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Functional polythiiranes: 5. Side chain liquid crystalline polythiiranes

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For the first time, a series of polythiiranes bearing in the side chain biphenyl and 4-alkoxybiphenyl mesogenic groups connected to the backbone with spacer groups of different lengths were prepared by anionic ring-opening polymerization of the corresponding thiirane derivatives. Unlike the corresponding polyoxiranes described in the literature, large methylene or oxyethylene spacers were needed in polythiiranes to observe liquid crystalline properties. But like the polyoxiranes, the polythiiranes exhibited mainly high ordered smectic A and E mesophases which were characterized by the usual techniques: d.s.c., polarized optical microscopy and X-ray diffraction. © 1997 Elsevier Science Ltd.

(Keywords: side chain liquid crystalline polymers; polythiiranes; anionic ring opening polymerization)

INTRODUCTION

Polythiiranes are well known polymers[1] but few attempts to functionalize these materials have been reported. For some years, we have performed studies in order to synthesize several types of functional polythiiranes with various properties according to the chemical groups present in the side chain[2–4]. We have obtained these functional polymers by thiirane ring opening with highly nucleophilic quaternary ammonium dithiobenzoates; the chimioselectivity of these salts towards the thiirane ring allows the polymerization of functional thiirane monomers in high yields. The goal of this work was to display the influence of the sulfur atom in the main chain on the properties of the functional side chains.

In spite of many papers dealing with side chain liquid crystal (SCLC) polymers[5], few studies have shown the dependence on phase transitions of the presence of a heteroatom in the main chain. Only a few examples of heteroatomic main chain SCLC polymers have been considered in the literature, e.g. polysulfones[6], polyamines[7,8], polyesters[9] and polyethers[10–14]. The flexibility of the ether backbone was used to explain the ordering of mesogenic pendent groups without spacer in SCLC polyoxiranes[11]. Polythiiranes SCLC appear not to have been studied until now. The substituents of polythiiranes, as for polyoxiranes, are located on every third atom along the main chain; these polymers containing C–S bonds larger than C–O bonds might also exhibit mesophases in the absence of a flexible spacer.

In a previous paper, we reported a new synthetic way to thiirane monomers bearing a biphenyl group as substituent and their ring opening polymerization[15]. As may be expected, these polymers do not behave as liquid crystals, as they do not bear any substituent on the mesogenic group. The synthesis was extended to a large kind of thiirane monomers and various structural modifications were realized.

We report in this paper the characterization of the corresponding polythiiranes bearing 4-alkyloxybiphenyl mesogenic group connected to the main chain through various spacers. We have studied the influence of the spacer on the thermal properties for this novel class of polymers, of the terminal group, of the distance between mesogenic groups (copolymers). Our results are compared with those described in the literature for identical mesogens.

EXPERIMENTAL

Materials

4,4′-Dihydroxy biphenyl (97%), 4-phenylphenol (97%), dimethylsulfate, bromobutane, 2-chloroethanol, 1,4-dibromobutane, 1,8-dibromooctane, bromoacetylbromide and 2,3-dimercaptopropanol were used as received, 6-Chloro-1-hexanol and 2-{2-[2-chloroethoxy]ethoxy} ethanol were commercial precursors for 6-iodo-1-hexanol and 8-iodo-3,6-dioxaoctanol. *N*,*N*-Dimethylformamide (99+%, spectrophotometric grade) was used as a solvent for polymerization.

Techniques

^1H and ^{13}C n.m.r. spectra were recorded on a Brucker AC 400 n.m.r. spectrometer; tetramethylsilane was used as a standard. Molecular weight of polymers were

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Table 1 ^{1}H n.m.r. chemical shifts for monomer precursors

Compound	Solvent	δ (ppm, reference TMS)
3	$CDCl_3$	3.94 (s, -O-CH_3), 4.62 (*s*, -CH_2Br), 6.92–7.58 (*m* aromatic H)
4	$CDCl_3$	1.00 (*t*, CH_3-), 1.60 (*m*, CH_3-CH_2-), 1.87 (*m*, CH_3-CH_2-CH_2-), 4.10 (*t*, -O-CH_2-), 4.62 (*s*, -CH_2Br), 6.90–7.60 (*m*, aromatic H)
7	$CDCl_3$	3.90 (*s*, CH_3-O-), 3.90 (*s*, -CH_2Br), 5.31 (*s*, -CH_2-O-) 6.94–7.60 (*m*, aromatic H)
8	$CDCl_3$	0.92 (*t*, CH_3-), 1.43 (*sx*, CH_3-CH_2-), 1.71 (*qn*, CH_3-CH_2-CH_2-), 3.82 (*s*, CH_2Br), 3.97 (*t*, -O-CH_2-), 5.25 (*s*, -CH_2-OCO-), 6.87–7.47 (*m*, aromatic H)
13	$CDCl_3$	0.91 (*t*, CH_3-), 1.48 (*sx*, CH_3-CH_2-), 1.72 (*qn*, CH_3-CH_2-CH_2-), 3.82 (*s*, Br-CH_2-), 3.92 (*t*, CH_3-CH_2CH_2-CH_2-), 4.16 (*m*, -Φ-O-CH_2-CH_2-O-), 4.47 (*m*, -COO-CH_2-), 6.88 (m, aromatic H *ortho* to substituents), 7.39 (*m*, aromatic H, *meta* to substituents)
14	$CDCl_3$	0.99 (*t*, CH_3-), 1.50–1.65 (*m*, CH_3-CH_2-, -COO-CH_2-CH_2-CH_2-CH_2-), 1.72–1.80 (*m*, CH_3-CH_2-CH_2-, -COO-CH_2-CH_2-CH_2-CH_2-CH_2-), 3.83 (*s*, Br-CH_2-), 3.99 (*t*, -CH_2-O-Φ-Φ-O-CH_2-), 4.19 (*t*, -COO-CH_2-), 6.94 (*m*, aromatic H *ortho* to substituents), 7.46 (*m*, aromatic H, *meta* to substituents)
19	$CDCl_3$	0.91 (*t*, CH_3-), 1.47 (*sx*, CH_3-CH_2-), 1.71 (*qn*, CH_3-CH_2-CH_2-), 1.87 (*m*, -OCO-CH_2-$(CH_2)_2$-), 3.80 (*s*, Br-CH_2-), 4.00 (*t*, -CH_2-O-Φ-Φ-O-CH_2-), 4.25 (*t*, -COO-CH_2), 6.86 (*m*, aromatic H *ortho* to substituents), 7.38 (*m*, aromatic H, *meta* to substituents)
20	$CDCl_3$	0.91 (*t*, CH_3-), 1.30 (*m*, -OCO-$(CH_2)_3$-$(CH_2)_2$-), 1.48–1.56 (*m*, -OCO-$(CH_2)_2$-CH_2-, -OCO-$(CH_2)_5$-CH_2-, CH_3-CH_2-), 1.62–1.76 (*m*, CH_3-CH_2-CH_2-, -OCO-$(CH_2)_6$-CH_2-, -OCO-CH_2-CH_2-), 3.76 (*s*, Br-CH_2-), 3.91–3.92 (*m*, -CH_2-O-Φ-Φ-O-CH_2-), 4.10 (*t*, -COO-CH_2-), 6.86 (*m*, aromatic H *ortho* to substituents), 7.37 (*m*, aromatic H, *meta* to substituents)
23	$CDCl_3$	1.36–1.49 (*m*, O-CH_2-CH_2CH_2-CH_2-), 1.71 (*qn*, -Φ-O-CH_2CH_2), 1.74 (*qn*, -COO-CH_2-CH_2-), 3.76 (*s*, Br-CH_2-), 3.77 (*s*, CH_3-), 3.91 (*t*, -Φ-O-C_2-), 4.12 (*t*, -COO-CH_2-), 6.87 (*m*, aromatic H *ortho* to substituents), 7.40 (*m*, aromatic H, *meta* to substituents)
24	$CDCl_3$	1.48–1.53 (*m*, -COO-$(CH_2)_2$-CH_2-CH_2-), 1.72 (*qn*, -COO-$(CH_2)_4$-CH_2-), 1.82 (*sx*, -COO-CH_2-CH_2-CH_2-), 3.83 (*s*, Br-CH_2-), 4.00 (*t*, -Φ-O-CH_2-), 4.20 (*t*, -COO-CH_2-), 6.95 (*d*, aromatic H *ortho* to substituents), 7.29 (*t*, aromatic H, 4′-position to substituent), 7.41 (*t*, aromatic H, 3-position to substituent), 7.52 (*m*, aromatic H, 2′- and 3′-position to substituent)
26	$CDCl_3$	0.91 (*t*, CH_3-), 1.41 (*sx*, CH_3-CH_2-), 1.72 (*qn*, CH_3-CH_2-CH_2-), 3.64–3.68 (*m*, -Φ-O-CH_2-CH_2-O-CH_2-CH_2-O-), 3.81 (*m*, Br-CH_2-COO-CH_2-CH_2-), 3.92 (*t*, -Φ-O-CH_2-CH_2-O-), 4.10 (*t*, CH_3-CH_2-CH_2-CH_2-), 4.27 (*t*, Br-CH_2-COO-CH_2-), 6.88 (*m*, aromatic H *ortho* to substituents), 7.38 (*m*, aromatic H, *meta* to substituents)

