# Semifluorinated polymers: 1. Synthesis and characterization of side chain liquid crystalline polymers containing semifluorinated oligooxyethylene based flexible spacers

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(*Received 22 November 1990; accepted 13 May 1990*)

The synthesis and characterization of polymethacrylates, polyacrylates and polysiloxanes containing 4-methoxy-4′-hydroxybiphenyl (4-BP), 4-methoxy-4′-hydroxy-α-methylstilbene (4-MS) and 4-hydroxy-4′-methoxy-α-methylstilbene (4′-MS) mesogenic groups and a semifluorinated triad based on tetrafluorooxetane, hexafluoropropylene oxide and trifluoroethylene oxide is described. All polymers display a $S_A$ mesophase and side chain crystallization. In the case of polymers based on 4-MS and 4′-MS the highest degree of decoupling seems to be displayed by the polymethacrylates. This result is in contrast to the behaviour of the corresponding polymers containing aliphatic spacers. The polymethacrylate based on 4-BP displays an unusual 'inverse' monotropic $S_A$-mesophase which to our knowledge was not previously encountered in any liquid crystal systems. The synthesis and characterization of copolymethacrylates and copolysiloxanes containing 4-methoxy-4′-hydroxy-α-methylstilbene and 4-hydroxy-4′-methoxy-α-methylstilbene constitutional isomers is also described.

**(Keywords: side chain liquid crystal polymers; semifluorinated spacers)**

## INTRODUCTION

The field of side chain liquid crystalline polymers was critically and extensively reviewed[1–10]. Nevertheless, still numerous problems remain contradictory or non-elucidated. One of the fundamental issues of this field refers to the mechanism by which the nature and molecular weight of the polymer backbone, and the nature and length of the flexible spacer determine the overall morphology of the resulting polymer and through it the type, the degree of order, and the dynamics of the mesophase formation.

Side chain liquid crystalline polymers containing paraffinic segments as flexible spacers are so far the most thoroughly investigated systems[1–10]. For this particular class of polymers the following general relationship seems to emerge. For polymers with molecular weights above which the phase transition temperatures are molecular weight independent[4,9,12] the length of the flexible spacer dictates the type of mesophase displayed by the polymer[9,13–16] and the degree of decoupling[2,17]. For the same spacer length, the nature of the polymer backbone determines the thermal stability of the mesophase (i.e., the isotropization temperature), its thermodynamic stability with respect to the crystalline phase (i.e., enantiotropic, monotropic, or virtual), and the degree of decoupling[12–16,18].

The effect of the polymer backbone can be explained based on thermodynamics[19]. Because the statistical random-coil conformation of the backbone gets distorted in the mesophase[20,21], its ease of distortion is determined by the backbone flexibility and seems to dictate the overall dynamics of the side chain liquid crystalline polymer[22]. Therefore, the highest degree of decoupling is provided by the most flexible polymer backbones. Smectic copolymers based on very flexible backbones and containing structural units with and without mesogenic groups display a microphase separated morphology in which the polymer backbone gets microsegregated between the smectic layers[9,23–28]. Such a polymer displays two glass transition temperatures[9,23–25]. One of these two glass transitions was assigned to the independent motion of the polymer backbone, the other to the cooperative motion of the side groups which in such systems is independent of the motion of the polymer backbone.

These polymer systems have the potential of providing side chain liquid crystalline polymers with very high degrees of decoupling. In such systems, by analogy to the known situation in immiscible polymer blends and microphase separated block and graft copolymers[29,30], we assume that the miscibility of the polymer backbone with the flexible spacer and the mesogenic groups should influence the overall morphology of the system and therefore, its dynamic behaviour. Based on these considerations, the investigation of side chain liquid

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0032-3861/91/101897-12

crystalline polymers containing novel types of flexible spacers is of both fundamental and practical interests. So far, in addition to paraffinic groups, only oligodimethylsiloxane[2] and oligooxyethylene[2,31–35] segments were investigated as flexible spacers.

The goal of this paper is to present our first series of experiments on the synthesis and characterization of side chain liquid crystalline polymers containing semifluorinated flexible spacers based on an oligooxyethylenic triad containing trifluoroethyleneoxide, hexafluoropropyleneoxide and tetrafluorooxetane structural units. 4-Methoxy-4′-hydroxybiphenyl (4-BP), 4-methoxy-4′-hydroxy-α-methylstilbene (4-MS), and 4-hydroxy-4′-methoxy-α-methylstilbene (4′-MS) were used as mesogenic side groups, while polymethacrylate, polyacrylate and poly(methylsiloxane) were used as polymer backbones.

A copolymethacrylate and a copoly(methylsiloxane) containing 4-MS and 4′-MS side groups were also synthesized and characterized. There are some additional reasons for which side chain liquid crystalline polymers containing semifluorinated flexible spacers can be of interest. Perfluorinated alkanes are highly immiscible with their hydrogenated alkane homologues and therefore exhibit high tendency towards microphase separation into distinct domains even when the molecular weights of the fluorocarbon and hydrocarbon segments are very low. Subsequently, semifluorinated *n*-alkanes display amphiphilic character, and behave as surfactants which exhibit both thermotropic and lyotropic (i.e., amphotropic) mesomorphism[36–40]. Polymerized liposomes based on fluorinated and non-fluorinated amphiphilic monomer pairs display also high tendency towards microphase separation[3,41,42].

Recently, it has been suggested that triphilic low molecular weight mesogens based on perfluorinated, paraffinic and biaryl segments may provide a new strategy towards the stabilization of a non-centrosymmetric arrangement within the layer of the smectic mesophase[43]. Therefore, polyphilic mesogens based on semifluorinated structures may also be of interest for the generation of materials displaying nonlinear optical and ferroelectric properties[43]. In conclusion, there are multiple fundamental reasons which justify the investigation of side chain liquid crystalline polymers containing semifluorinated flexible spacers.

To our knowledge this paper represents the first report on the synthesis and characterization of side chain liquid crystalline polymers containing semifluorinated flexible spacers.

## EXPERIMENTAL

### *Materials*

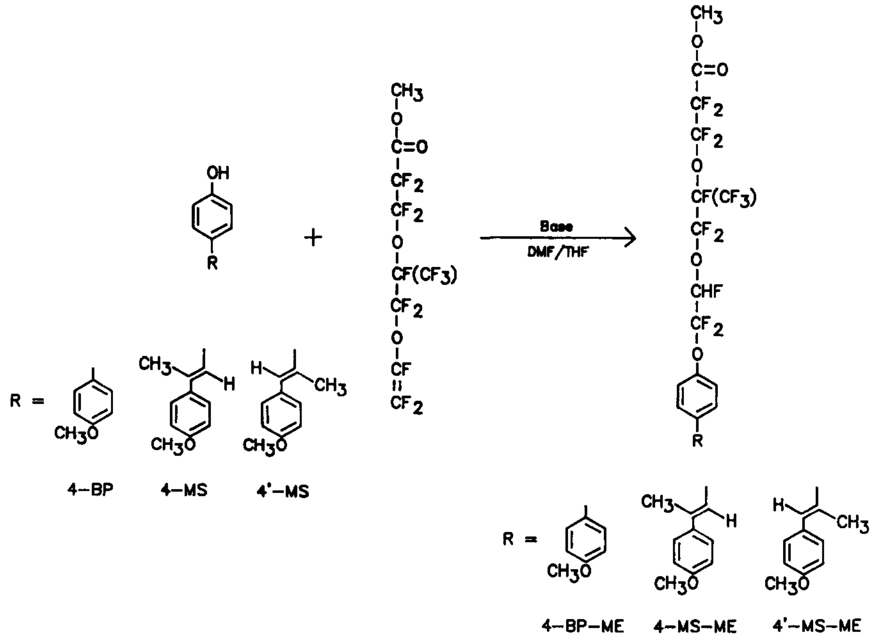
4-Methoxy-4′-hydroxybiphenyl (4-BP) was synthesized and purified as described previously[31]. 4-Methoxy-4′-hydroxy-α-methylstilbene (4-MS) and 4-hydroxy-4′-methoxy-α-methylstilbene (4′-MS) were synthesized by synthetic procedures developed previously[14,15]. Methyl 3-[2-(trifluoroethenoxy)-1-(trifluoromethyl)trifluoroethoxy]tetrafluoropropionate was synthesized according to a literature procedure[46]. Poly(methylhydro siloxane) ($\overline{DP}=10$) was synthesized as described in a previous publication from our laboratory[25]. Tetramethyldivinyldisiloxane platinum complex (Petrarch) used as catalyst in the hydrosilation reaction was diluted to 5% solution in xylene. All the other reagents were commercially available products and were used as received or purified by conventional methods.

