Functional polythiiranes: 3. Synthesis and characterization of polythiiranes containing biphenyl units in the side chain

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The synthetic route to polythiiranes bearing side chain biphenyl groups is described. [(4-Biphenyl)methylthio]methylthiirane afforded relatively low molecular weight polymers in 50% yield, while (4-biphenyl)methyl 2-[(2,3 epithiopropyl)-thio]ethanoate afforded high molecular weight polymers in high yields.

(Keywords: polythiiranes; side chain liquid crystalline polymers)

Introduction

Side chain liquid crystalline polymers (SCLCPs) have been the topic of many studies (reviewed in ref. 1). Numerous mesogenic groups have been introduced as side chains but only a few types of main chain are used, namely polyacrylates, poly(vinylether)s and polysiloxanes, i.e. the repeat units contain two atoms in the main chain. Only a few examples of three-atom main chain repeat units have been reported[2–4] and a unique example of SCLCPs with sulfur in the backbone has been described, i.e. polysulfones[5].

Carbon-based backbones are often obtained by chain polymerization of suitable monomers: radical polymerization and, more recently, cationic living polymerization are the most convenient methods that have been used. The molecular weight distributions of polymers obtained by radical polymerization are often quite broad. Cationic living processes yield polymers with narrower distributions but the molecular weights remain generally low: number average degree of polymerization, $DP_n < 30$ for the SCLCPs described[6,7]. Anionic polymerization is not widely used[8] because mesogenic groups or spacers often contain ester groups which are reactive towards nucleophilic displacement.

The formation of thermotropic liquid crystalline phases and the extent of the side group organization are strongly dependent on the nature of the main chain. The influence of the polymer backbone with two-atom units on phase transitions has been studied by Percec and Pugh[9]. The general trends observed by comparison of various studies were that the most flexible backbones give the highest isotropization temperatures and the lowest glass transition temperatures, i.e. the broadest ranges of mesophases. As polysiloxanes achieve better flexibility than carbon-based main chain polymers, they often exhibit broader mesophase ranges. The insertion of sulfur in the carbon-based main chain, affording polymers with three-atom structural units, should thus enhance the flexibility of the main chain owing to the C–S bond length. Larger ranges of mesophases may be expected for these new polymers by comparison with previously described SCLCPs. Our present aim is the synthesis of new polymers containing the polythiirane backbone and some of the usual biphenyl mesogenic units as side chains from readily obtained monomers, which should lead to SCLCPs.

In the previous paper[10] we reported new polythiiranes with ester side chain groups efficiently obtained by anionic polymerization of a suitable monomer: methyl 2-[(2,3-epithiopropyl)-thio]ethanoate (METE) using the chemoselective tetramethylammonium dithiobenzoate (TMATB) as initiator. In this paper we report a synthetic route to prepare polythiiranes containing biphenyl units in the side chain from three new monomers: [(4-biphenyl)methylthio]methylthiirane **4**, 4-biphenyl 2-[(2,3-epithiopropyl)-thio]ethanoate **5**, (4-biphenyl)methyl 2-[(2,3-epithiopropyl)-thio]ethanoate **6**.

Results

Although there are numerous methods for the preparation of thiiranes[11], substituted thiiranes are difficult to obtain with high yields, owing to the reactivity of this heterocycle towards electrophilic as well as nucleophilic opening.

The synthetic route used for preparation of the new monomers is described in *Scheme 1*. The linkage between thiirane ring and biphenyl unit is realized by the efficient reaction[10] of mercaptomethylthiirane (MMT) on activated bromides, and derived from the thiol alkylation method[12]. The yields and the characterization of these monomers are described in the Experimental section and n.m.r. data are given in *Table 1*.

