\langle\!\bigcirc\!\rangle\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!Cl \;+\; HO\!-\!\langle\!\bigcirc\!\rangle\!-\!CH_2CH_2\!-\!\langle\!\bigcirc\!\rangle\!-\!OH$$

$DMAP / CH_2Cl_2$

$$H_2C\!=\!\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\parallel}}{C}}\!-\!C\!-\!O\!\leftarrow\!CH_2\!\xrightarrow{}_m\!O\!-\!\langle\!\bigcirc\!\rangle\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!O\!-\!\langle\!\bigcirc\!\rangle\!-\!CH_2CH_2\!-\!\langle\!\bigcirc\!\rangle\!-\!OH \;+\; HO\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!\overset{*}{C}HCH_2CH\!\langle\!\begin{array}{l}CH_3\\CH_3\end{array}$$

17-20: m = 8 - 11, X = H
21-24: m = 8 - 11, X = Cl

$DCC, DMAP / CH_2Cl_2$

$$H_2C\!=\!\overset{\overset{CH_3}{|}}{\underset{\underset{O}{\parallel}}{C}}\!-\!C\!-\!O\!\leftarrow\!CH_2\!\xrightarrow{}_m\!O\!-\!\langle\!\bigcirc\!\rangle\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!O\!-\!\langle\!\bigcirc\!\rangle\!-\!CH_2CH_2\!-\!\langle\!\bigcirc\!\rangle\!-\!O\!-\!\overset{\overset{O}{\parallel}}{C}\!-\!\overset{*}{C}HCH_2CH\!\langle\!\begin{array}{l}CH_3\\CH_3\end{array}$$

1M-4M: m = 8 - 11, X = H
5M-8M: m = 8 - 11, X = Cl

4-[2-(4-Hydroxyphenyl)ethyl]phenyl 4-(ω-methacryloyloxyalkan-1-yloxy)benzoate (**17–20**) and 4-[2-(4-hydroxyphenyl)ethyl]phenyl 3-chloro-4-(ω-methacryloyloxyalkan-1-yloxy)benzoate (**21–24**)

Compounds **17–24** were prepared by esterification of the corresponding compounds **9–16** with 4,4′-ethylenediphenol. The synthesis of compound **18** is described below:

4-(9-Methacryloyloxynonan-1-yloxy)benzoic acid (3.09 g, 8.6 mmol) was reacted at room temperature with excess thionyl chloride (2 mL) containing 2,6-di-*tert*-butylphenol (0.5 g) and a few drops of *N,N*-dimethylformamide (DMF) in methylene dichloride (30 mL) for 2 h. The solvent and excess thionyl chloride were removed under reduced pressure to give the corresponding acyl chloride. The product was dissolved in 30 mL of methylene dichloride and slowly added to a cold solution of 4,4'-ethylenediphenol (9.2 g, 43 mmol) and 4-dimethylaminopyridine (DMAP, 1.4 g) in 20 mL of methylene dichloride. The solution was stirred at room temperature for 2 h. The solvent was then distilled. The obtained crude product was purified by means of column chromatography (silica gel, ethyl acetate/hexane (volume ratio 1/4 as eluent) to yield 1.96 g (42%) of white crystals; ^{1}H NMR (CDCl$_3$, δ, ppm): 1.34–1.90 (m, 14H, —(CH$_2$)$_7$—), 1.95 (s, 3H, =(C—)—CH$_3$), 2.90 (s, 4H, —Ph—CH$_2$—CH$_2$—Ph—), 4.03 (t, 2H, —CH$_2$—OPh—), 4.12 (t, 2H, —COOCH$_2$—), 4.66 (s, 1H, —OH), 5.54 and 6.10 (2d, 2H, =CH$_2$), 6.72–8.15 (m, 12 aromatic protons).