### *Synthesis of monomers and polymers*

*Schemes 1* and *2* outline the synthesis of monomers.

### *Mesogens containing semifluorinated spacers terminated with a methyl ester group (4-BP-ME, 4-MS-ME, 4′-MS-ME)*

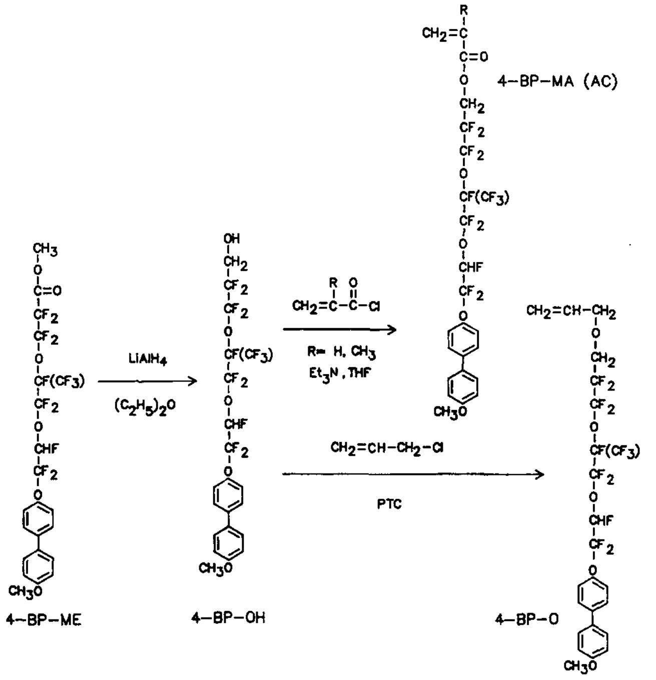
Short notations used for these compounds are presented in *Scheme 1 and Table 1*. In all cases the short



**Scheme 1** Synthesis of 4-methoxy-4′-hydroxybiphenyl (4-BP-ME), 4-methoxy-4′-hydroxy-α-methylstilbene (4-MS-ME) and 4-hydroxy-4′-methoxy-α-methylstilbene (4′-MS-ME) methyl ester derivatives containing the semifluorinated flexible spacer

notation used for the mesogenic group is followed by ME, which stands for methyl ester.

All methyl ester derivatives were prepared by the nucleophilic addition of phenolic -OH to the vinyl ether group of the fluorinated ester vinyl ether. An example is outlined below. To a solution of 5.0 g (0.025 mol) of 4-methoxy-4′-hydroxybiphenyl in 15 ml of DMF was added 0.52 g (0.0046 mol) of potassium t-butoxide. After stirring for 10 min, this solution was added over 1 h to a solution of 15.1 g (0.036 mol) of methyl 3-[2-(trifluoroethenoxy)-1-(trifluoromethyl)trifluoroethoxy]tetrafluoropropionate in 10 ml of anhydrous THF while maintaining the solution temperature at 20–22°C. After addition, the solution was stirred at room temperature for 5 h and poured into 200 ml of ice water containing three drops of conc. HCl. The aqueous mixture was extracted with 3 × 200 ml of ether. The combined ether extracts were dried over $MgSO_4$ and concentrated on a rotary evaporator to 20.4 g of oil. Kugelrohr distillation of the oil at 0.2 mm gave, after removing a small forerun, 13.3 g (86%) of product (4-BP-ME) which distilled at a bath temperature of 160–170°C. The white solid was sufficiently pure to use directly in the next step.



**Scheme 2** Synthesis of methacrylate (4-BP-MA), acrylate (4-BP-AC), and allyl ether (4-BP-O) containing semifluorinated flexible spacers and 4-methoxy-4′-hydroxybiphenyl based mesogens

### *Mesogens containing semifluorinated spacers terminated with an alcohol group (4-BP-OH, 4-MS-OH, 4′-MS-OH)*

The short notations used for these compounds consist of the short notation used to characterize the mesogenic group, followed by OH which stands for alcohol.

All alcohol derivatives were prepared by the reduction of the corresponding methyl esters with $LiAlH_4$ in dry diethyl ether. An example is as follows. In a 500 ml three neck round bottom flask equipped with condenser, drying tube, and addition funnel, and containing 3.00 g (0.0783 mol) of $LiAlH_4$ in 50 ml dry diethyl ether, a solution of 4-BP-ME (9.74 g, 0.0157 mol) in 30 ml dry diethyl ether was added dropwise with stirring. After the

**Table 1** Characterization of monomers

| Compound | Yield (%) | M.p. (°C) | 200 MHz $^1H$ n.m.r. ($CDCl_3$, $\delta$, ppm) |
|---|---|---|---|
| 4-BP-ME | 86 | 63 | $^{b}$3.76 (*s*, $C\underline{H}_3O$–); 3.88 (*d*, –$CO_2C\underline{H}_3$); 5.96 and 6.14 (2*s*, –$C\underline{H}F$–); 6.88–7.46 (*m*, 8 aromatic protons) |
| 4-BP-OH | 92 | 76 | 3.86 (*s*, $C\underline{H}_3O$–); 4.06 (*t*, –$C\underline{H}_2OH$); 5.94 and 6.21 (2*s*, –$C\underline{H}F$–); 6.97–7.54 (*m*, 8 aromatic protons) |
| 4-BP-MA | 65 | 34 | 1.94 (*s*, $C\underline{H}_3$–C–COO); 3.83 (*s*, $C\underline{H}_3O$–); 4.57 (*t*, –$C\underline{H}_2O$–); 5.64 and 6.17 (2*s*, $C\underline{H}_2$=); 5.93 and 6.20 (2*s*, –$C\underline{H}F$–); 6.94–7.51 (*m*, 8 aromatic protons) |
| 4-BP-AC | 84 | 45 | 3.86 (*s*, $C\underline{H}_3O$–); 4.63 (*t*, –$C\underline{H}_2O$–); 5.90–6.54 (*m*, $C\underline{H}_2=C\underline{H}$–); 5.97 and 6.23 (2*s*, –$C\underline{H}F$–); 6.97–7.56 (*m*, 8 aromatic protons) |
| 4-BP-O | 71 | 49 | 3.84 (*s*, $C\underline{H}_3O$–); 3.87 (*t*, –$C\underline{H}_2$–); 4.09 (*bs*, $CH_2=CH-C\underline{H}_2$–); 5.23 and 5.83 (*m*, $C\underline{H}_2=C\underline{H}$–); 5.93 and 6.20 (2*s*, –$C\underline{H}F$–); 6.94–7.51 (*m*, 8 aromatic protons) |
| 4-MS-OH | 78 | 62$^{a}$ | 2.23 (*s*, $C\underline{H}_3$–C=); 3.84 (*s*, $C\underline{H}_3O$–); 4.04 (*t*, –$C\underline{H}_2OH$); 5.94 and 6.21 (2*s*, –$C\underline{H}F$–); 6.73 (*s*, Ph–$C\underline{H}$=); 6.90–7.46 (*m*, 8 aromatic protons) |
| 4-MS-MA | 83 | 11 | 1.94 (*s*, $C\underline{H}_3$–C–COO); 2.23 (*s*, $C\underline{H}_3$–C=); 3.84 (*s*, $C\underline{H}_3O$–); 4.59 (*t*, –$C\underline{H}_2O$–); 5.67 and 6.20 (2*s*, $C\underline{H}_2$=); 5.94 and 6.20 (2*s*, –$C\underline{H}F$–); 6.73 (*s*, Ph–$C\underline{H}$=); 6.90–7.46 (*m*, 8 aromatic protons) |
| 4-MS-AC | 78 | 15 | 2.23 (*s*, $C\underline{H}$–C=); 3.84 (*s*, $C\underline{H}_3O$–); 4.60 (*t*, –$C\underline{H}_2O$–); 5.91–6.54 (*m*, $C\underline{H}_2=C\underline{H}$–); 5.97 and 6.21 (2*s*, –$C\underline{H}F$–); 6.73 (*s*, Ph–$C\underline{H}$=); 6.90–7.44 (*m*, 8 aromatic protons) |
| 4-MS-O | 81 | 19 | 2.24 (*s*, $C\underline{H}_3$–C=); 3.84 (*s*, $C\underline{H}_3O$–); 3.89 (*t*, –$C\underline{H}_2O$–); 4.10 (*bs*, $CH_2=CH-C\underline{H}_2$–); 5.27 and 5.87 (*m*, $C\underline{H}_2=C\underline{H}$–); 5.94 and 6.21 (2*s*, –$C\underline{H}F$–); 6.73 (*s*, Ph–$C\underline{H}$=); 6.91–7.46 (*m*, 8 aromatic protons) |
| 4′-MS-ME | 79 | 31$^{a}$ | $^{b}$2.18 (*s*, $C\underline{H}_3$–C=); 3.78 (*s*, $C\underline{H}_3O$–); 3.89 (*d*, –$CO_2C\underline{H}_3$); 5.95 and 6.13 (2*s*, –$C\underline{H}F$–); 6.73 (*s*, Ph–$C\underline{H}$=); 6.86–7.45 (*m*, 8 aromatic protons) |
| 4′-MS-OH | 85 | 46$^{a}$ | 2.27 (*s*, $C\underline{H}_3$–C=); 3.86 (*s*, $C\underline{H}_3O$–); 4.06 (*t*, –$C\underline{H}_2OH$); 5.99 and 6.24 (*s*, –$C\underline{H}F$–); 6.80 (*s*, Ph–$C\underline{H}$=); 6.94–7.53 (*m*, 8 aromatic protons) |
| 4′-Ms-MA | 83 | −9 | 1.97 (*s*, $C\underline{H}_3$–C–COO); 2.29 (*s*, $C\underline{H}_3$–C=); 3.88 (*s*, $C\underline{H}_3O$–); 4.65 (*t*, –$C\underline{H}_2O$–); 5.73 and 6.26 (2*s*, $C\underline{H}_2$=); 6.01 and 6.26 (2*s*, –$C\underline{H}F$–); 6.83 (*s*, Ph–$C\underline{H}$=); 7.00–7.58 (*m*, 8 aromatic protons) |
| 4′-MS-AC | 64 | 3 | 2.26 (*s*, $C\underline{H}_3$–C=); 3.84 (*s*, $C\underline{H}_3O$–); 4.61 (*t*, –$C\underline{H}_2O$–); 5.95 and 6.21 (2*s*, –$C\underline{H}F$–); 5.91–6.54 (*m*, $C\underline{H}_2=C\underline{H}$–); 6.77 (*s*, Ph–$C\underline{H}$=); 6.91–7.50 (*m*, 8 aromatic protons) |
| 4′-MS-O | 75 | 7 | 2.26 (*s*, $C\underline{H}_3$–C=); 3.84 (*s*, $C\underline{H}_3O$–); 3.87 (*t*, –$C\underline{H}_2O$–); 4.10 (*bs*, $CH_2=CH-C\underline{H}_2$–); 5.26 and 5.84 (*m*, $C\underline{H}_2=C\underline{H}$–); 5.93 and 6.20 (2*s*, –$C\underline{H}F$–); 6.74 (*s*, Ph–$C\underline{H}$=); 6.90–7.49 (*m*, 8 aromatic protons) |