These monomers have been processed, by our previously developed method, to prepare the corresponding polymers, using TMATB as an initiator and dimethyl formamide (DMF) as a solvent. Monomer **5** did not afford

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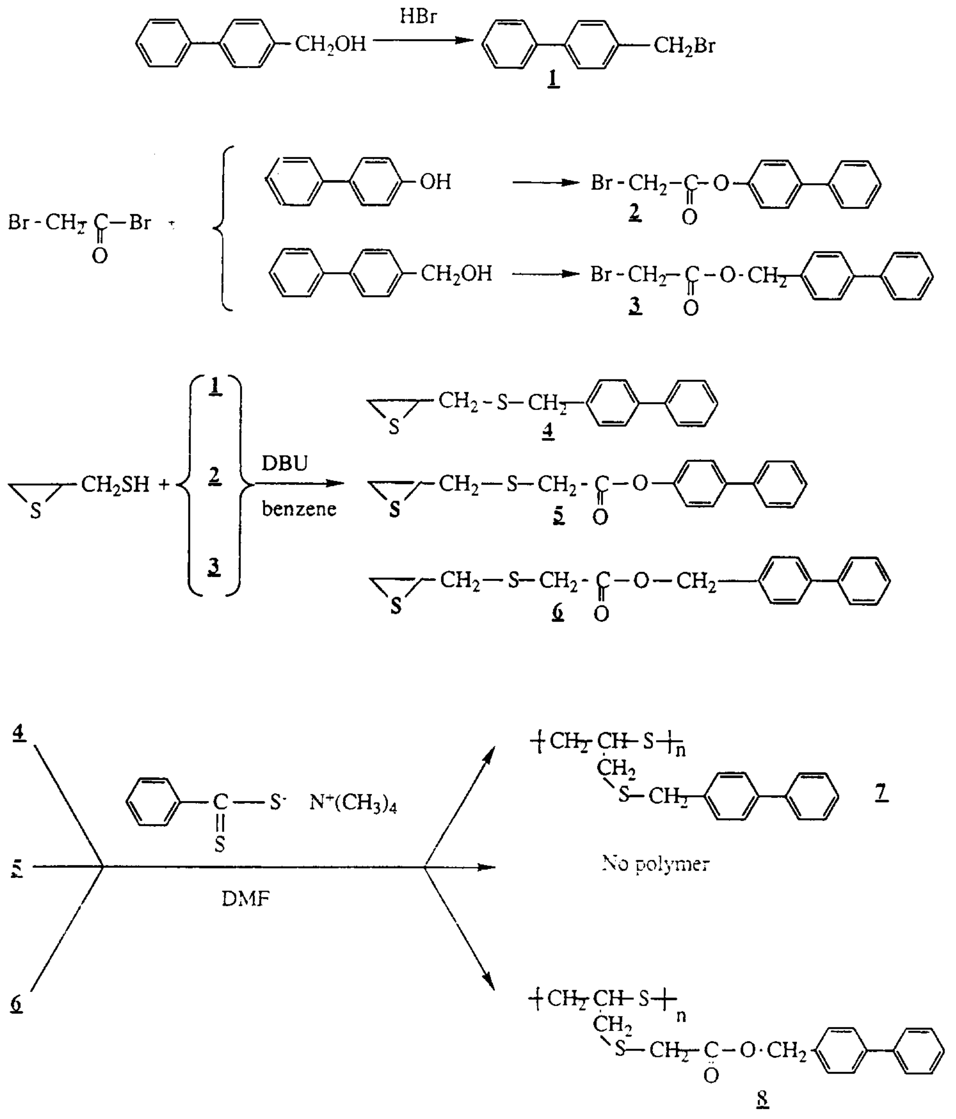