determined by size exclusion chromatography (s.e.c.) on Styragel columns calibrated with standard polystyrene samples. A Perkin-Elmer DSC 4 differential scanning calorimeter was used to determine the thermal transitions; heating and cooling rates were 10°C min^{-1}. A Leitz Ortho-Plan polarizing microscope equipped with a Mettler FP 82 hot stage was used to observe the textures of mesophases. The X-ray patterns were obtained using a CPS-120 curved counter from inel. The localized $CuK_{\alpha 1}$ X-ray beams were produced by a XRG-2500 generator (inel).

Synthesis of monomers

Schemes 1 and *2* outline the synthetic routes used for the preparation of the monomers showing the notation used in the text for the intermediate compounds. The ^{1}H n.m.r. spectra were in accordance with the structures of the whole intermediates. *Table 1* presents the ^{1}H n.m.r. data for the halogenated compounds used in the monomers synthesis.

4-Methoxy biphenyl (**1**). Synthesized according to ref. 25. Yield: 80%; mp 85°C.

4-Butoxy biphenyl (**2**). Synthesized according to ref. 26. Yield: 70%; m.p. 73–74°C.

4-Bromomethyl-4′-methoxybiphenyl (**3**) and *4-bromomethyl-4′-butoxybiphenyl* (**4**). Both were synthesized according to ref. 27 from **1** and **2** with bromomethyl methylether in acetic acid. Yields > 90%; **3**: mp 96°C; **4** mp 58°C.

4-Methoxy-4′-hydroxymethylbiphenyl (**5**) and *4-butoxy-4′-hydroxymethybiphenyl* (**6**). Both synthesized according to a procedure described in ref. 28; **5**: yield: 77%; mp 68°C and **6**: yield: 46%; mp 51°C.

4-Methoxy-4′-hydroxybiphenyl (**9**). Synthesized according to ref. 29; yield: 34%; mp 182°C.

4-Butoxy-4′-hydroxybiphenyl (**10**). Synthesized according to ref. 30; yield: 35%; mp 172°C.

6-Iodo-1-hexanol and *8-iodo-3,6-dioxaoctanol*. Synthesized from the corresponding commercial chlorides according to the well known procedure[31] using NaI in acetone. Crude products were purified by fractional distillation. 6-iodo-1-hexanol: Eb_5: 120°C; 8-iodo-3,6-dioxaoctanol: Eb_5: 140°C.

2-[(4′-Butoxy-4-biphenylyl)oxy]ethanol (**11**), *6-[(4′-butoxy-4-biphenylyl)oxy]hexanol* (**12**), *6-[(4′-methoxy-4-biphenylyl)oxy]hexanol* (**21**) and *6-(biphenylyloxy)hexanol* (**22**). Synthesized with a literature procedure described for similar compounds[19]. The crude products were purified by recrystallization in ethanol. **11**: yield: 30%; mp 167°C; **12**: yield 55%; mp 142°C; **21**: yield: 50%; mp 148°C; **22**: yield: 58%; mp 101°C.

8-[(4′-Butoxy-4-biphenylyl)oxy]-3,6-dioxaoctanol (**25**). A mixture of 30.45 mmol **10** (6% excess), 25 ml ethanol and 48.7 mmol KOH in 9 ml of water were heated and stirred until complete dissolution. 8-Iodo-3,6-dioxaoctanol (48.7 mol) was added dropwise. The mixture was refluxed for 15 h. After cooling the mixture solidified. Ethanol was evaporated in a rotavapor. The pasty solid was solubilized in hot toluene. The organic phase was decanted, dried and evaporated. A white solid was recuperated, washed with ether, dried and was

Table 2 Yields and melting points of bromoethanoates

Compound	Yield (%)	Melting point (°C)	Solvent
7	90	not crystallized	ether
8	88	not crystallized	ether
13	76	91	benzene
14	73	95	benzene
19	78	96	benzene
20	80	97	toluene
23	75	72–73	toluene
24	94	49–50	toluene
26	87	84	toluene

Table 3 Overall yields for the synthesis of monomers **M1**–**11** and their melting points

Compound	Overall yield (%)	Melting point (°C)
M1	41	liquid
M2	27	liquid
M3	40	liquid
M4	12	liquid
M5	8	67–68
M6	5.5	73–74
M7	3	78
M8	12	83–84
M9	4	87–88
M10	9.5	60–63
M11	38	53–54

further purified by column chromatography (silica gel, toluene/THF, 90/10 eluent); yield 44%, mp 111°C.

4-[(4′-Butoxy-4-biphenylyl)oxy]butanol (**17**) and *8-[(4′-butoxy-4-biphenylyl)oxy]octanol* (**18**). According to a procedure described in the literature for similar compounds[32], **10** was reacted with commercial 1,4-dibromobutane and 1,8-dibromooctane affording 4-(4-bromobutoxy)-4′-butoxybiphenyl (**15**): yield: 60%; mp 110°C and 4-(8-bromooctyloxy)-4′-butoxybiphenyl (**16**): yield: 45%; mp 129°C. The hydrolysis method of the literature[33] was applied to compounds **15** and **16**, and gave the corresponding alcohols, **17**: yield: 30%; mp 159°C; **18**: yield: 58%; mp: 142°C.

(4-Methoxy-4′-biphenylyl)methyl bromoethanoate (**7**), *(4-butoxy-4′-biphenylyl)methyl bromoethanoate* (**8**), *2-[(4-butoxy-4′-biphenylyl)oxy]ethyl bromoethanoate* (**13**), *6-[(4-butoxy-4′-biphenylyl)oxy]hexyl bromoethanoate* (**14**), *4-[(4-butoxy-4′-biphenylyl)oxy]butyl bromoethanoate* (**19**), *8-[(4-butoxy-4′-biphenylyl)oxy]octyl bromoethanoate* (**20**), *6-[(4-methoxy-4′-biphenylyl)oxy]hexyl bromoethanoate* (**23**), *6-(biphenylyloxy)hexyl bromoethanoate* (**24**), and *8-[(4-butoxy-4′-biphenylyl)oxy]-3,6-dioxaoctyl bromoethanoate* (**26**). The whole bromoethanoates were prepared by a suitable procedure used in our laboratory[4] using bromoacetylbromide and alcohols. Solvents varied with the solubility of compounds. *Table 2* presents yields and melting points of bromoethanoates.