[a] $T_m = T_i$
[b] $CD_2Cl_2$

**Table 2** Characterization of polymers containing semifluorinated flexible spacers and 4-methoxy-4′-hydroxybiphenyl based mesogens

| Polymer | $\bar{M}_n \times 10^{-3}$ | $\bar{M}_w/\bar{M}_n$ | Thermal transitions (°C) and thermodynamic parameters [ΔH (kcal mru$^{-1}$)/ΔS (cal mru$^{-1}$ K$^{-1}$)]$^a$ |
|---|---|---|---|
| 4–BP–PMA | 49.0 | 2.1 | *k* 114(0.89/2.29) $S_A$ 124(1.97/4.97) *i*<br>*i* 107(2.82/7.41) *k* |
| 4–BP–PMA$^b$ | 49.0 | 2.1 | *k* 109(0.79/2.06) $S_A$ 124(1.99/5.01) *i*<br>*i* 107(2.82/7.41) *k* |
| 4–BP–PAC | 15.4 | 2.0 | *k* 112(1.61/4-19) $S_A$ 142(1.38/3.33) *i*<br>*i* 130(1.39/3.44) $S_A$ 104(1.50/3.99) *k* |
| 4–BP–PS$^c$ | 12.7 | 3.1 | *k* 91(2.55/7.00) *i*<br>*i* 82(1.46/4.11) $S_A$ 74(1.30/3.74) *k* |
| 4–BP–PS | 12.7 | 3.1 | *k* 85(1.26/3.53) $S_A$ 95(1.47/4.01) *i*<br>i 82(1.46/4.11) $S_A$ 74(1.30/3.74) *k* |

[a] First line corresponds to heating d.c.s. scan; second line corresponds to cooling d.s.c. scan

[b] Heating scan after quenching to −30°C

[c] First heating scan

Mole repeat unit, mru

addition was completed, the reaction mixture was stirred under reflux for 3 h. The excess of $LiAlH_4$ was decomposed by dropwise addition of 50 ml of water, followed by 100 ml of 10% aqueous HCl solution. The ether layer was separated, washed with water, dried over $MgSO_4$ and evaporated to dryness to yield 8.53 g (92%) of product, m.p. 76°C (d.s.c.). The yields, melting points, and 200 MHz $^1H$ n.m.r. spectral characterization of all derivatives are presented in *Table 1*.

### *Mesogens containing semifluorinated spacers terminated with a methacrylate (4-BP-MA, 4-MS-MA, 4′-MS-MA) or acrylate (4-BP-AC, 4-MS-AC, 4′-MS-AC) group*

Short notations for these compounds contain the notation for the mesogenic group followed by MA or AC which stand for methacrylate and acrylate respectively.

All monomers were synthesized by the esterification of the corresponding alcohol derivatives with acryloyl or methacryloyl chloride. An example is as follows. 4-BP-OH (2.50 g, 0.0042 mol) was dissolved in 30 ml of dry THF, followed by 0.68 ml (0.0049 mol) of dry triethylamine. The resulting solution was cooled to 0°C in an ice-water bath and 0.38 ml (0.0046 mol) of acryloyl chloride was added dropwise. The reaction mixture was allowed to warm up to room temperature and was kept stirring overnight. The precipitated $Et_3N \cdot HCl$ was filtered and THF was evaporated in a rotary evaporator at room temperature. The crude product was dissolved in $CH_2Cl_2$, washed with aqueous $NaHCO_3$ solution, water, dried over $MgSO_4$, and purified by column chromatography (silica gel, $CH_2Cl_2$ eluent) to yield 2.30 g (84%) of white product. Purity >99% (h.p.l.c.); m.p. 45°C (d.s.c.). The characterization of all methacrylates and acrylates is summarized in *Table 1*.

### *Radical polymerization and copolymerization of methacrylates and acrylates*

All monomers were polymerized or copolymerized in dry benzene using AIBN as initiator at 60°C for 24 h. Polymerizations were carried out in Schlenk tubes under nitrogen atmosphere after 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 benzene and precipitated into methanol. The filtered polymers were dried under vacuum and then were purified by successive reprecipitations from THF solutions into methanol until g.p.c. analysis showed no traces of unreacted monomer, or oligomers. Conversions were higher than 90% in all cases. *Tables 2* and *3* summarize the characterization of all polyacrylates, polymethacrylates and copolymethacrylates.

### *Mesogens containing semifluorinated spacers terminated with an allyl ether group (4-BP-O, 4-MS-O, 4′-MS-O)*

The short notations used for these compounds consist of the short name of the mesogenic unit followed by O which stands for olefin.

All compounds were synthesized by the phase-transfer catalysed etherification of the corresponding alcohols with allyl chloride. An example is presented below. A solution of 4-BP-OH (1.50 g, 0.0025 mol), 2.0 ml of 50% (w/v) aqueous NaOH solution, TBAH (0.086 g, 0.0003 mol), and allyl chloride (0.31 ml, 0.0038 mol) in 6 ml of solvent (benzene/DMSO, 5/1 v/v) was stirred at 60°C for 5 h. The reaction mixture was cooled to room temperature, diluted with benzene, washed with water, dried with $MgSO_4$ and the solvent was evaporated in a rotary evaporator. The crude product was purified by column chromatography (silica gel, $CH_2Cl_2$ eluent) to yield 1.15 g (71%) of pure product. Purity >99% (h.p.l.c.); m.p. 49°C. *Table 1* presents the characterization of all allyl ethers synthesized.