Synthesis of monomers 1M–8M

All methacrylate monomers 1M–8M were synthesized by the esterification of the corresponding phenol derivatives 17–24 with (2S)-2-chloro-4-methylvaleric acid. The synthesis of 2M is described as follows:

Compound 18 (1.8 g, 3.3 mmol), dicyclohexylcarbodiimide (DCC) (0.84 g, 4.0 mmol), 4-dimethylaminopyridine (DMAP, 0.2 g) and (2S)-2-chloro-4-methylvaleric acid (0.6 g,

Scheme 2: Synthesis of polymers 1P-8P

1M-4M: m = 8 - 11 , X = H

5M-8M: m = 8 - 11 , X = Cl

AIBN
1,4-dioxane
60°C
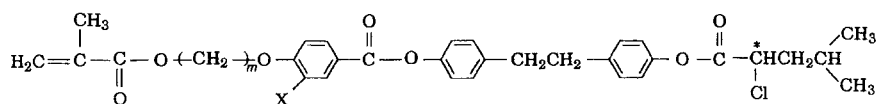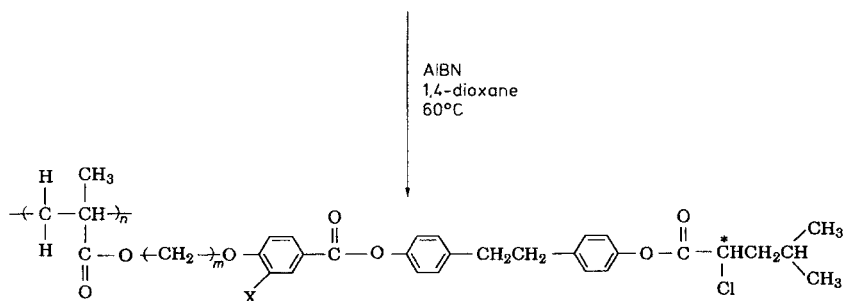
1P-4P: m = 8 - 11 , X = H

5P-8P: m = 8 - 11 , X = Cl

4.0 mmol) were dissolved in 20 mL of methylene dichloride under nitrogen. The result-
ing solution was stirred at room temperature overnight, and then filtered. The solvent
was then evaporated. The crude product was purified using column chromatography
(silica gel, ethyl acetate/hexane (volume ratio 1/10 as eluent) to yield 1.29 g (58%) of
white crystals. ^{1}H NMR (CDCl$_3$, δ, ppm): 0.85–1.06 (m, 6H, —CH(C$\underline{H}_3$)$_2$), 1.22–1.90
(m, 14H, —(C$\underline{H}_2$)$_7$—), 1.95 (s, 3H, =(C—)—C$\underline{H}_3$), 1.90–2.03 (m, 3H,
—C$\underline{H}_2$—C$\underline{H}$(CH$_3$)$_2$), 2.91 (s, 4H, —Ph—C$\underline{H}_2$C$\underline{H}_2$—Ph—), 4.01 (t, 2H, —C$\underline{H}_2$—OPh—),
4.15 (t, 2$\underline{H}$, —COO—C$\underline{H}_2$—), 4.48 (m, 1$\underline{H}$, —C$\underline{H}$Cl—) 5.57 and 6.06 (2d, 2$\underline{H}$, =C$\underline{H}_2$),
6.90–8.12 (m, 12 aromatic protons). The thermal transitions and optical rotations are
reported in Tab. 1 (see Results and discussion).

Synthesis of polymethacrylates 1P–8P

The radical polymerizations of the monomers were carried out in Schlenk tubes
equipped with septa, under argon. The polymerization tube containing the 1,4-dioxane
solution of the monomer (10 g/100 mL) and the initiator (AIBN, 1 wt.-% vs. monomer)
was first degassed by several freeze-pump-thaw cycles under vacuum and then filled
with argon. All polymerizations were carried out at 60 °C for 15 h. After the polymeriza-
tion time, the polymers were precipitated into methanol, filtered, and purified by repreci-
pitation from tetrahydrofuran (THF) solutions into methanol. The polymerization results
have been summarized in Tab. 2 in section Results and discussion.