(4-Alkoxy-4′-biphenylyl)methylthiothiiranes **M1**–**3** and (2,3-epithiopropyl)thioethanoate monomers **M2**, **M4**–**11** were obtained by the procedure described in ref. 3 from mercaptomethylthiirane[34] prepared with 2,3-dimercaptopropanol and bromides **3**, **4**, **7**, **8**, **13**, **14**, **19**, **20**, **23**, **24** and **26**. They were purified by silica gel chromatography with cyclohexane/acetone mixtures as eluent, the amount of acetone depending on each product (varying from 5 to 15%). *Table 3* presents the yields and the melting points of the whole series of monomers. Their ^1H n.m.r. data in $CDCl_3$ are described in *Table 4*.

Polymerizations

Polymerizations were carried out in solution in *N,N*-dimethylformamide (monomer concentration = 0.25 mol^{-1}), under nitrogen, at 30°C, for 10 min. The glassware was dried. Before adding the initiator (tetramethylammonium dithiobenzoate)[2] in solution in DMF with a syringe, the monomer in solution was degassed and the polymerization flask purged with nitrogen; this operation was repeated five times and the flask finally maintained under a nitrogen atmosphere. The ratio monomer/initiator ($[M_O]/[I_O] = 50$) would determine the polymer molecular weight. Bromobutane was added at the end of the reaction to avoid an increase in molecular weights by oxidation of thiolate end groups in disulfides; the reaction mixture was precipitated in ether. The filtered polymers were dried under vacuum, dissolved in chloroform at ambient temperature (hot chloroform for **P8** and **P9**) and purified by further precipitation in methanol. This treatment was repeated three times. The conversions were quantitative in almost all cases; but yields were sometimes lower due to losses during the purification process.

RESULTS AND DISCUSSION

Monomer synthesis

Monomers with short spacers: **M1**–**4** (*Scheme 1*) were prepared from the corresponding 4-(4′-alkyloxy)biphenyl bromomethane as previously described. For monomers **M1** and **3**, a direct link to the thiirane ring using a sulfur function was obtained in one step by nucleophilic substitution of mercaptomethylthiirane (MMT) on 4-(4′-alkyloxy) biphenyl bromomethanes. Monomers **M2** and **4** were prepared in two steps from 4-(4′-alkyloxybiphenyl) methanol; the ester linkage was introduced by reaction with bromoacetylbromide; in a second step the thiirane ring was attached by nucleophilic substitution of MMT on the corresponding bromoacetates.

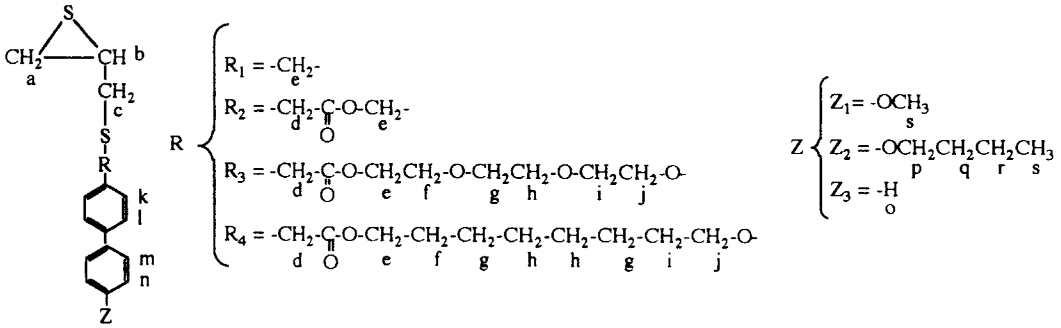
The monomers with larger spacers **M5**–**11** (*Scheme 2*) were prepared according to the same synthetic method with an additional step to link the spacer to the mesogenic core.

For this purpose, the 4-(4′-alkyloxyphenyl)phenols were reacted with the corresponding chloroalcohol; in order to improve some yields, iodoalcohols were also used. The reactions with the appropriate dihalide were also performed; in this case an hydrolysis step is needed. Both methods gave similar yields. The best overall yields (40%) were obtained for the shortest synthesis **M1**, **3** and for **11**. The spectroscopic data (^1H, ^{13}C n.m.r.) were in accordance with the proposed structures and are described in the Experimental section.

Polymerizations

The polymer structures are summarized in *Scheme 3*. The polymerizations were carried out for all monomers under the same conditions: at 30°C, in DMF as a solvent and with tetramethylammonium dithiobenzoate as an initiator. The polymerizations were rapidly completed[2]. The results of the polymerizations are reported in *Table 5*. Some polymers: **P7**–**9** were not quite soluble in DMF and precipitated out during the polymerization; furthermore, **P8** and **9** were not soluble in usual solvents at

Table 4 ^1H n.m.r. data of monomers thiirane ($CDCl_3$, δ, TMS)

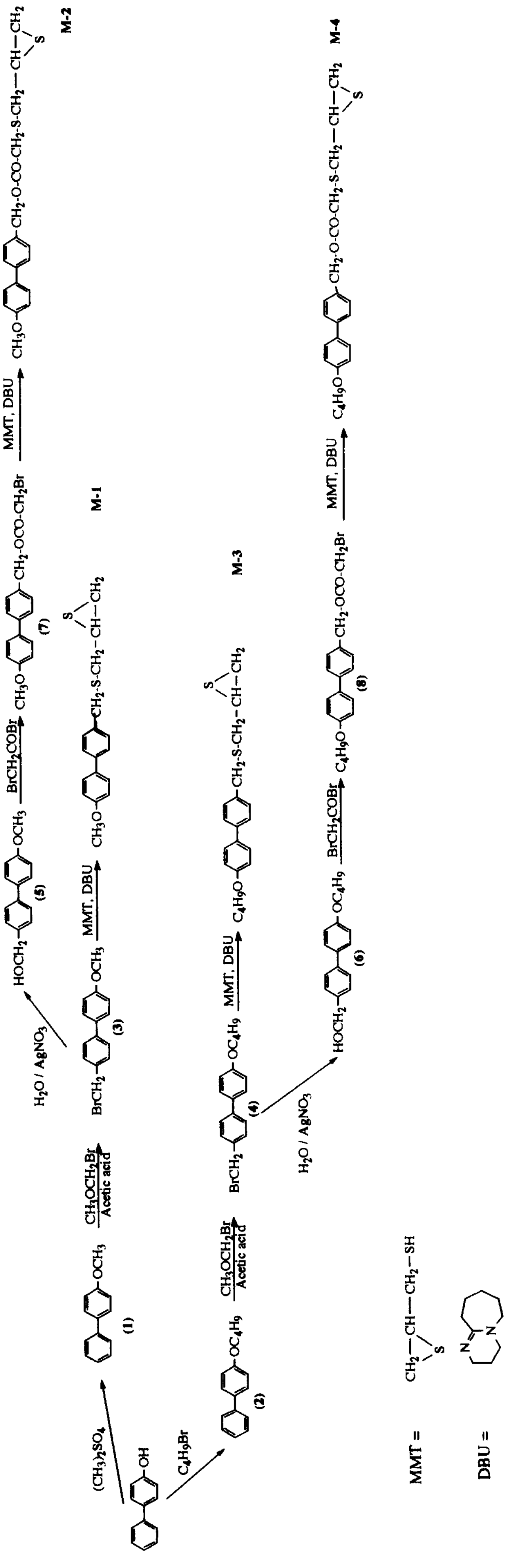


$$R\begin{cases} R_1 = \text{-}\underset{e}{CH_2}\text{-} \\ R_2 = \text{-}\underset{d}{CH_2}\text{-}\underset{O}{\overset{\|}{C}}\text{-O-}\underset{e}{CH_2}\text{-} \\ R_3 = \text{-}\underset{d}{CH_2}\text{-}\underset{O}{\overset{\|}{C}}\text{-O-}\underset{e}{CH_2}\underset{f}{CH_2}\text{-O-}\underset{g}{CH_2}\underset{h}{CH_2}\text{-O-}\underset{i}{CH_2}\underset{j}{CH_2}\text{-O-} \\ R_4 = \text{-}\underset{d}{CH_2}\text{-}\underset{O}{\overset{\|}{C}}\text{-O-}\underset{e}{CH_2}\text{-}\underset{f}{CH_2}\text{-}\underset{g}{CH_2}\text{-}\underset{h}{CH_2}\text{-}\underset{h}{CH_2}\text{-}\underset{g}{CH_2}\text{-}\underset{i}{CH_2}\text{-}\underset{j}{CH_2}\text{-O-} \end{cases}$$