### *Synthesis of polymethylsiloxanes and copolymethylsiloxanes*

Liquid crystalline polymethylsiloxanes were synthesized using the following representative procedure. The olefinic derivative (4-BP-O) (0.80 g, 20 mol% excess *versus* the Si–H groups present in the polymethylhydrosiloxane) was dissolved in 30 ml of dry, freshly distilled toluene together with the proper amount of poly(methylhydrosiloxane) ($\overline{DP} = 10$). The reaction mixture was heated to 60°C under nitrogen, and 100 $\mu$g of tetramethyldivinyldisiloxane platinum catalyst were then added with a syringe as solution in xylene (5%). The reaction mixture was stirred at that temperature until both i.r. and

**Table 3** Characterization of polymers and copolymers containing semifluorinated flexible spacers and 4-methoxy-4'-hydroxy-α-methylstilbene and/or 4-hydroxy-4'-methoxy-α-methylstilbene based mesogens

| Polymer | $\bar{M}_n \times 10^{-3}$ | $\bar{M}_w/\bar{M}_n$ | Thermal transitions (°C) and thermodynamic parameters [ΔH (Kcal mru$^{-1}$)/ΔS (cal mru$^{-1}$ K$^{-1}$)][a] |
|---|---|---|---|
| 4-MS-PMA[a] | 35.2 | 2.0 | $k$ 54(1.07)/3.28) $\mathrm{S_A}$ 118(0.86/2.19) $i$<br>$i$ 99(0.84/2.26) $\mathrm{S_A}$ −4 $g$ |
| 4-MS-PMA | 35.2 | 2.0 | $g$ 2 $\mathrm{S_A}$ 115(0.86/2.23) $i$<br>$i$ 99(0.84/2.26) $\mathrm{S_A}$ −4 $g$ |
| 4-MS-PAC[b] | 6.1 | 1.2 | $k$ 50(1.71/5.31) $i$<br>$i$ 25(0.06/0.18) $\mathrm{S_A}$ 0 $g$ |
| 4-MS-PAC | 6.1 | 1.2 | $g$ 1 $\mathrm{S_A}$ 37(0.26/0.82) $i$<br>$i$ 25(0.06/0.18) $\mathrm{S_A}$ 0 $g$ |
| 4-MS-PS[b] | 35.4 | 2.4 | $k$ 50(3.31/10.23) $i$<br>$i$ 36(0.20/0.64) $\mathrm{S_A}$ 31(2.31/7.59) $k$ |
| 4-MS-PS | 35.4 | 2.4 | $k$ 44(0.76/2.41) $k$ 50(1.86/5.75) $i$<br>$i$ 36(0.20/0.64) $\mathrm{S_A}$ 31(2.31/7.59) $k$ |
| 4'-MS-PMA[b] | 25.3 | 1.8 | $g$ 1 $k$ 43(0.16/0.49) $\mathrm{S_A}$ 75(0.52/1.49) $i$<br>$i$ 62(0.61/1.82) $\mathrm{S_A}$ −5 $g$ |
| 4'-MS-PMA | 25.3 | 1.8 | $g$ −3 $k$ 54(0.05/0.15) $\mathrm{S_A}$ 74(0.67/1.92) $i$<br>$i$ 62(0.61/1.82) $\mathrm{S_A}$ −5 $g$ |
| 4'-MS-PAC[b] | 18.0 | 1.7 | $k$ 48(0.66/2.06) $i$<br>$i$ 45(0.19/0.61) $\mathrm{S_A}$ 2 $g$ |
| 4'-MS-PAC | 18.0 | 1.7 | $g$ 9 $\mathrm{S_A}$ 52(0.33/1.02) $i$<br>$i$ 45(0.19/0.61) $\mathrm{S_A}$ 2 $g$ |
| 4'-MS-PS | 36.0 | 2.9 | $k$ 39(2.09/6.69) $i$<br>$i$ 28(0.36/1.20) $\mathrm{S_A}$ 18(1.88/6.46) $k$ |
| 4'-MS-PS | 36.0 | 2.9 | $k$ 26(0.15/0.49) $k$ 34(2.03/6.60) $i$<br>$i$ 28(0.36/1.20) $\mathrm{S_A}$ 18(1.88/6.46) $k$ |
| 4,4'(1/1)-MS-coPMA[b] | 31.5 | 2.9 | $g$ −5 $k$ 48(0.74/2.30) $\mathrm{S_A}$ 107(0.89/2.33) $i$<br>$i$ 89(0.80/2.21) $\mathrm{S_A}$ −3 $g$ |
| 4,4'(1/1)-MS-coPMA | 31.5 | 2.9 | $g$ 2 $\mathrm{S_A}$ 104(0.86/2.29) $i$<br>$i$ 89(0.80/2.21) $\mathrm{S_A}$ −3 $g$ |
| 4,4'(1/1)-MS-coPS[b] | 43.6 | 2.3 | $k$ 43(2.16/6.84)[c] $i$<br>$i$ 24(1.76/5.93) $k$ |
| 4,4'(1/1)-MS-coPS | 43.6 | 2.3 | $k$ 38(1.96/6.30) $\mathrm{S_A}$ 44[d] $i$<br>$i$ 24(1.76/5.93) $k$ |

[a] First line corresponds to heating d.s.c. scan; second line corresponds to cooling d.s.c. scan
[b] First heating scan
[c] Multiple endotherms
[d] Overlapped transition

200 MHz $^1$H n.m.r. analyses showed that all Si–H groups were consumed (about 4–6 h). The white polymers were separated by precipitation into methanol, and were purified by successive precipitations from chloroform solutions into methanol until g.p.c. analysis showed that the polymers were free of unreacted 4-BP-O derivative. To avoid contamination of the resulting polymers with polydimethylsiloxane from silicon grease, only teflon tape and teflon gaskets were used in the hydrosilation equipment. The characterization of polymethylsiloxanes and copolymethylsiloxanes is presented in *Tables 2* and *3*.

### *Techniques*

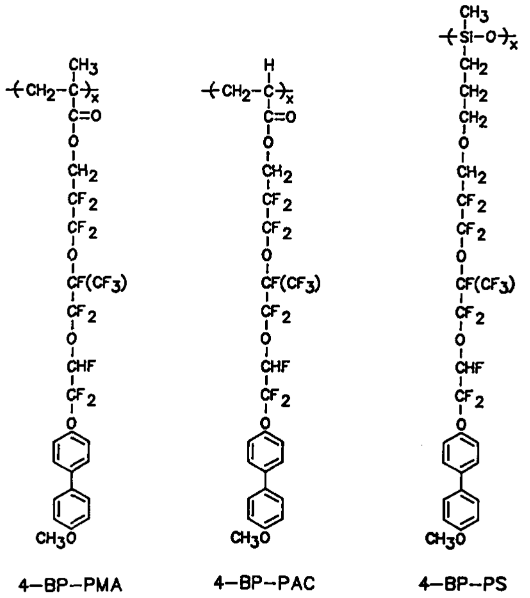
$^1$H n.m.r. spectra (200 MHz) were recorded on a Varian XL-200 spectrometer. All specra were recorded in $CDCl_3$ solutions with TMS as internal standard.

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 rates were 20°C min$^{-1}$. Glass transition temperatures ($T_g$) were read at the middle of the change in heat capacity. 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 to explain it will be made. 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 FP80 central processor was used to observe the thermal transitions and to analyse the anisotropic textures[44,45]. Molecular weights were determined by gel permeation chromatography (g.p.c.) with a Perkin–Elmer series 10 LC instrument equipped with LC-100 column oven, LC-600 autosampler, and a Nelson Analytics 900 series data acquisition system. High pressure liquid chromatography (h.p.l.c.) determinations were performed with the same instrument. The molecular weight measurements were made using a u.v. detector, THF as solvent (1 ml min$^{-1}$; 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 with polystyrene standards.

## RESULTS AND DISCUSSION

*Scheme 1* outlines the synthesis of the 4-BP, 4-MS and 4′-MS derivatives containing a semifluorinated flexible spacer terminated with a methyl ester group, i.e. 4-BP-ME, 4-MS-ME and 4′-MS-ME. The introduction of the semifluorinated spacer group is accomplished through the base catalysed addition of the phenolic -OH to the vinyl ether of the fluorinated ester vinyl ether[46]. Although nucleophilic additions to fluorinated olefins are well known[47], few examples of the addition of -OH[48] or other nucleophiles[49] to fluorovinyl ethers have been reported. The addition reaction occurs selectively with the vinyl ether in the presence of a reactive fluorinated ester. Although the esters could be purified by column chromatography, substantial amounts of material were lost, presumably due to the hydrolysis of the ester group. Better yields were generally obtained by reduction of the crude ester to the alcohol which was easily purified.