Results and discussion

The synthetic route used for the preparation of monomers 1M–8M is outlined in
Scheme 1. (2S)-2-Chloro-4-methylvaleric acid was prepared from L-leucine through
a Sandmeyer reaction. The reaction was performed with retention of configura-
tion[33]. The esterification of (2S)-2-chloro-4-methylvaleric acid with the corre-
sponding phenol derivatives 17–24 was also achieved with retention of configura-
tion. The prepared methacrylate monomers 1M–8M were characterized by differen-
tial scanning calorimetry (DSC) and optical polarizing microscopy. Since the mono-

Tab. 1.   Specific optical rotatory power $[\alpha]_D^{23}$, phase transitions, and phase transition
enthalpies for monomers 1M–8M

Monomer	$m^{a)}$	$\dfrac{[\alpha]_D^{23}}{deg \cdot dm^{-1} \cdot g^{-1} \cdot cm^3}$ [b)	Phase transitions in °C (correspond-ing enthalpy changes in kcal/mol)$^{c)}$
1M	8	−10.3	K 49.5 (0.42) S$_A$ 75.0 (1.88) I
2M	9	−10.3	K 41.6 (1.34) S$_A$ 52.5 (1.08) I
3M	10	−10.3	K 59.4 (1.84) S$_A$ 84.4 (1.84) I
4M	11	−10.3	K 53.8 (7.10) S$_A$ 80.2 (0.95) I
5M	8	−6.3	K 45.6 (8.06) N* 75.4 (0.10) I
6M	9	−6.3	K 38.9 (3.54) N* 72.6 (0.10) I
7M	10	−6.3	K 13.9 (1.21) N* 39.9 (0.67) I
8M	11	−6.3	K 37.3 (2.06) N* 43.5 (0.55) I

[a)] According to Scheme 1.
[b)] 23 °C; sodium D-line; concentration c = 1 g/cm^3, chloroform.
[c)] K = crystalline, S$_A$ = smectic A, N* = cholesteric, I = isotropic; 1 cal = 4.18 J.

mers were easily polymerized when they were heated over 100 °C, their thermal transitions were reported based on the DSC first heating scan. Tab. 1 summarizes the thermal transitions and thera modynamic parameters of monomers **1M–8M**. Monomers **1M–4M** reveal a smectic A phase while monomers **5M–8M** which contain a lateral chloro substituent, present a cholesteric mesomorphic behavior. The results demonstrate that introducing a lateral chloro substituent into the mesogenic core will cause a significant depression in melting point and the order of the mesophase of a monomer.

The free-radical polymerization results of the monomers are summarized in Tab. 2. The molecular weights of these polymers were determined by means of gel-permeation chromatography (GPC), using a calibration based on polystyrene stan-

Tab. 2. Number-average molecular weight $\bar{M}_n$, weight-average molecular weight $\bar{M}_w$, phase transitions, and phase transition enthalpies for polymers **1P–8P**

Polymer	$m^{a)}$	$10^{-3} \cdot \bar{M}_n$	$10^{-3} \cdot \bar{M}_w$	Phase transitions in °C (corresponding enthalpy changes in kcal/mol)[b] heating cooling
1P	8	14.7	27.8	G 22.4 S_B 75.8 (0.47) S_A 141.9 (1.59) I I 128.1 (1.04) S_A 60.8 (0.51) S_B 7.0 G
2P	9	22.9	31.8	G 7.0 S_B 64.1 (0.71) S_A 114.9 (0.93) I I 114.0 (0.93) S_A 59.6 (0.69) S_B − 6.1 G
3P	10	17.1	37.1	G 25.0 S_B 80.4 (0.74) S_A 150.0 (1.99) I I 142.9 (1.72) S_A 77.1 (0.70) S_B 15 G
4P	11	28.4	54.4	G 3.1 S_B 82.3 (1.16) S_A 148.1 (1.83) I I 145.4 (1.53) S_A 78.3 (1.11) S_B − 3.1 G
5P	8	6.7	13.6	G 15.0 S_C^* 74.0 (0.05) S_A 108.7 (0.26) I I 100.1 (0.23) S_A 72.8 (0.05) S_C^* 11.5 G
6P	9	18.7	47.6	G 11.2 S_C^* 68.0 $(-)^{c)}$ S_A 115.6 (1.20) I I 110.4 (1.11) S_A 63.0 $(-)^{c)}$ S_C^* 6.7 G
7P	10	19.1	46.2	G 14.0 S_C^* 76.0 $(-)^{c)}$ S_A 113.5 (1.01) I I 107.9 (0.87) S_A 73.0 $(-)^{c)}$ S_C^* 7.6 G
8P	11	12.1	24.0	G 11.7 S_C^* 63.2 $(-)^{c)}$ S_A 113.6 (1.32) I I 110.0 (0.81) S_A 59.5 $(-)^{c)}$ S_C^* 9.1 G