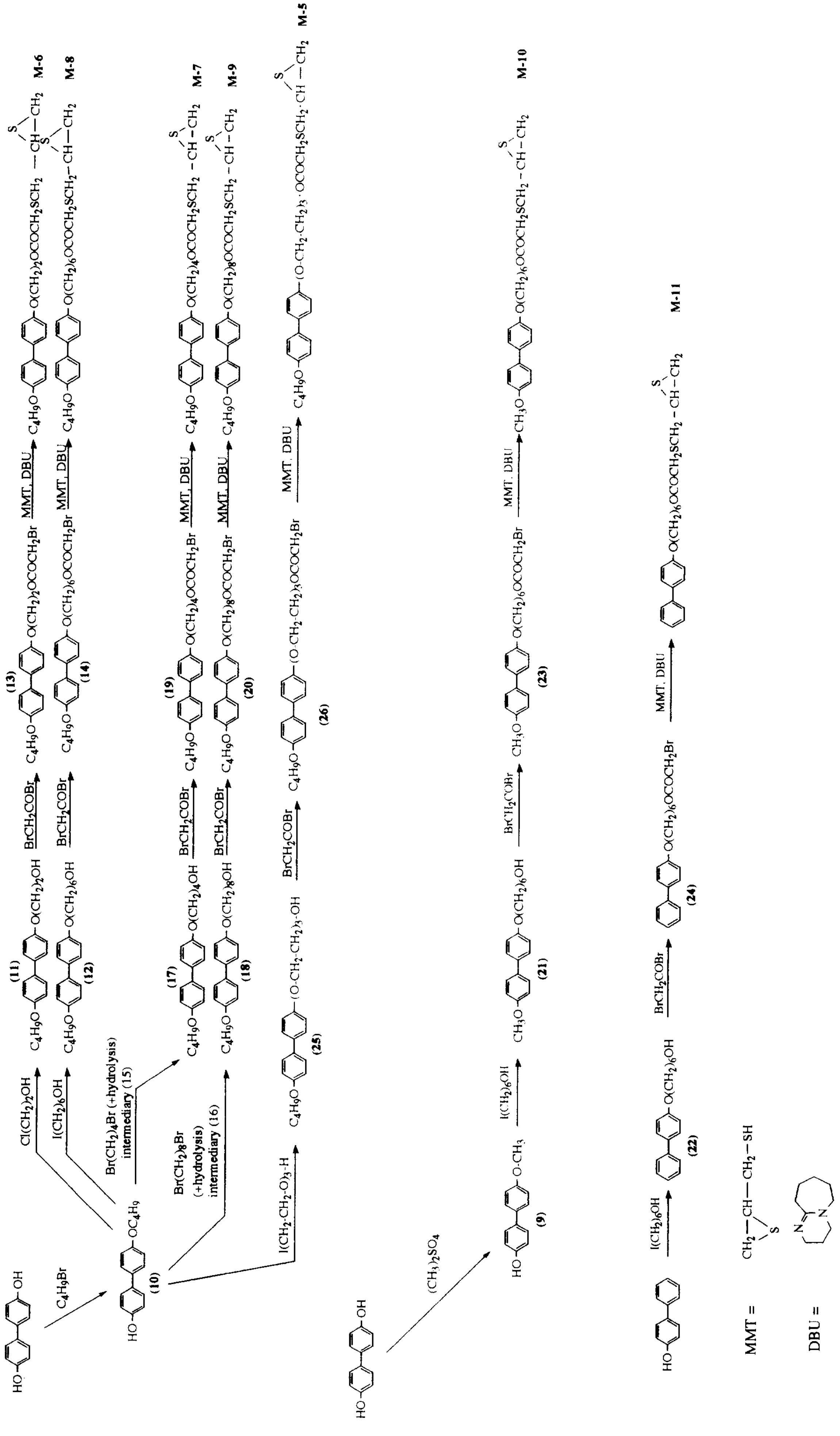
$$Z\begin{cases} Z_1 = \text{-O}\underset{s}{CH_3} \\ Z_2 = \text{-O}\underset{p}{CH_2}\underset{q}{CH_2}\underset{r}{CH_2}\underset{s}{CH_3} \\ Z_3 = \text{-}\underset{o}{H} \end{cases}$$

Monomer	a: 2H	b: 1H	c: 2H	d: 2H	e: 2H	f: 2H	g	h	i: 2H	j: 2H	k: 2H	l: 2H	m: 2H	n: 2H	o: 1H	p: 2H	q: 2H	r: 2H	s: 3H
M1 R_1, Z_1	2.22 *d* 2.53 *m*	3.05 *m*	2.48 *m* 3.02 *m*		3.90 *s*						7.52 *t*	7.45 *m*	7.45 *m*	6.97 *d* 7.31 *t*	3.90 *s*				
M2 R_2, Z_1	2.21 *d* 2.50 *d*	3.10 *m*	2.68 *m* 3.06 *m*	3.39 *s*	5.29 *s*						7.41 *t*	7.55 *m*	7.55 *m*	6.99 *d* 7.32 *t*	3.90 *s*				
M3 R_1, Z_2	2.22 *d* 2.56 *d*	3.10 *m*	2.47 *m* 3.01 *m*		3.91 *s*						7.53 *t*	7.42 *m*	7.42 *m*	6.90 *d* 7.31 *t*		4.06 *t*	1.81 *sp*	1.50 *sx*	1.02 *t*
M4 R_2, Z_2	2.14 *d* 2.41 *d*	3.00 *m*	2.62 *m* 3.00 *m*	3.31 *s*	5.22 *s*						7.35 *t*	7.47 *m*	7.47 *m*	6.87 *d* 7.24 *t*		3.97 *t*	1.71 *qn*	1.43 *sx*	0.92 *t*
M5 R_3, Z_2	2.20 *d* 2.50 *d*	3.03 *m*	2.63 *m* 3.01 *m*	3.27 *s*	4.23 *t*	3.80 *t*	3.66 *m* 2H	3.66 *m* 2H	3.62 *m*	4.09 *m*	6.88 *t*	7.38 *d*	7.38 *d*	6.88 *t*	3.92 *t*	1.71 *qn*	1.43 *sx*	0.91 *t*	
M6 R_4, Z_2	2.19 *d* 2.48 *d*	3.03 *d*	2.65 *m* 3.00 *m*	3.30 *s*	4.43 *t*					4.14 *t*	6.86 *d*	7.39 *d*	7.39 *d*	6.86 *d*		3.91 *t*	1.70 *q*	1.42 *sx*	0.91 *t*
M7 R_4, Z_2	2.20 *d* 2.49 *d*	3.01 *d*	2.63 *m* 2.98 *m*	3.24 *s*	4.15 *t*	1.80 *m*			1.80 *m*	3.93 *t*	6.88 *d*	7.39 *d*	7.39 *d*	6.88 *d*		3.91 *t*	1.75 *m*	1.45 *sx*	0.91 *t*
M8 R_4, Z_2	2.21 *d* 2.50 *d*	3.02 *d*	2.63 *m* 3.02 *m*	3.28 *s*	4.08 *t*	1.75 *q*	1.45 *m* 4H		1.63 *m*	3.90 *t*	6.88 *d*	7.40 *d*	7.40 *d*	6.88 *d*		3.90 *t*	1.71 *m*	1.30 *m*	0.94 *t*
M9 R_4, Z_2	2.21 *d* 2.49 *d*	3.03 *d*	2.63 *m* 3.00 *m*	3.25 *s*	4.06 *t*	1.59 *m*	1.43 *m* 4H	1.30 *m* 4H	1.71 *m*	3.91 *t*	6.90 *d*	7.40 *d*	7.40 *d*	6.90 *d*		3.92 *t*	1.71 *m*	1.30 *m*	0.94 *t*
M10 R_4, Z_1	2.21 *d* 2.50 *d*	3.03 *d*	2.63 *m* 3.00 *m*	3.25 *s*	4.09 *t*	1.75 *q*	1.42 *m* 4H		1.63 *q*	3.92 *t*	6.88 *d*	7.40 *d*	7.40 *d*	6.88 *d*					3.77 *s*
M11 R_4, Z_3	2.29 *d* 2.55 *d*	3.11 *d*	2.71 *m* 3.08 *m*	3.31 *s*	4.18 *t*	1.81 *q*	1.50 *m* 4H		1.70 *q*	4.00 *t*	6.96 *d*	7.40 *t*	7.53 *m*	7.53 *m*	7.30 *t*				