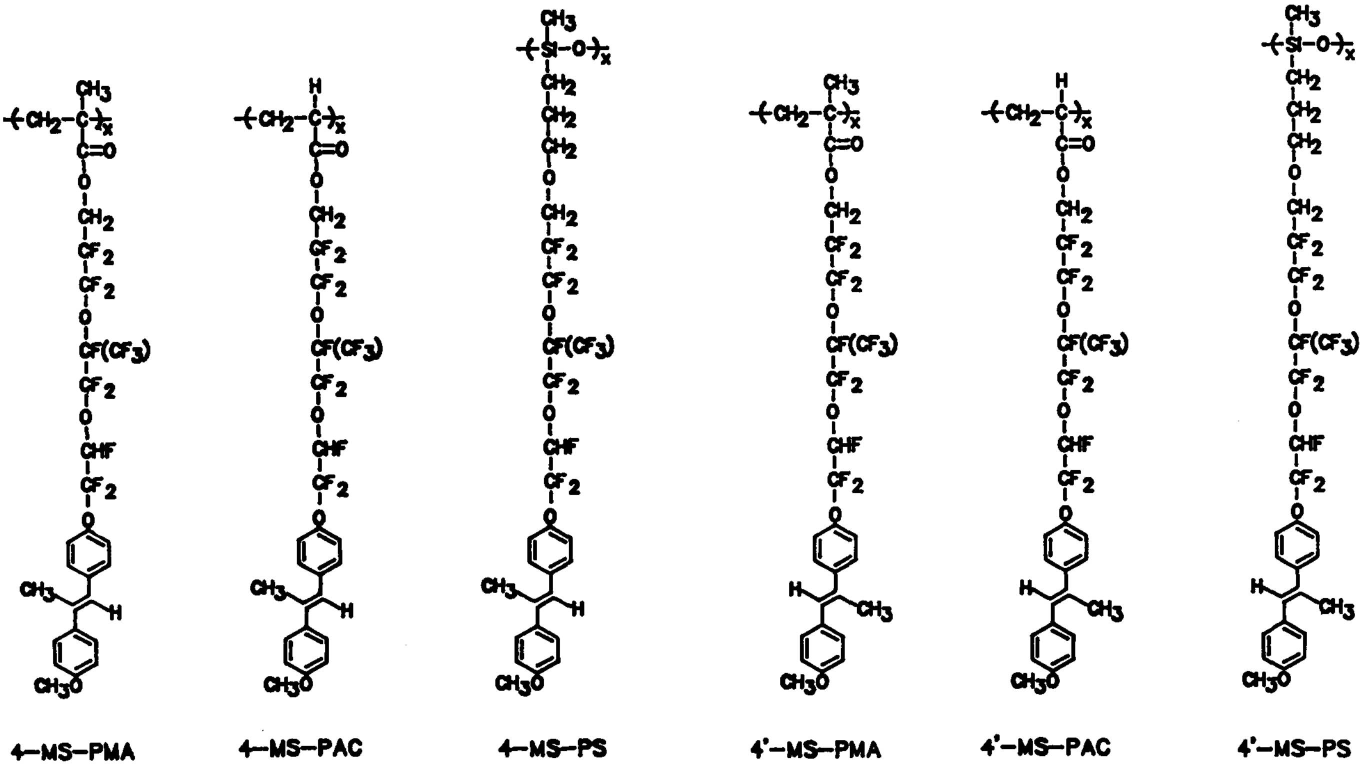


**Scheme 3** Polymethacrylate (4-BP-PMA), polyacrylate (4-BP-PAC), and polymethylsiloxane (4-BP-PS) containing semifluorinated flexible spacers and 4-methoxy-4′-hydroxybiphenyl based mesogens

*Scheme 2* presents the synthesis of 4-BP-OH, 4-BP-MA, 4-BP-AC and 4-BP-O. The methyl ester derivatives were reduced to the corresponding alcohols with $LiAlH_4$–diethyl ether. The resulting alcohols were esterified with methacryloyl or acryloyl chloride to yield the corresponding methacrylate and acrylate monomers. Alternatively, they were etherified with allyl chloride under phase transfer catalysed conditions[50] to provide the corresponding allyl ethers. The semifluorinated alcohol derivatives are more acidic than their aliphatic analogues and therefore, they can be easily deprotonated and etherified under liquid–liquid phase transfer catalysed conditions. Under phase transfer catalysed reaction conditions the reactivity of these semifluorinated alcohols resembles more the reactivity of phenols rather than that of aliphatic alcohols.

The acrylate and methacrylate monomers were polymerized using AIBN as a radical initiator. The allyl ether derivatives were hydrosilylated with a poly(methylhydrosiloxane) to provide poly(methylsiloxane)s containing mesogenic side groups. The structure of the polymers containing 4-BP mesogenic side groups is outlined in *Scheme 3*. *Scheme 4* presents the structure of the polymers containing 4-MS and 4′-MS mesogenic side groups.

The molecular weights and the thermotropic behaviour of all polymers are summarized in *Tables 2* and *3*. These molecular weights were obtained by using a g.p.c.



**Scheme 4** Polymethacrylates (4-MS-PMA, 4′-MS-PMA), polyacrylates (4-MS-PAC, 4′-MS-PAC), and polymethylsiloxanes (4-MS-PS, 4′-MS-PS) containing semifluorinated flexible spacers and 4-methoxy-4′-hydroxy-α-methylstilbene or 4-hydroxy-4′-methoxy-α-methylstilbene based mesogens

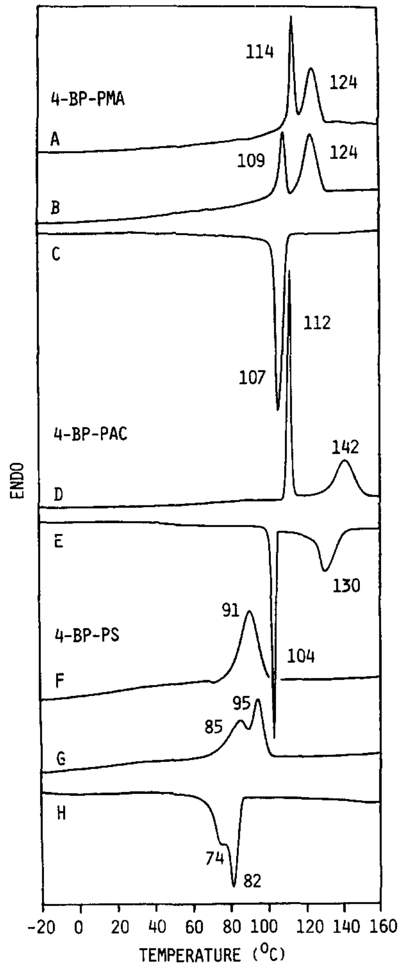


**Figure 1** Normalized d.s.c. scans (20°C min$^{-1}$) of: curve A, 4-BP-PMA, first and subsequent heating scans; curve B, 4-BP-PMA, heating scan after quenching the isotropic liquid to −30°C; curve C, 4-BP-PMA, first and subsequent cooling scans; curve D, 4-BP-PAC, first and subsequent heating scans; curve E, 4-BP-PAC, first and subsequent cooling scans; curve F, 4-BP-PS, first heating scan; curve G, 4-BP-PS, second and subsequent heating scans; curve H, 4-BP-PS, first and subsequent cooling scans

calibration based on polystyrene standards and therefore are only relative. Nevertheless, based on our previous experience with similar polymers containing aliphatic spacers[12,25], with the exception of 4-BP-PS from *Table 2* and 4-MS-PAC from *Table 3*, all polymers have molecular weights which are higher than those below which their phase transitions are molecular weight dependent. Therefore, the phase transition temperatures and the thermodynamic parameters of polymers based on different backbones and similar mesogenic side groups, or different mesogenic side groups but identical polymer backbones can be quantitatively considered.