[a] According to *Scheme 2*.
[b] Per mole repeating units. G = glassy, S_A = smectic A, S_B = smectic B, S_C^* = chiral smectic C, I = isotropic; 1 cal = 4.18 J.
[c] Enthalpy is very small and the transition temperature has been determined by optical microscopic observation.

dards, and therefore they are only relative. Thermal transitions and thermodynamic parameters of polymers **1P–8P** are also reported in Tab. 2. Polymers **1P–4P** reveal enantiotropic smectic A and B phases. Fig. 1 presents the representative DSC heating and cooling traces of polymer **1P**. In the heating scan (curve A), it shows a glass transition temperature at 22.4 °C, a smectic B to smectic A phase transition at
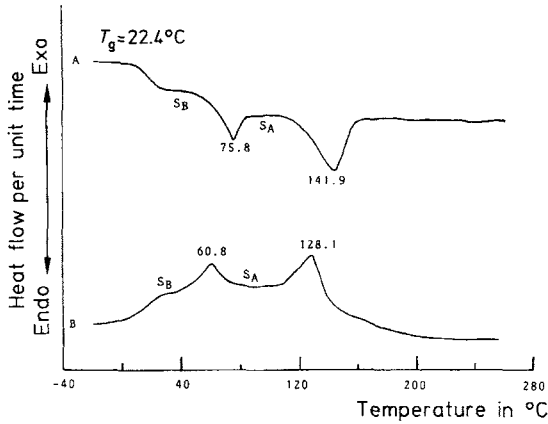

Fig. 1. Differential scanning calorimetry curves of polymer **1P** (10 °C/min): (A) second heating scan; (B) cooling scan
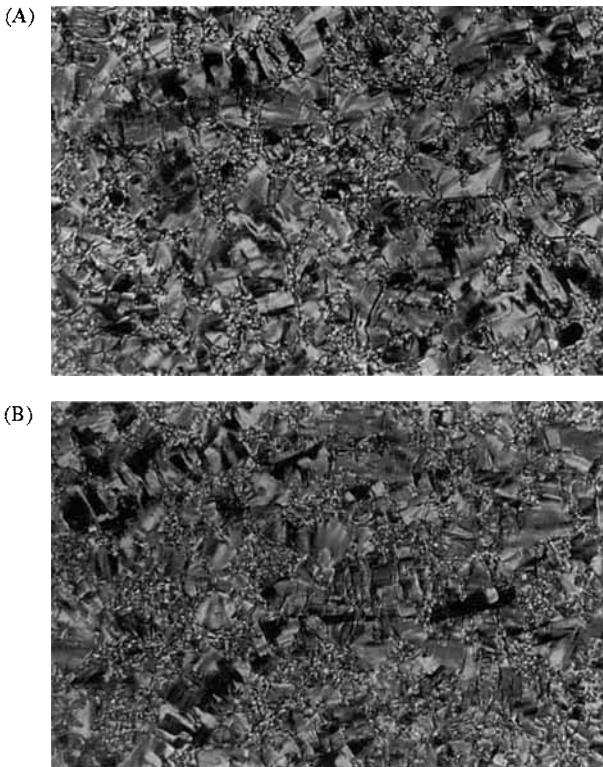
Fig. 2. Optical polarizing micrographs (original magnification: 320 ×) displayed by polymer **1P**: (A) S_A texture obtained after cooling to 116 °C; (B) S_B texture obtained after cooling to 35 °C