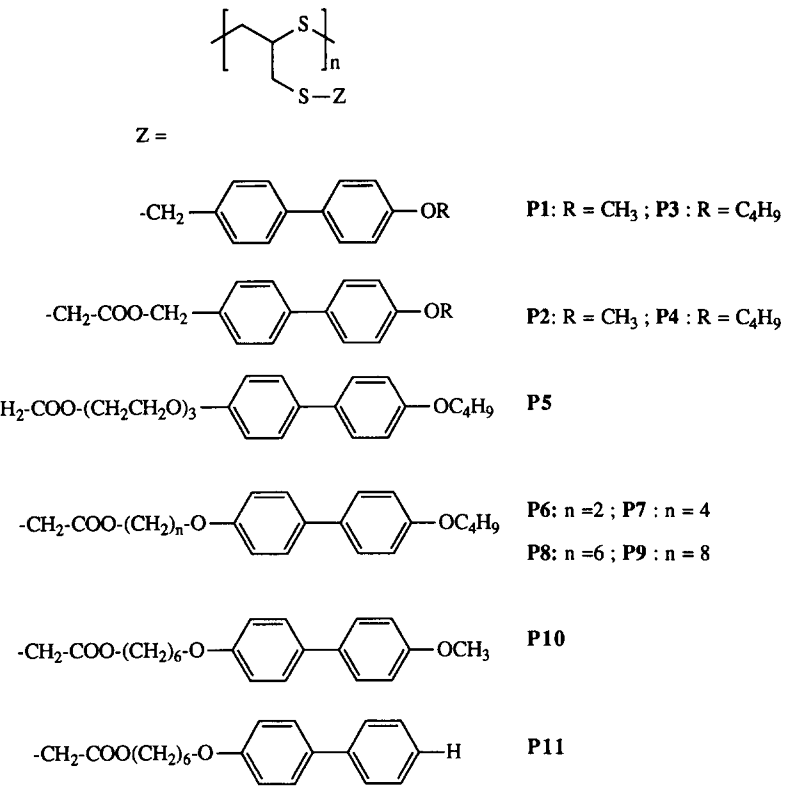
d: doublet; *m*: multiplet; *q*: quadruplet; *qn*: quintuplet; *s*: singlet; *sx*: sextuplet; *t*: triplet



Scheme 1 Synthetic route used for the preparation of the thiirane monomers M1–4



Scheme 2 Synthetic route for the preparation of the thiirane monomers M5–11



Scheme 3 The studied polymers

Table 5 Results of polymerizations: $[M_O] = 0.25\,\mathrm{mol\,l^{-1}}$; solvent: DMF; 20°C

Polymer	$[M_O]/[I_O]^a$	Yield	M_n calculated ($\mathrm{g\,mol^{-1}}$)	$M_n{}^b$ (Eq PS)	$M_w{}^b$ (Eq PS)	$I_p{}^b$ (M_w/M_n)
P1	50	95%	15000	16400	22300	1.36
P2	17	98%	6000	3190	5780	1.81
P3	50	97%	17000	7000	11000	1.57
P4	67	98%	27000	28000	55000	1.98
P5	50	93%	26000	18000	38000	2.11
P6	50	91%	21600	14500	32340	2.23
P7	50	92%	23000	5849	20740	3.55
P8^c	50	98%	24400			
P9^c	50	94%	25800			
P10	50	92%	22350	11590	14980	1.29
P11	50	95%	20800	30550	58930	1.93

[a] Calculated assuming a living polymerization: $DP_n = [M_O]/[I_O]$

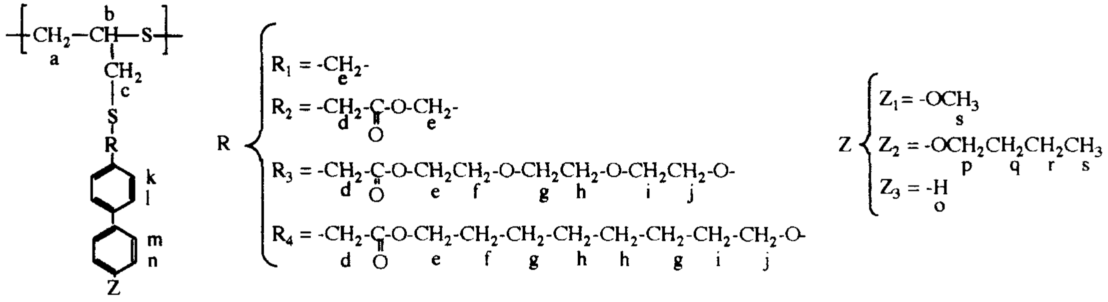
[b] These results are obtained from s.e.c. analysis (THF) and expressed in equivalent polystyrene

[c] **P8** and **P9** are insoluble in THF

ambient temperature and could not be analysed either by s.e.c. or by light scattering. The large polydispersity index for **P7** probably results from the low solubility of the polymer in the polymerization mixture. The average number molecular weights M_n calculated by s.e.c. (expressed in polystyrene standard) are rather different than those expected for a polymerization. An accurate measurement of the average molecular weights was difficult for both reasons. As for methylthiirane and other thiirane monomer polymerizations[16], the initiation step is slower than the propagation step. So, for low $[M_O]/[I_O]$ the entire initiator is not consumed and the average molecular weights observed may be larger than the expected ones. Furthermore, underestimated molecular weights were observed by ourselves[4] and by others[17] on s.e.c. determinations resulting from a decrease of hydrodynamic volumes because of the comb-like structure of these polymers. Although phase transitions are influenced by molecular weight[18] we did not study this problem in this work. We consider that polymers studied here have degrees of polymerization high enough to hinder molecular weight dependence of the phase transitions.

All polymers were fully characterized by their ^1H and ^{13}C n.m.r. spectra (*Tables 6* and *7*). Statistical copolymers with methylthiirane (MT) were prepared from **M3** (34, 57, 82, 86 mol%). Their ^1H and ^{13}C n.m.r. spectra clearly showed the signals of both monomer units. Their characteristic data are given in the Experimental section.