We will first discuss the thermotropic behaviour of the polymers containing 4-BP mesogenic side groups. Representative differential scanning calorimetric traces displayed by different heating and cooling scans of these polymers are presented in *Figure 1*. First and subsequent heating and cooling scans of 4-BP-PMA are always identical and perfectly reproducible (curves A, C, *Figure 1*). On the first or subsequent heating scans 4-BP-PMA presents a melting transition at 114°C, followed by a $S_A$ mesophase which undergoes isotropization at 124°C. On cooling 4-BP-PMA presents the isotropic–crystalline transition at 107°C. Upon quenching the polymer from the isotropic phase to −30°C, the first transition temperature shifts to a slightly lower temperature i.e. 109°C. The isotropization transition temperature remains unchanged (curve B, *Figure 1*).

A characteristic focal conic texture displayed by the $S_A$ mesophase of 4-BP-PMA is presented in *Figure 2a*. We could not obtain a different texture for the crystalline phase of 4-BP-PMA because the motion of the polymer within this range of temperatures is frozen. The crystalline phase of 4-BP-PMA was confirmed by X-ray diffraction experiments.

The thermotropic behaviour of 4-BP-PMA is quite similar to that of the corresponding polymethacrylate containing 4-BP mesogenic side groups and a paraffinic flexible spacer consisting of 11 methylenic units[51]. For example, in the case of 4-BP-PMA, the degree of supercooling of the lowest temperature transition is only 7°C while that of the isotropic–liquid crystalline phase transition is 17°C. The corresponding polymethacrylate with a paraffinic spacer exhibits two smectic mesophases. The one at lower temperature displays a degree of supercooling of 5°C while the one at higher temperature a degree of supercooling of 10°C[51]. The enthalpy change of the peaks at 114 and 124°C from the heating scan is equal to that of the peak at 107°C from the cooling scan (*Table 2*). Therefore, the peak at 107°C is due to both isotropic-$S_A$ and $S_A$-crystalline transitions which are overlapped.

This behaviour transforms the $S_A$ mesophase exhibited by 4-BP-PMA into a monotropic mesophase which appears as an inverse monotropic mesophase. In the case of polymers containing paraffinic flexible spacers or of low molar mass liquid crystals, a monotropic mesophase (i.e., thermodynamically metastable with respect to the crystalline phase) is obtained as a result of the fact that the crystallization transition is supercooled more than the corresponding isotropic–mesomorphic transition. Subsequently, the monotropic mesophase can be observed only on cooling scans, and is thermodynamically metastable.

In the case of 4-BP-PMA the situation is reversed and the mesophase can be observed only on the heating scans; 4-BP-PMA displays a high ability towards side chain crystallization. In the case of most polymethacrylates containing flexible spacers based on 11 methylenic units, the side chain crystallization process is kinetically controlled while the mesophase formation is thermodynamically controlled[14,15]. In many cases, the side chain crystallization process requires extensive annealing above the $T_g$ of the polymer. Subsequently, most of the time no crystallization exotherm can be observed on the cooling scan. At the same time, the melting transition temperature and the enthalpy change associated with this transition are thermal history dependent. In the case of 4-BP-PMA, the melting and crystallization transition temperatures and the enthalpy changes associated with them are very little affected by the thermal history of the sample.

The high rate of crystallization of 4-BP-PMA suggests that the polymer based on the semifluorinated spacer exhibits a higher degree of decoupling than the similar polymers based on aliphatic spacers. The lower degree of supercooling of the crystalline phase *versus* that of the $S_A$ phase indicates that the difference of order between the isotropic and $S_A$ phase is higher than that between

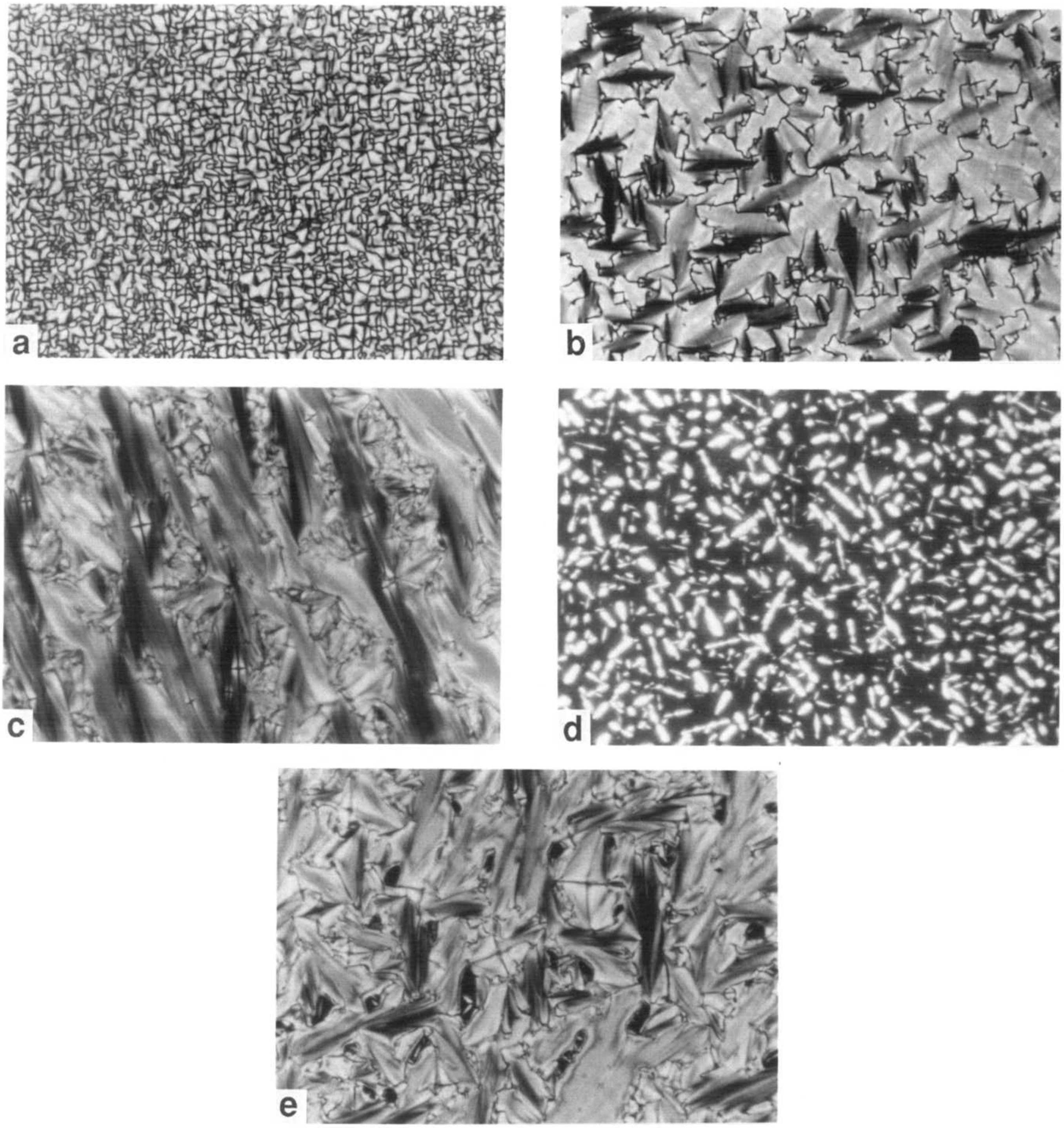


**Figure 2** Representative optical polarized micrographs ( × 100) of (a) 4-BP-PMA, after 5 min of annealing at 116°C on heating scan (below 107°C this texture remains unchanged); (b) 4-BP-PAC, after 5 min of annealing at 135°C on heating scan (below 100°C this texture remains unchanged); (c) 4-MS-PMA, after 10 min of annealing at 94°C on cooling scan; (d) 4-MS-PS, after 1 min at 46°C on cooling scan; (e) 4,4'-(1/1)-MS-coPMA, after 10 min of annealing at 90°C on cooling scan

the $S_A$ and crystalline phase. The thermodynamic data from *Table 2* support this statement.

Curves D and E in *Figure 1* present representative heating and cooling d.s.c. traces of 4-BP-PAC. First and subsequent heating and cooling scans are identical. This polymer displays also a crystalline phase followed by an enantiotropic $S_A$ mesophase. The degree of supercooling of the crystalline phase transition is lower (8°C) than that of the $S_A$-isotropic phase transition (12°C). Nevertheless, the isotropization temperature of 4-BP-PAC is higher than that of 4-BP-PMA, although the enthalpy and entropy changes associated with isotropization transitions are higher for polymethacrylate than for polyacrylate. Both trends are in agreement with the behaviour of the polymethacrylates and polyacrylates containing aliphatic flexible spacers[51].