75.8 °C and a smectic A to isotropic phase transition at 141.9 °C. The cooling scan (curve B) looks almost identical to the heating scan, except that a very small super-cooling is observed for both exothermic transitions. Fig. 2 shows the typical smectic A and B textures exhibited by polymer 1P. The phase assignment was also con-ducted by X-ray diffraction measurements. Fig. 3 presents the temperature-depen-dent X-ray diffraction diagrams obtained from the powder sample of 1P at 100, 55 and 25 °C. Curve A reveals a diffuse reflection at about 4.69 Å, which corresponds to the lateral spacing of two mesogenic side groups, and a sharp first-order reflection at 34.16 Å, which corresponds to a d-spacing of smectic layers. The results verify
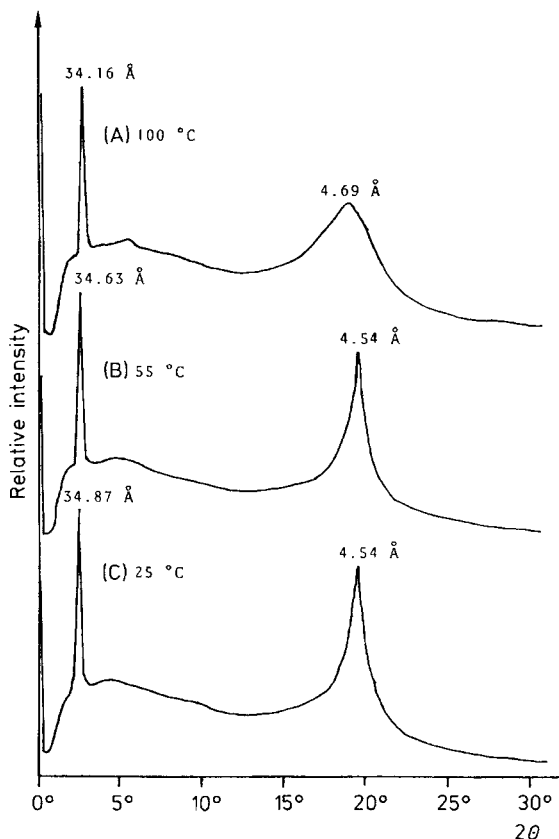
Fig. 3. Temperature-dependent X-ray mea-surements for polymer 1P at (A) 100, (B) 55, (C) 25 °C

the formation of a smectic A phase. When the measurement temperature was low-ered from 100 to 55 °C, the d-spacing of first-order reflection increases from 34.16 to 34.63 Å and the wide-angle reflection becomes very sharp (curve B). These results indicate the formation of a smectic B phase.

Polymers 5P–8P which contain, respectively, a lateral chloro substituent, reveal enantiotropic smectic A and chiral smectic C phases. Representative DSC traces for polymer 8P are presented in Fig. 4. A glass transition at 11.7 °C is displayed here, followed by a chiral smectic C to smectic A phase transition at 63.2 °C and a smectic
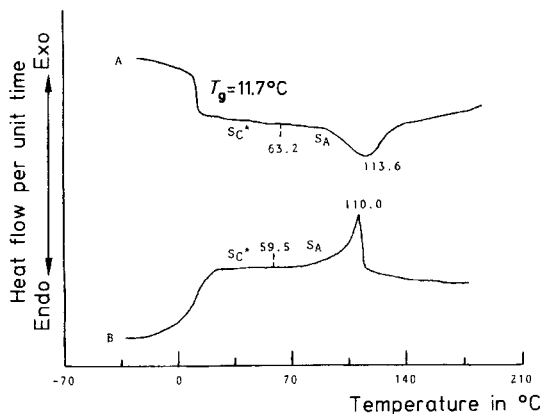
Fig. 4. Differential scanning calorimetry curves of polymer **8P** (10 °C/min): (A) second heating scan; (B) cooling scan. (S_C^*-S_A transitions were determined by optical microscopic observation)