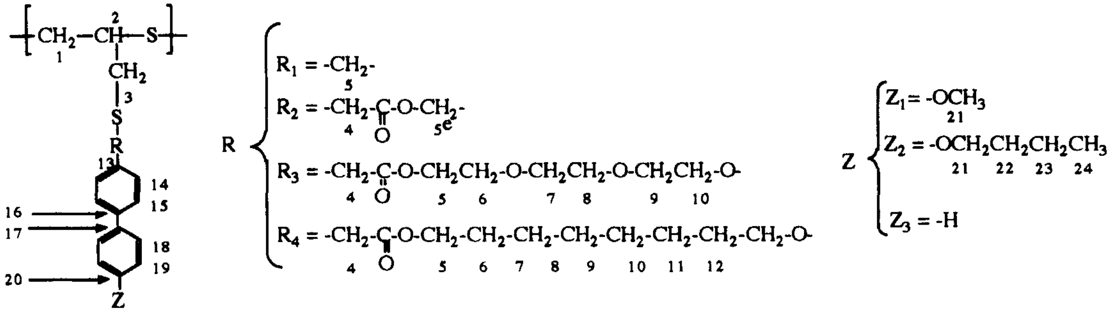
Table 6 ^{1}H n.m.r. data of polymers in $CDCl_3$ (TMS, δ, ppm)



Polymer	a: 2H	b: 1H	c: 2H	d: 2H	e: 2H	f: 2H	g: 2H	h	i: 2H	j: 2H	k: 2H	l: 2H	m: 2H	n: 2H	o	p: 2H	q: 2H	r: 2H	s: 3H
P1 R_1, Z_1	2.75 *m*	2.75 *m*	2.75 *m*		2.88 *m*						7.65 *t*	7.31 *qd*	7.31 *qd*	6.72 *d* 7.20 *t*					3.70 *s*
P2 R_2, Z_1	2.70 *m*	2.85 *m*	2.85 *m*	3.15 *s*	5.18 *s*						7.25 *m*	7.40 *m*	7.40 *m*	6.72 *d* 7.15 *m*					3.75 *s*
P3 R_1, Z_2	2.75 *m*	2.75 *m*	2.75 *m*		3.69 *m*						7.42 *m*	7.25 *m*	7.25 *m*	6.72 *d* 7.20 *t*		3.88 *m*	1.69 *m*	1.40 *m*	0.90 *t*
P4 R_2, Z_2	2.68 *m*	2.83 *m*	2.83 *m*	3.11 *s*	5.10 *s*						7.27 *m*	7.40 *m*	7.40 *m*	6.72 *d* 7.12 *m*		3.82 *m*	1.65 *m*	1.45 *m*	0.85 *t*
P5 R_3, Z_2	2.90 *m*	3.10 *m*	2.98 *m*	3.25 *s*	4.21 *m*	3.72 *m*	3.60 *m*	3.60 *m* 2H	3.56 *m*	4.05 *m*	6.88 *m*	7.38 *m*	7.38 *m*	6.88 *m*		3.90 *m*	1.69 *qt*	1.41 *sx*	0.91 *t*
P6 R_4, Z_2	2.95 *m*	3.11 *m*	3.02 *m*	3.30 *s*	4.41 *s*					4.09 *m*	6.88 *d*	7.39 *qd*	7.39 *qd*	6.88 *d*		3.91 *t*	1.73 *qt*	1.45 *sx*	0.95 *t*
P7 R_4, Z_2	3.00 *m*	3.14 *m*	3.04 *m*	3.28 *s*	4.16 *s*	1.81 *s*			1.81 *m*	3.92 *m*	6.87 *m*	7.41 *m*	7.41 *m*	6.87 *m*		3.92 *m*	1.75 *m*	1.48 *m*	0.95 *t*
P8 R_4, Z_2	3.01 *m*	3.13 *m*	3.05 *m*	3.29 *s*	4.10 *t*	1.75 *m*	1.46 *m*		1.75 *m*	3.93 *t*	6.89 *m*	7.40	7.40 *d*	6.89 *m*		3.91 *t*	1.64 *m*	1.46 *m*	0.96 *t*
P9 R_4, Z_2	3.00 *m*	3.12 *m*	3.05 *m*	3.29 *s*	4.10 *t*	1.75 *m*	1.45 *m*	1.34 *m* 4H	1.75 *m*	3.94 *t*	6.90 *m*	7.42 *d*	7.42 *d*	6.90 *m*		3.91 *t*	1.63 *m*	1.4 *m*	0.96 *t*
P10 R_4, Z_1	3.00 *m*	3.12 *m*	3.04 *m*	3.28 *s*	4.10 *m*	1.76 *m*	1.46 *m*		1.64 *m*	3.91 *m*	6.90 *m*	7.42 *d*	7.42 *d*	6.90 *m*					3.78 *s*
P11 R_4, Z_3	2.99 *m*	3.12 *m*	3.04 *m*	3.27 *s*	4.10 *m*	1.76 *m*	1.41 *m*		1.65 *m*	3.92 *m*	6.92 *d*	7.36 *t*	7.50 *m*	7.50 *m*	7.25 *t*				

d: doublet; *m*: multiplet; *qd*: quadruplet; *qt*: quintuplet; *s*: singulet; *sx*: sextuplet; *t*: triplet

Table 7 ^{13}C n.m.r. data of polymers in $CDCl_3$ (TMS, δ, ppm)



Polymer	COO	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C17	C18	C19	C20	C21	C22	C23	C24
P1 R_1, Z_1		35.70	47.00	36.56		26.95								133.38	129.04	128.74	140.48	140.48	126.85	126.72	156.82	55.67			
P2 R_2, Z_1	170.22	35.72	46.64	37.45	31.51	62.83								156.57	128.96	128.51	133.28	140.57	126.92	126.89	156.62	68.12			
P3 R_1, Z_2		35.52	46.87	36.30										132.98	128.84	128.68	140.48	140.48	126.65	126.89	156.25	67.91	31.35	19.35	13.98
P4 R_2, Z_2	170.23	35.74	46.63	37.05	31.40	62.77								156.65	128.93	128.47	133.29	140.54	126.91	126.84	156.65	68.10	31.40	19.44	14.08
P5 R_3, Z_2	170.09	35.54	46.27	36.82	33.99	64.36	69.60	67.56	67.28	68.80	70.59			158.10	114.69	127.44	133.41	133.90	127.44	114.58	157.64	70.39	31.0	19.11	13.74
P6 R_4, Z_2	170.26	35.81	46.58	37.12	31.38	65.81							67.72	158.33	114.87	127.67	133.89	132.87	127.61	114.77	157.39	63.78	34.11	19.27	13.88
P7 R_4, Z_2	170.26	35.80	46.79	37.24	31.38	65.19	25.46					25.90	67.73	158.25	114.74	127.61	133.40	133.10	127.61	114.74	157.96	67.30	34.31	19.27	
P8 R_4, Z_2	170.28	35.79	46.27	37.07	31.38	65.49	28.56	25.74			25.81	29.26	67.73	158.22	114.73	127.59	133.28	133.18	127.59	114.71	158.12	67.81	34.33	19.27	13.88
P9 R_4, Z_2	170.28	35.80	46.74	37.06	31.38	65.61	29.25	28.61	25.87	26.07	28.61	26.36	67.98	158.22	114.73	127.59	133.22	133.22	127.59	114.73	158.18	67.74	34.34	19.27	13.88
P10 R_4, Z_1	170.28	35.76	46.36	37.05	29.24	65.48	28.55	23.73			25.80	34.31	67.80	158.15	114.14	127.63	133.18	133.39	127.63	114.71	158.62				55.29
P11 R_4, Z_3	170.28	35.76	46.56	37.04	29.21	65.48	28.54	25.72			25.79	34.31	67.80	158.61	114.74	128.71	133.50	140.75	126.60	128.07	126.64				

Table 8 Phases transitions in °C (enthalpy in J g $^{-1}$)