Because the enthalpy changes of the transition peak from the heating d.s.c. scan at 112°C (curve D, *Figure 1*) and cooling scan at 104°C (curve E, *Figure 1*) are equal, we would tend to assign this peak to a transition from a $S_A$ mesophase into a highly ordered smectic mesophase rather than into a crystalline phase. However,

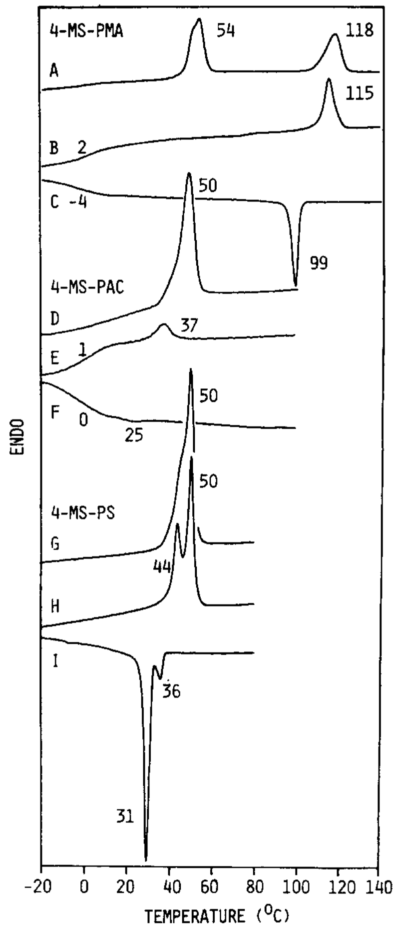


**Figure 3** Normalized d.s.c. scans (20°C min$^{-1}$) of: curve A, 4-MS-PMA, first heating scan; curve B, 4-MS-PMA, second and subsequent heating scans; curve C, 4-MS-PMA, first and subsequent cooling scans; curve D, 4-MS-PAC, first heating scan; curve E, 4-MS-PAC, second and subsequent heating scans; curve F, 4-MS-PAC, first and subsequent cooling scans; curve G, 4-MS-PS, first heating scan; curve H, 4-MS-PS, second and subsequent heating scans; curve I, 4-MS-PS, first and subsequent cooling scans

preliminary X-ray diffraction experiments show the low temperature phase to be crystalline. A representative focal conic texture exhibited by the $S_A$ mesophase of 4-BP-PAC is presented in *Figure 2b*.

Curves H and I in *Figure 1* present second and subsequent heating and cooling d.s.c. scans of 4-BP-PS. This polymer exhibits side chain crystallization and an enantiotropic $S_A$ mesophase. The degree of supercooling of the $S_A$ mesophase is again higher than that of the crystallization process. However, both melting and isotropization transition temperatures are lower than those of the 4-BP-PMA and 4-BP-PAC. The first heating scan of 4-BP-PS (curve G, *Figure 1*) or the heating scan after annealing above $T_g$ shows only a melting transition and the $S_A$-isotropic transition at 91°C. This demonstrates that under equilibrium conditions the $S_A$ mesophase of 4-BP-PS is only monotropic. At first sight, the lower isotropization and melting transition temperatures displayed by 4-BP-PS in comparison to those of 4-BP-PMA and 4-BP-PAC represent a reversed trend when compared to the influence of the polymer backbone on the phase transition temperatures of the corresponding polymers containing aliphatic spacers[51,52]. However, the spacer of 4-BP-PS contains three more methylenic units than that of the corresponding 4-BP-PMA and 4-BP-PAC. Therefore, it could be that the lower isotropization temperature of the polysiloxane is due to a combination of both longer spacer length (*Scheme 3*) and lower polymer molecular weight (*Table 2*).

*Figure 3* presents representative heating and cooling d.s.c. scans of 4-MS-PMA, 4-MS-PAC and 4-MS-PS. The corresponding phase transitions and their associated thermodynamic parameters are summarized in *Table 3*. All three polymers display a melting transition at about 50°C. In the case of 4-MS-PMA and 4-MS-PAC, this melting transition appears only in the first heating scan or after suitable annealing above $T_g$. In the case of 4-MS-PS, the melting process is very little dependent on the thermal history of the sample and appears on each heating or cooling scan regardless of their previous thermal history. All three polymers display a $S_A$ mesophase. This mesophase is enantiotropic in the case of 4-MS-PMA and monotropic in the case of 4.MS-PS. In the case of 4-MS-PAC, the mesophase is enantiotropic when recorded from second or subsequent heating and cooling scans (curves E and F, *Figure 3*). However, it is only monotropic under equilibrium conditions (curves D and F, *Figure 3*). The side chain crystallization process of the polymers based on 4-MS and semifluorinated spacers resembles that of the corresponding polymers based on aliphatic spacers. However, the isotropization transition temperatures of the polymers based on semifluorinated spacers and 4-MS decrease with increasing flexibility of the polymer backbone. This trend is reversed in the case of the polymers based on 4-MS and aliphatic flexible spacers[14].

At the present time we do not have any good explanation for this behaviour. In the case of 4-MS-PAC, the isotropization temperature is lower than that of 4-MS-PS most probably due to the fact that the molecular weight of the polyacrylate is below values where phase transition temperatures are molecular weight independent (*Table 3*). *Figure 2c* shows the focal conic texture exhibited by the $S_A$ phase of 4-MS-PMA, while *Figure 2d* the formation of batonnetes on cooling 4-MS-PS from the isotropic into the $S_A$ phase.

Representative d.s.c. traces of 4′-MS-PMA, 4′-MS-PAC and 4′-MS-PS are presented in *Figure 4*. The phase transition temperatures of these polymers and the corresponding thermodynamic parameters are summarized in *Table 3*. 4′-MS-PMA displays side chain crystallization and an enantiotropic $S_A$ mesophase. The side chain melting process of 4′-MS-PMA is thermal history dependent (curves A, B, *Figure 4*). The melting peak of 4′-MS-PAC appears only on the first heating scan or after suitable annealing. Therefore, under equilibrium conditions, the $S_A$ mesophase displayed by 4′-MS-PAC is only monotropic (curves D, F, *Figure 4*) although it appears enantiotropic when determined from second or subsequent heating and cooling scans (curves E, F, *Figure 4*).

The side chain crystallization process of 4′-MS-PS is very little dependent on the thermal history of the sample (curves G, H, and I, *Figure 4*) and is observable in every heating scan. The $S_A$ mesophase of 4′-MS-PS is only monotropic. As in the case of the polymers based on 4-MS, the polymers based on 4′-MS and semifluorinated spacers present isotropic transition temperatures which decrease with the increase of the polymer backbone flexbility. This result is opposite to the one obtained with the same mesogenic group and aliphatic flexible spacers[15]. For all polymer backbones, the isotropization

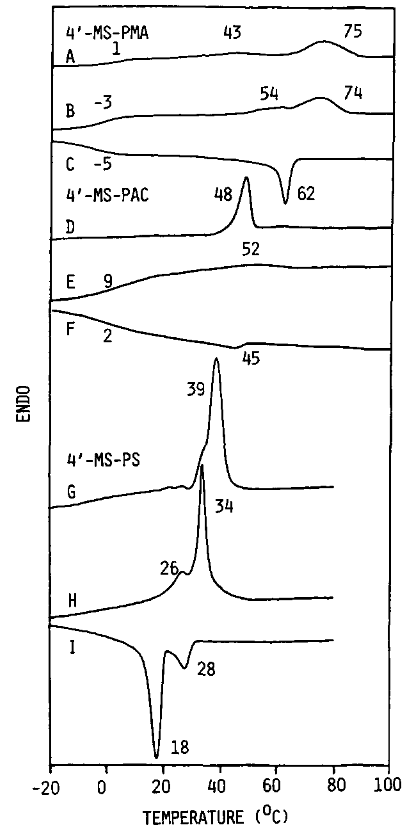
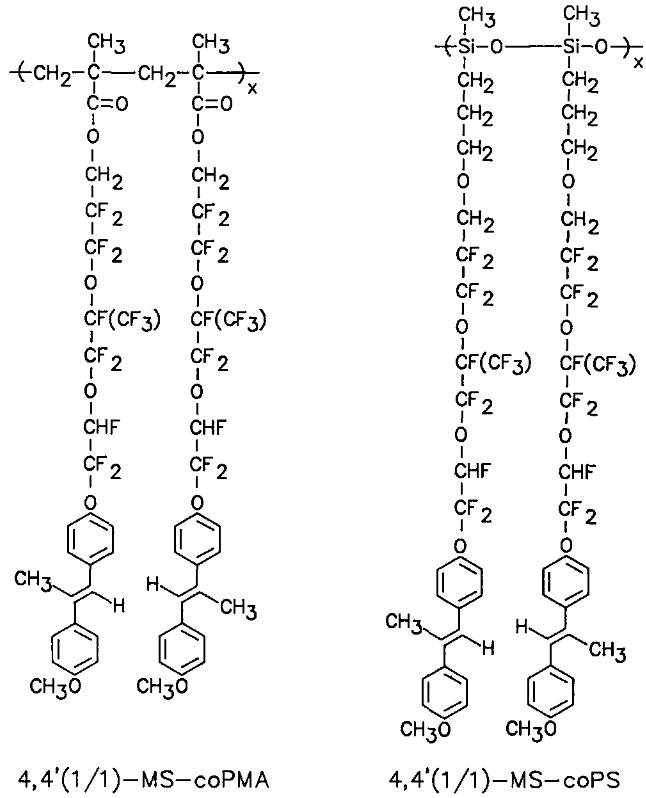