A to isotropic phase transition at 113.6 °C on the heating scan (curve A). The cooling scan (curve B) looks almost identical to the heating scan, except that a very small supercooling (less than 5 °C) is observed for both exothermic transitions. The temperature-dependent X-ray diffraction diagrams obtained from powder samples of **8P**
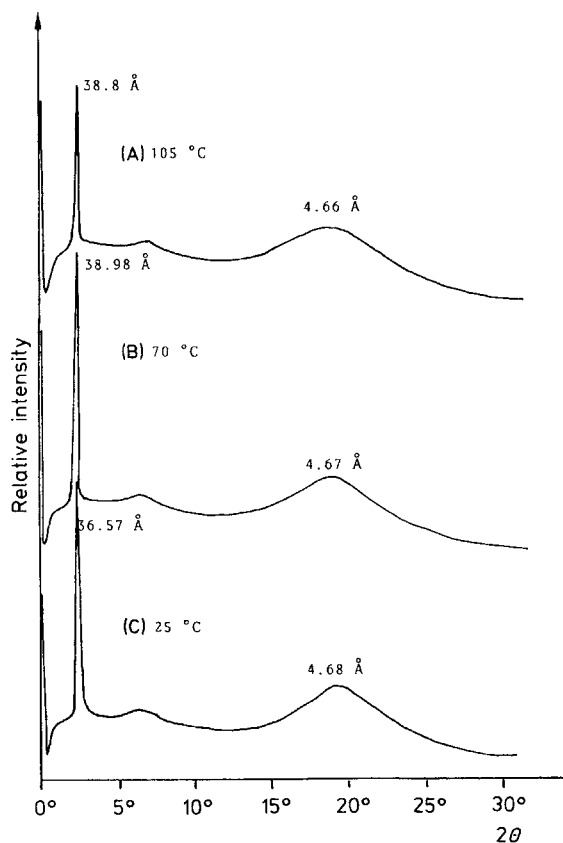
Fig. 5. Temperature-dependent X-ray measurements for polymer **8P** at (A) 105, (B) 70, (C) 25 °C

at 105, 70 and 30 °C are presented in Fig. 5. A broad reflection at wide angles (associated with the lateral packings) and a sharp reflection at low angles (associated with the smectic layers) are shown by all curves. Curve A presents a diffuse reflection at about 4.66 Å and a sharp first-order reflection at 38.80 Å. The optical polarizing micrograph (Fig. 6 A) reveals a focal-conic fan texture for polymer **8P** in this temperature range. Both results are consistent with a smectic A structure. When the measurement temperature is lowered from 105 to 70 °C, the d-spacing of the first-order reflection retains about the same value (Fig. 5, curve B). However, when the measurement temperature is further decreased from 70 to 30 °C, the d-spacing of the
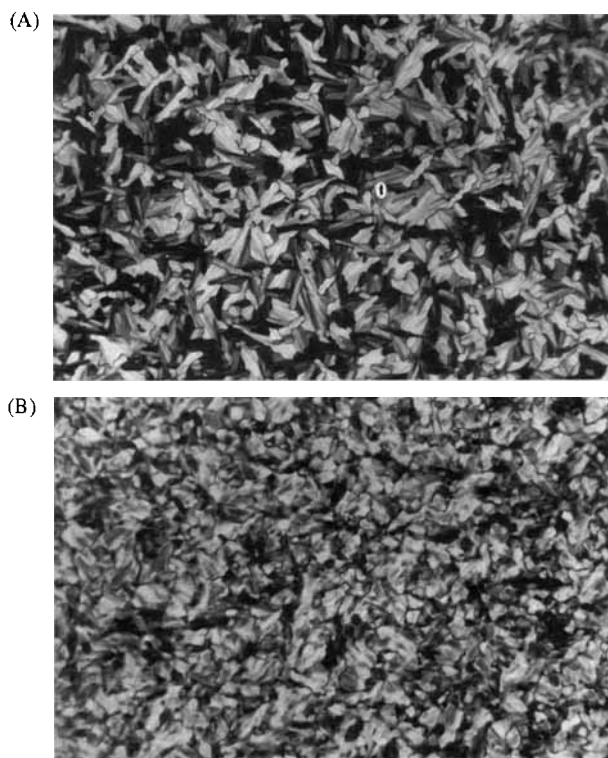
(A)