Scheme 1

any polymer, probably because the highly nucleophilic thiolate ion gave a transesterification reaction with the biphenyl ester owing to the good leaving group ability of (4-phenyl)phenolate anion. Monomers **4** and **6** afforded polymers with the structures expected, as indicated by the ^{1}H and ^{13}C n.m.r. data presented in *Table 1*. The polymerization conditions and values of DP_n are summarized in *Table 2*. Monomer **4** led to polymers **7** with observed DP_n (g.p.c.) lower than theoretical values for a living polymerization and independent of the initiator concentration. The polymerization yield has been evaluated at 50% by monitoring the disappearance of the thiirane doublet at 2.15 ppm in ^{1}H n.m.r. spectroscopy; this yield is obtained in 1 h. At present, we consider that the decrease of the polymerization rate and the low yield with respect to other thiirane monomers[10,13] may result from conformational effects in organization of the growing chain of polymer 7. On the contrary, monomer **6** gave rise to quantitative yields in less than 2 min (^{1}H n.m.r. disappearance of the thiirane doublet at 2.25 ppm). For high $(M_0)/(I_0)$ ratios (where M_0 is monomer concentration and I_0 is ionomer concentration), monomer **6** led to polymer **8** with observed DP_n values in accordance with those calculated in living polymerization. For the lowest ratios, the initiator was not completely consumed, the purple colour of the initiator persisted, and the obtained DP_n values are higher than the calculated ones. Identical results have been obtained for methyl thiirane (MT)[13] and METE[10]. The introduction of an ester group in the side chain has led to easier conformational ordering and has lowered steric effects in the growing polymer chain.

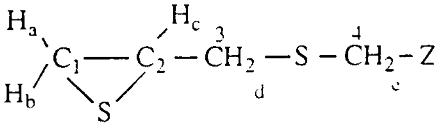
Identical mesogenic units have been used by Sagane and Lenz[6] with comparable spacers, on a poly(vinylether) main chain; these authors studied the relationships between the molecular weight distribution and the thermal properties of the polymers. Duran and Gramain[14] used identical mesogenic units on a polyacrylate main chain. The average molecular weights of polymer **7** are in the same range as those reported in ref. 6, but these values are higher for polymer **8** than those reported for similar mesogenic units and spacers[6,14].

Conclusions

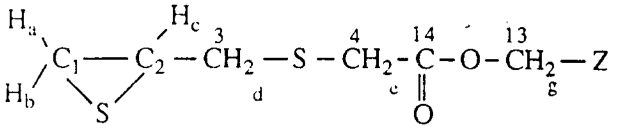
A series of new substituted thiiranes has been prepared. Their anionic polymerization in DMF with TMATB as initiator has afforded a new class of polythiiranes with side chains containing biphenyl units that might exhibit liquid crystalline properties, some with high molecular weights. These efficient synthetic methods have been

Table 1 ^1H and ^{13}C n.m.r. data for monomers **4** and **6** and the corresponding polymers

Monomers:

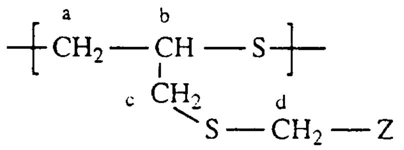


δ (ppm)	^1H	δ (ppm)	^{13}C
2.15 (d, 1H)	a	25.80	1
2.40–2.55 (m, 2H)	b, c	33.80	2
2.90–3.10 (m, 2H)	d	36.40	3
3.85 (s, 2H)	e	37.60	4
7.20–7.70 (9H)		126.99	7, 10
		127.29	12
		128.26	11
		129.26	6
		137.05	5
		140.11	8
		140.63	9

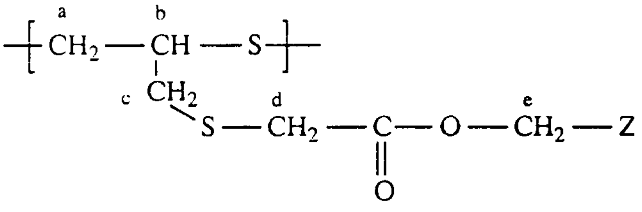


δ (ppm)	^1H	δ (ppm)	^{13}C
2.25 (d, 1H)	a	25.69	1
2.50 (d, 1H)	b	33.29	2
2.70 (m, 1H)	c	33.80	3
3.05 (m, 2H)	d	38.59	4
3.40 (s, 2H)	e	66.94	13
5.25 (s, 2H)	g	127.11	7, 10
		127.37	12
		127.51	11
		128.87	6
		134.36	5
		140.54	8
		141.47	9
		170.0	14