P5	$\mathrm{Sm\,X} \xleftarrow[99(1.26)]{} \mathrm{Sm\,E} \xleftrightarrow[105(23.85)]{115(41.84)} \mathrm{Iso}$
P6	$\mathrm{Sm\,E} \xleftrightarrow[139(52.30)]{148(51.04)} \mathrm{Iso}$
P7	$\mathrm{Sm\,E} \xleftrightarrow[100.5(1.97)]{114.6(5.42)} \mathrm{Sm\,A} \xleftrightarrow[133(13.74)]{136.8(15.03)} \mathrm{N} \xleftrightarrow[145(15.16)]{150.6(15.62)} \mathrm{Iso}$
P8	$\mathrm{Sm\,X} \xleftrightarrow[114.8(3.79)]{122(2.38)} \mathrm{Sm\,E} \xleftrightarrow[124.4(12.64)]{128.3(12.40)} \mathrm{Sm\,A} \xleftrightarrow[144.1(16.01)]{149(15.78)} \mathrm{Iso}$
P9	$\mathrm{Sm\,X} \xleftrightarrow[120.5^{a}]{125.1^{a}} \mathrm{Sm\,E} \xleftrightarrow[124.1^{a}]{127.6^{a}} \mathrm{Sm\,A} \xleftrightarrow[143.8(16.95)]{149.7(16.58)} \mathrm{Iso}$
P10	$\mathrm{Sm\,E} \xleftrightarrow[107(10.88)]{110(10.88)} \mathrm{Sm\,A} \xleftrightarrow[123(12.55)]{127(12.55)} \mathrm{Iso}$
P11	$\mathrm{Sm\,X} \xleftrightarrow[43(1.25)]{45(1.67)} \mathrm{Sm\,A} \xleftrightarrow[49(12.37)]{55(13.39)} \mathrm{Iso}$

Sm X = No identified smectic, Sm E = smectic E, Sm A = smectic A, N = nematic, Iso = isotrope liquid

[a] The corresponding enthalpies cannot be evaluated as both peaks are too close

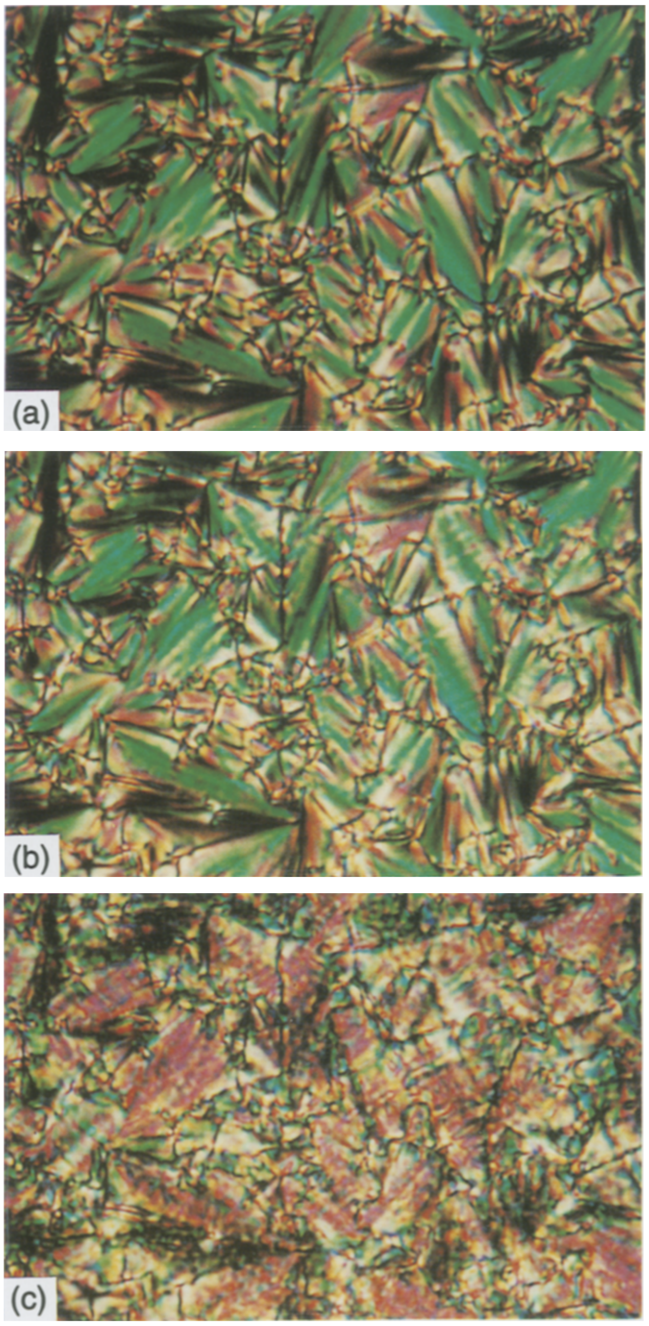


Figure 1 Observed textures in polymer **P8**. (a) 144.1°C (microscopy): smectic A mesophase, focal conics. (b) 126°C (microscopy): smectic E mesophase, striated focal conics. (c) 118.6°C (microscopy): ultimate change of texture, not identified

Thermal properties and optical textures

Investigations of the LC properties of polymers **P1–4** which contain short spacers gave no results. These spacers do not appear large enough to decouple efficiently the motions of the main chain from those of the side chains. The **M3/MT** copolymers did not give any LC properties: the extension of the distance between two mesogenic groups along the main chain did not produce any effect on the LC properties.

The other polymers **P5–11**, exhibit mesophases even with an unsubstituted biphenyl group (**P11**). The phase transition temperatures of the polymers are summarized in *Table 8*. Some of them show several transitions. Glass transition temperatures were not easily assigned for the whole series of polymers but this is usual for smectic SCLC polymers[8,19,20]. The mesophases were identified by observation of their typical textures on polarized optical microscope and by X-ray diffraction patterns. All these polymers exhibit at least one mesophase: smectic A but also highly ordered smectic E. Under the smectic E mesophase, polymers **P5**, **8**, **9**, **11**, have shown a slight transition which could correspond to another smectic mesophase. But the corresponding changes of texture were only observed on the optical microscope in the case of **P8** and **9**. At the present time we cannot say anything more about these transitions.

The typical focal-conic texture was observed for the smectic A mesophases (*Figure 1a*) of polymers **P7**, **8**, **10** and **11**. On cooling the focal-conic appeared striated (*Figure 1b*); this modification of the texture is characteristic of a transition from a smectic mesophase to a highly ordered mesophase which was identified by the X-ray pattern as a smectic E. The optical texture of the smectic E mesophase of polymer **P5** was not at all characteristic and was identified by X-ray diffraction; the same texture has already been observed in polyoxetanes[14]. Concerning **P8** and **9**, the last transition observed on cooling smectic E is signalled by an increase of the striations to such an extent that the focal conics are almost completely hidden (*Figure 1c*).

X-ray diffraction

In the X-ray diffraction patterns of polymers **P5–11**, sharp diffractions characteristic of smectic monolayer structures were observed in the small angles region (*Figure 2*). A broad diffraction in the wide angle region confirmed the presence of a smectic A mesophase. The other smectic mesophase observed at lower temperatures, exhibited three sharp diffractions over the wide angle region. The positions of the diffraction are characteristic of a pseudo rectangular network of mesogenic groups in the layers owing to the pgg no. 8