(B)

Fig. 6.   Optical polarizing micrographs (original magnification: 320 ×) displayed by polymer **8P**: (A) S_A texture obtained after cooling to 95 °C; (B) S_C^* texture obtained after cooling to 40 °C

first-order reflection decreases from 38.98 to 36.57 Å (curve C). This gives strong evidence for the formation of a tilted smectic C phase. Fig. 6 B displays the smectic C texture exhibited by polymer **8P**. The formation of a chiral smectic C phase was further verified by spontaneous polarization (P_s) measurements. A voltage of 70 V was applied to a 5 µm thick cell. Fig. 7 represents the polarization (P_s) as a function of temperature for polymer **8P**. The maximum P_s value of polymer **8P** was about 44 nC/cm^2 at 50 °C. The experimental results in this study indicate that all four polymers without lateral chloro substituent exhibit enantiotropic smectic A and smectic B phases and show no chiral smectic C phase. The reason could be that the 1,2-diphenylethane mesogenic group is flexible and undergoes free rotation about the
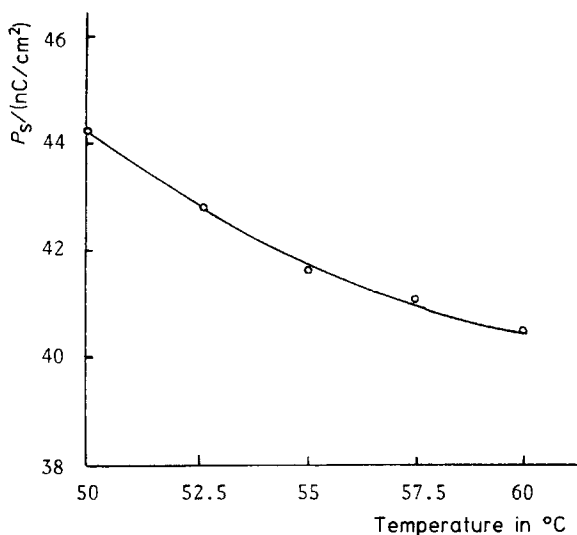
Fig. 7. Spontaneous polarization P_s versus temperature for polymer **8P** (70 V, cell thickness 5 µm)

ethane C—C bond leading to a number of different conformational isomers[36-38]. The presence of conformational isomers hinders the formation of a tilted chiral smectic C phase. Nevertheless, all four polymers containing the lateral chloro substituent reveal enantiotropic smectic A and chiral smectic C phases. Upon comparison of the mesomorphic behavior of polymers **5P–8P** with that of their corresponding polymers **1P–4P**, it is clear that introducing the lateral chloro substituent into the mesogenic core changes the length-to-breadth ratio of the molecule and therefore enhances the formation of a tilted chiral smectic C phase even if the 1,2-diphenylethane unit would form several conformational isomers.

In conclusion, two series of new side-chain liquid-crystalline polymethacrylates containing (2S)-2-chloro-4-methylvaleric acid end groups and 1,2-diphenylethane based mesogens have been prepared. All the obtained polymers show only smectic mesomorphism and do not undergo side-chain crystallization even if eleven methylene units are used to connect the polymer backbone and the mesogenic units. All four polymers without the lateral chloro substituent show smectic A and B phases while all the other four polymers with the chloro substituent present smectic A and chiral smectic C phases. The results seem to demonstrate that the flexible 1,2-diphenylethane based mesogen hinders the formation of a chiral smectic C phase. However, incorporating a lateral chloro substituent into the mesogenic core can enhance dramatically the tendency to form a chiral smectic C phase for the polymers prepared in this study.

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