Polymers:

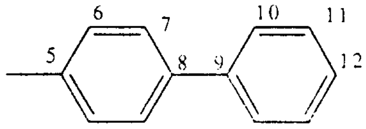


δ (ppm)	^1H	δ (ppm)	^{13}C
2.60–3.00 (m, 5H)	a, b, c	36.10	a
3.60–3.85 (m, 2H)	d	36.24	c
7.10–7.60 (m, 9H)	Z	36.97	d
		47.30	b
		126.99	7, 10
		127.26	12
		128.78	11
		129.43	6
		137.16	5
		139.92	8
		140.55	9



δ (ppm)	^1H	δ (ppm)	^{13}C
2.85 (s, 2H)	a	34.33	a
2.95 (s, 2H)	c	35.86	b
3.05 (s, 1H)	b	37.18	d
3.25 (s, 2H)	d	46.57	dyad b
5.10 (s, 2H)	e	46.83	
7.20–7.60 (9H)	Z	66.85	e
		127.09	7, 10
		127.29	12
		127.46	11
		128.81	6
		131.51	5
		140.40	8
		141.21	9
		170.06	C=O

Z:



extended to monomers with 4′-substituted biphenyl units, since polymers with unsubstituted units do not often exhibit liquid crystalline properties. At present, their polymerization is being studied as well as the thermal behaviour of these new materials. Several aspects of the polymerization reactions will also be examined in the future.

Experimental

^1H and ^{13}C n.m.r. spectra were obtained on a Brucker AC 400 MHz n.m.r. spectrometer. Samples were run in $CDCl_3$ with tetramethylsilane as standard. I.r. spectra were recorded on a Fourier transform Perkin–Elmer 1750. Satisfactory analyses of the monomers were carried out in the CNRS Laboratory at Solaize (France).

Table 2 Polymerization of monomers **4** and **6** and characterization of the resulting polymers ($t = 20°C$; DMF (2 ml); $M_0 = 10^{-2}$ mol; polymerization time 1 h)

Monomer	$[M_0]/[I_0]$	Polymer yield (%)[a]	G.p.c. $M_n \times 10^{-3}$	G.p.c. DP_n	G.p.c. M_w/M_n
4	161	48[b]	5.1	19	1.48
	100	46[b]	4.9	18	1.43
	49	49	3.7	14	1.83
	32	52	3.5	13	2.03
	24	46	3.4	12.5	1.81
	20	45	3.4	12.5	1.83
6	160	95	45.4	138	1.54
	100	92	37.7	114	1.50
	50	89	30.6	93	1.50
	33	91	23.0	70	1.70
	14	67	16.2	49	1.46

[a] After a second precipitation

[b] Identical results with higher polymerization time

Molecular weights were determined by g.p.c. on Styragel columns calibrated with standard polystyrene samples.

Bromobiphenyl methane **1** was prepared from biphenyl methanol and according to ref. 15. Yield 75%; m.p. 84°C (lit. 84–85°C).

4-Biphenyl(2-bromo)acetate **2** was prepared from 4-phenyl phenol and 2-bromo acetylbromide according to ref. 16. The crude product was recrystallized from cyclohexane. Yield 90%; m.p. 112°C; ^1H n.m.r.: $\delta = 4.10$ (s, 2H), 7.15–7.65 (m, 9H).

(4-Phenyl)benzyl(2-bromo)acetate **3** was prepared from biphenyl methanol and 2-bromoacetyl bromide according to ref. 16. The crude product was purified by recrystallization from cyclohexane. Yield 95%; m.p. $< 50°C$; ^1H n.m.r.: $\delta = 3.90$ (s, 2H), 5.25 (s, 2H), 7.30–7.70 (m, 9H).

Mercaptomethylthiirane was prepared according to ref. 17. The reactions with compounds **1**, **2**, **3** were carried out in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), under the experimental conditions reported previously[10].