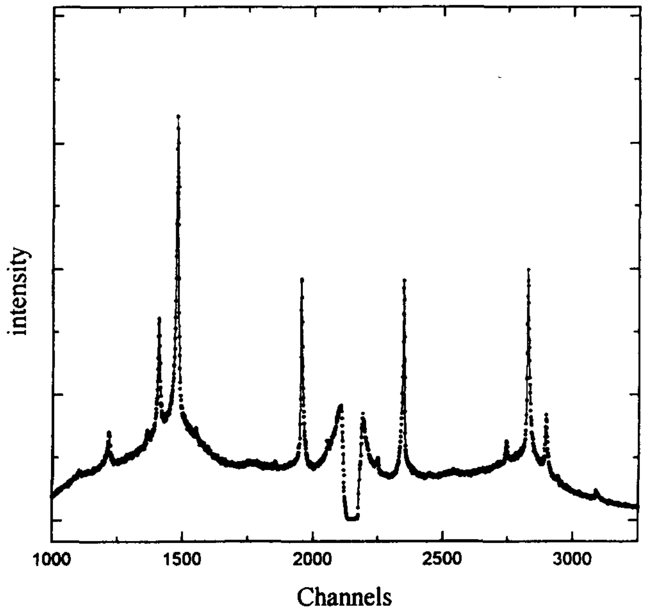


Figure 2 X-ray diffraction pattern of polymer **P7** at 120°C

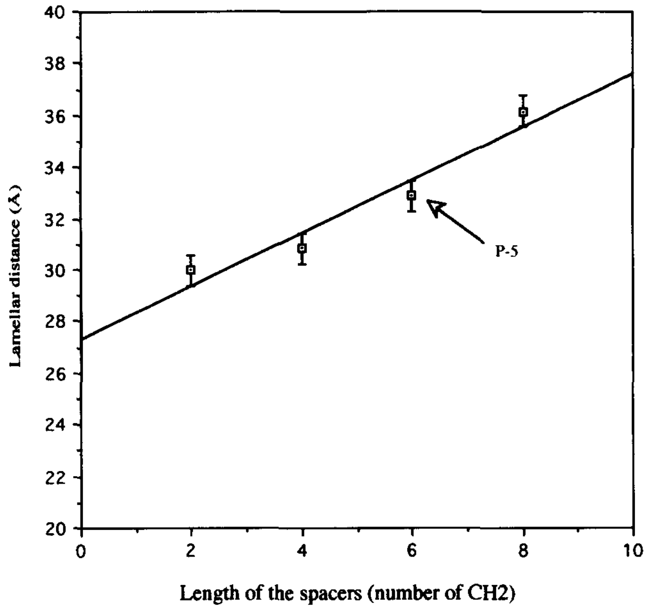


Figure 3 Lamellar distances of polythiiranes smectic mesophases vs length of spacers

space group. This kind of ordering fits with a smectic E mesophase. The *d*-spacing determined from both mesophases were very similar but varies with the length of the spacer; a good correlation appears for the lamellar distance as a function of the spacer length in polymers **P6–9** (*Figure 3*). For polymer **P8** the *d*-spacing derived from X-ray diffraction (32.9 Å) is consistent with the length of the lateral group: 27.98 Å calculated from a computer drawn model. Polymer **P5** whose spacer length lies probably between **P8** and **9** exhibits a *d*-spacing (33.48 Å) which effectively takes place on the graph between **P8** and **9**. The *d*-spacing determined for **P10** and **11** are, respectively, 32.24 and 28.01 Å. To summarize our results, a consistent scheme of thermotropic liquid crystal polymorphism is drawn (*Figure 4*).

DISCUSSION

In this series of polymers, the presence of large and flexible spacers is necessary to achieve LC properties. Many reports have treated the effect of a spacer on the mesomorphic properties of SCLC polymers[21]. Most of them deal with carbon main chains and the spacer effect on a heteroatomic main chain is seldom examined. Polyoxiranes which have been extensively described[11] exhibited smectic phases without a spacer, while in polymers **P2** and **4** a spacer constituted of five atoms -CH_2-S-CH_2CO-O-CH_2- cannot efficiently decouple the motions of the main and side chains. This kind of spacer with an ester and a thioether linkage appears rather rigid and is not useful for decoupling the side group from the polythiirane chain; this is all the more so, as the polythiirane chain itself is less flexible than polyoxirane.

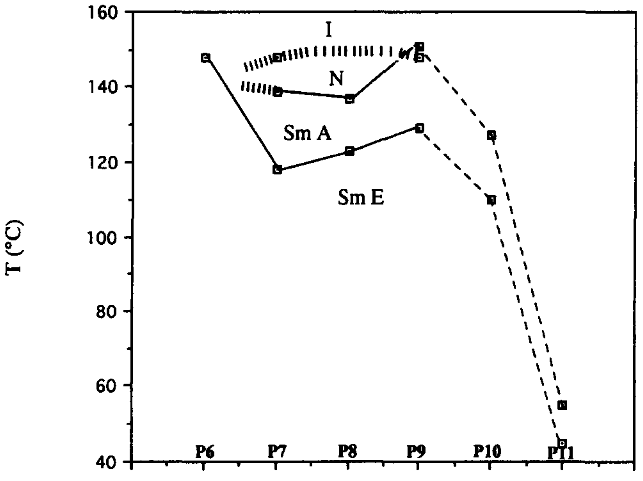


Figure 4 Thermotropic liquid crystal polymorphism for polymers **P6–11**

The behaviour of alkoxy-biphenyl polythiiranes may be also compared to the behaviour of alkoxy-biphenyl polyoxetanes[14]; effectively, polyoxetanes linked to alkoxy–biphenyl groups by various spacers do not behave as LC. The flexibility of the polyoxirane main chain seems to be involved in explaining the easy ordering of mesogenic cores when LC properties are observed with short spacers. In the case of the polythiiranes, on the contrary, the presence of the large sulfur atom in the backbone and in the side chain seems to decrease the anisotropic orientation of the mesogenic side-chains. A molecular drawing of polymer **P8** exhibits a steric hindrance between both sulfur atoms which perhaps reduces the flexibility of the main chain. Furthermore, the flexibility and the conformational mobility of a polymer backbone are larger for lower molecular weights. The polythiiranes described here have rather high degrees of polymerization while molecular weights of the corresponding polyoxiranes were not reported. When the spacer is large enough to allow the building of mesophases, its length controls the nature and the number of mesophases (**P6–9**) as was previously described, but the isotropization temperatures are nearly in the same range. Changing the nature of the spacer also leads to significant modifications in LC properties; polymers **P5** and **9** may be compared in relation to the number of atoms in the spacer. The oxyethylene spacer (**P5**) affords a single ordered mesophase at a lower temperature.

The influence of the terminal group in the mesogen was studied for carbon main chains by some authors but it is difficult to rationalize their results because different mesogens, different spacers and different main chains were examined. Using biphenyl as a mesogen and polymethacrylate as a main chain, Finkelman *et al.*[19] observed the absence of mesophase when the terminal group is an hydrogen atom and the change from a nematic mesophase to a smectic one when the terminal group grew from a methoxyl group to ethoxyl, pentoxyl or hexyloxyl groups. On the contrary, Rodekirch *et al.*[22] observed the same smectic phase with methoxyl or butoxyl terminal groups in the case of a phenylbenzoate mesogen and a polymethacrylate main chain. In the described polythiiranes, the influence of the terminal group appears obvious on comparing the LC properties of polymers **P8**, **10** and **11**. Without an alkoxy terminal group, the transitions temperatures decrease drastically and the smectic E phase disappears. As was observed by other authors with polyoxiranes[12], the length of the alkoxy terminal group does not influence the nature of the mesophases but a slight increase of the transition temperatures is observed when we substituted -OC_4H_9 for -OCH_3.

CONCLUSION

We have demonstrated in this study the ability of polythiiranes to act as main chains for liquid crystalline polymers. Unlike the previously described polyoxiranes, large and flexible spacers were needed to observe the liquid crystalline properties of biphenyl mesogens linked to polythiiranes. The mesophases obtained in polythiiranes are essentially smectic and the highly ordered smectic E phase was observed with nearly all of the polymers as in the corresponding polyoxiranes.

This obvious dependence of the behaviour of SCLC polyoxiranes and polythiiranes with the nature of the main chain is in accordance with the findings of Bresci *et al.*[23] but is also in accordance with the contradictory assumption of Finkelman *et al.*[24] since the same mesogens gave the same mesophases

At the present time, we are continuing with this work, considering the effects of various mesogenic groups on the thermal properties of polythiiranes and investigating the macroscopic orientation by mechanic effects of some polythiiranes.

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