**Figure 4** Normalized d.s.c. scans ($20°C\,min^{-1}$) of: curve A, 4'-MS-PMA, first heating scan; curve B, 4'-MS-PMA, second and subsequent heating scans; curve C, 4'-MS-PMA, first and subsequent cooling scans; curve D, 4'-MS-PAC, first heating scan; curve E, 4'-MS-PAC, second and subsequent heating scans; curve F, 4'-MS-PAC, first and subsequent cooling scans; curve G, 4'-MS-PS, first heating scan; curve H, 4'-MS-PS, second and subsequent heating scans; curve I, 4'-MS-PS, first and subsequent cooling scans

and melting transition temperatures of the polymers based on 4-MS mesogenic group are higher than those based on 4'-MS. These data are in agreement with those obtained with 4-MS and 4'-MS mesogens, polymethacrylate, polyacrylate and polysiloxane backbones and paraffinic flexible spacers[14,15].

Previous experiments performed in our laboratory have demonstrated that copolymerization of the parent polymers' monomer pair containing 4-MS and 4'-MS constitutional isomeric mesogenic side groups suppresses the crystalline melting transition temperature more than the isotropization transition temperature. Therefore, these copolymerization experiments were used to transform monotropic or even virtual mesophases into enantiotropic mesophases[18,53]. This result is due to the fact that the structural units of the copolymer were isomorphic in the mesophase but not in the crystalline phase.

To see whether this concept applies to the liquid crystalline polymers and copolymers based on semifluorinated spacers we have synthesized the two copolymers described in *Scheme 5*. We can assume that the reactivities of 4-MS-MA ($M_1$) and 4'-MS-MA ($M_2$) are equal, and therefore, $r_1 = r_2 = 1$. Under these circumstances the copolymer composition is equal to the monomer feed and is independent of conversion (i.e., azeotropic copolymerization). Consequently, starting with a 1:1 mole ratio between 4-MS-MA and 4'-MS-MA in the reaction mixture we obtained 4,4'(1/1)-MS-coPMA copolymer from *Scheme 5*. Its d.s.c. traces are presented as curves A, B and C in *Figure 5*. In the first heating scan (curve A, *Figure 5*) this copolymer displays a melting transition at 48°C followed by an $S_A$ phase which



**Scheme 5** Copolymethacrylate [4,4'(1/1)-MS-coPMA], and copolymethylsiloxane [4,4'(1/1)-MS-coPS] containing semifluorinated flexible spacers and a 1/1 molar ratio of 4-methoxy-4'-hydroxy-α-methylstilbene/4-hydroxy-4'-methoxy-α-methylstilbene based mesogens

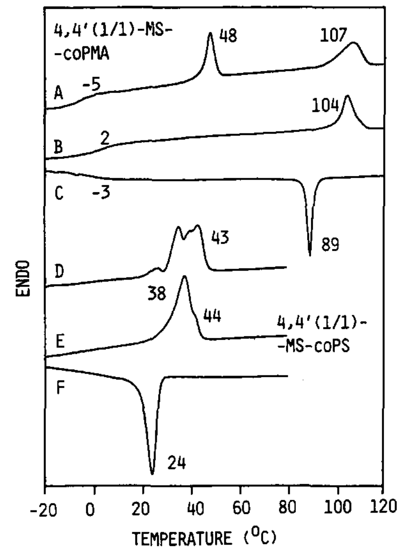


**Figure 5** Normalized d.s.c. scans ($20°C\,min^{-1}$) of: curve A, 4,4'(1/1)-MS-coPMA, first heating scan; curve B, 4,4'(1/1)-MS-coPMA, second and subsequent heating scans; curve C, 4,4'(1/1)-MS-coPMA, first and subsequent cooling scans; curve D, 4,4'(1/1)-MS-coPS, first heating scan; curve E, 4,4'(1/1)-MS-coPS, second and subsequent heating scans; curve F, 4,4'(1/1)-MS-coPS, first and subsequent cooling scans

undergoes isotropization at 107°C. Subsequent heating and cooling scans show only the enantiotropic smectic mesophase. *Figure 2e* presents the texture of the smectic mesophase exhibited by 4,4′(1/1)-MS-coPMA. Regardless of the thermal history of the sample, one of the parent homopolymers of this copolymer, i.e., 4′-MS-PMA, exhibits a melting transition (curves A, B, *Figure 4*). Therefore, for the case of polymethacrylates containing semifluorinated flexible spacers, copolymerization of the parent polymers' monomer pair containing 4-MS and 4′-MS constitutional isomeric mesogenic side groups suppresses the side chain crystallization tendency, as in the case of the copolymers based on paraffinic spacers. At the same time, this copolymerization experiment affects very little the formation of the mesophase.

However, this is not the case for the copolysiloxane 4,4′(1/1)-MS-coPS from *Scheme 5*. Its d.s.c. traces are presented in curves D, E and F of *Figure 5*. The first heating scan of 4,4′(1/1)-MS-coPS (curve D, *Figure 5*) displays multiple transitions which are difficult to assign. The second heating scan (curve E, *Figure 5*) presents a melting transition at 38°C followed by a smectic mesophase which undergoes isotropization at 44°C. On the cooling scan we can observe only a crystallization exotherm (curve F, *Figure 5*). Therefore, 4,4′(1/1)-MS-coPS presents an inverse monotropic mesophase which resembles the one displayed by 4-BP-PMA from *Figure 1* (curves A, B, C).

A previous publication from our laboratory[25] discusses the dependence of the smectic–isotropic transition peak width on the polymer molecular weight and on the composition of copolymers containing mesogenic and non-mesogenic structural units. The broadening of the peak was attributed to a higher miscibility between the polymer backbone and the mesogenic side groups in the smectic phase. These results were recently supported by additional experiments[28,54].

An inspection of the d.s.c. traces from *Figures 1, 2* and *3* shows that the isotropic-$S_A$ transition peak width is narrower in the case of polymethacrylates than in the case of polyacrylates and polysiloxanes. Therefore, it could be that the semifluorinated oligooxyethylene flexible spacer is more miscible with the last two polymer backbones than with the polymethacrylate backbone. This different miscibility may contribute to the overall mesomorphic behaviour of these polymers. The solubility of this semifluorinated oligooxyethylene spacer does not resemble that of perfluorinated paraffins. All intermediary compounds, monomers and polymers based on this semifluorinated spacer are much more soluble especially in basic solvents like tetrahydrofuran, alcohols, etc. This might be due to the presence of a very acidic proton in the trifluoroethoxy segment of the mesogenic group (*Schemes 1–3*). In addition, the formation of the textures of the polymethacrylates with semifluorinated spacers is much faster than that of the corresponding polyacrylates or polysiloxanes. At the same time, the isotropization enthalpies of polymethacrylates are higher than those of polyacrylates and polysiloxanes (*Tables 2* and *3*). Therefore, the peak widths, the dynamics of mesophase formation, the isotropization transition temperatures and their corresponding enthalpy changes, suggest a higher degree of decoupling for polymethacrylates than for polyacrylates and polysiloxanes. This result is in contrast to the behaviour of the corresponding polymers containing aliphatic flexible spacers[14,15,18,22,51–54]. The only two polymers which behave similar to the corresponding polymers based on aliphatic spacers[51] are 4-BP-PMA and 4-BP-PAC.

## ACKNOWLEDGEMENTS

Financial support from the Office of Naval Research is gratefully acknowledged.

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