[(4-Biphenyl)methylthio)]methylthiirane **4**. The crude product was purified by chromatography on silica gel with ether as eluent. Yield, quantitative; m.p. 58°C; i.r. (CH_2Cl_2): 1519 and 1488 (aromatic), 641 (C–S thiirane).

4-Biphenyl 2-[(2,3-epithiopropyl)-thio]ethanoate **5**. The crude product was purified by silica gel chromatography with ether/petroleum ether (50/50) as eluent. Yield 60%; m.p. 50°C; ^1H n.m.r.: $\delta = 2.40$ (d, $J = 6$ Hz, 1H), 2.65 (d, $J = 6$ Hz, 1H), 2.85 (m, 1H), 3.20 (m, 2H), 3.6 (s, 2H), 7.15–7.65 (m, 9H); i.r. (CCl_4): 3035 (CH aromatic), 1757 (C=O), 1515 and 1485 (aromatic), 621 (C–S thiirane).

(4-Biphenyl)methyl 2-[(2,3-epithiopropyl)-thio]ethanoate **6**. The crude product was purified by silica gel chromatography with cyclohexane/ether as eluent (95/5). Yield 70%; m.p. 41°C; i.r. (CH_2Cl_2): 1734 (C=O), 1511 and 1488 (aromatic), 621 (C–S thiirane).

Monomers were polymerized with different amounts of initiator in DMF as previously described[10]. The polymers were precipitated, polymer **7** in diethylether and polymer **8** in ethanol; they were then washed, dissolved in tetrahydrofuran and precipitated once again. Polymerization data are reported in *Table 2*. The ^{13}C n.m.r. signals (*Table 1*) have been attributed by 'off resonance' experiments, by comparison with other thiiranes[10] and with calculated values[18].

References

1 McArdle, C. B. (Ed.) 'Side Chain Liquid Crystal Polymers' Blackie, Glasgow, 1989
2 Cser, F., Nyitrai, K., Horwath, J. and Hardy, G. *Eur. Polym. J.* 1985, **21**, 259
3 Piercourt, S., Lacoudre, N., Le Borgne, A. and Spassky, N. *Makromol. Chem.* 1992, **193**, 705
4 Pugh, C. and Percec, V. *Polym. Bull.* 1986, **16**, 521
5 Arnold, N., Braun, D., Hirschmann, H. and Wendorff, J. H. *Makromol. Chem., Rapid Commun.* 1988, **9**, 331
6 Sagane, T. and Lenz, R. *Polym. J.* 1988, **20**, 923
7 Percec, V., Lee, M. and Ackerman, C. *Polymer* 1992, **33**, 703
8 Hahn, B., Wendorff, J. H., Portugall, M. and Ringsdorf, H. *Colloid Polym. Sci.* 1981, **259**, 875
9 Percec, V. and Pugh, C. in 'Side Chain Liquid Crystal Polymers' (Ed. C. B. McArdle), Blackie, Glasgow, 1989, p. 66
10 Bonnans-Plaisance, C., Courric, S. and Levesque, G. *Polym. Bull.* 1992, **28**, 489
11 Sander, M. *Chem. Rev.* 1966, 297
12 Ono, N., Miyake, H., Saito, T. and Kaji, A. *Synthesis* 1980, 952
13 Bonnans-Plaisance, C. and Levesque, G. *Polymer* 1991, **32**, 1318
14 Duran, R. and Gramain, P. *Makromol. Chem.* 1987, **188**, 2001
15 Birkeland, S., Daub, G., Hayes, F. N. and Ott, D. G. *J. Org. Chem.* 1961, **26**, 2662
16 Vollmar, A. and Dunn, M. S. *J. Org. Chem.* 1960, **25**, 387
17 Doyle, F. P., Holland, D. O., Mansford, K. R. L., Nayler, J. H. C. and Queen, A. *J. Chem. Soc.* 1960, 2660
18 Breitmaier, E. and Voelter, W. in 'Carbon 13 n.m.r. Spectroscopy', VCH mbH, Weinheim, 1987, p. 315