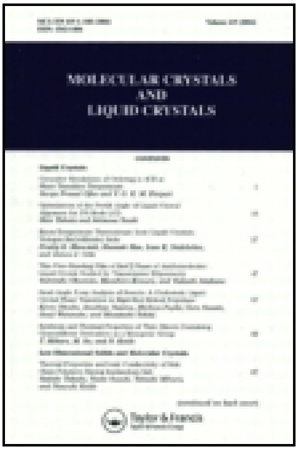


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

The Synthesis of Oxetane Monomers and their Polymerisation to give Side-Chain Liquid-Crystalline Polymers with Broad Smectic C Phases

Stephen J. Cowling [a] , Kenneth J. Toyne [a] & John W. Goodby [a]

[a] Department of Chemistry, Faculty of Science and the Environment, University of Hull, Hull, HU6 7RX, U.K.

Version of record first published: 24 Sep 2006

To cite this article: Stephen J. Cowling, Kenneth J. Toyne & John W. Goodby (1999): The Synthesis of Oxetane Monomers and their Polymerisation to give Side-Chain Liquid-Crystalline Polymers with Broad Smectic C Phases, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 332:1, 471-483

To link to this article: http://dx.doi.org/10.1080/10587259908023793

Mol. Cryst. Liq. Cryst., 1999, Vol. 332, pp. 471-483
Reprints available directly from the publisher
Photocopying permitted by license only

The Synthesis of Oxetane Monomers and their Polymerisation to give Side-Chain Liquid-Crystalline Polymers with Broad Smectic C Phases

STEPHEN J. COWLING, KENNETH J. TOYNE and
JOHN W. GOODBY

Department of Chemistry, Faculty of Science and the Environment, University of Hull, Hull, HU6 7RX, U.K.

A series of side-chain liquid-crystalline polymers has been synthesised from monomeric oxetanes. The synthesis and liquid crystal properties of the monomers and the polymers are discussed and it is shown that a short spacer unit can be used to obtain polymers with a flexible backbone which give broad liquid crystalline phases and low glass transition temperatures. Various initiators were used for the polymerisation but the photoinitiator "SARCAT KI 85^{TM}", a disulfonium salt, yielded the best results.

Keywords: side-chain liquid crystal polymers; oxetanes; cationic ring-opening polymerisation

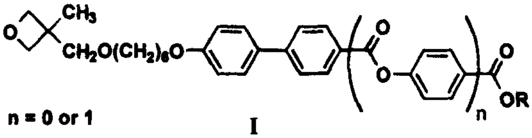
INTRODUCTION

The synthesis and properties of side-chain liquid-crystalline polymers (SCLCP's) has been an area of active research for 20 years. One of the aims of research in SCLCP's is the desire to synthesise polymers with either low or high glass transition temperatures (Tg) and broad ferroelectric or antiferroelectric phase ranges which are of interest as piezoelectric, pyroelectric and display device materials. Most of the SCLCP's which have been synthesized are based on polyacrylates, polymethacrylates and polysiloxanes[1].

Previous work on polyacrylates[2-5] has shown that they have high Tg values which arise because the backbone is rather rigid and has a dense population of the pendant groups along the backbone, *i.e.*, the side-chains are attached at every second atom along the backbone. On the other hand it is well established that in order to generate liquid-crystalline mesophases in side-chain polymers, a flexible spacer group[6,7] is needed which is long enough to separate the rigid mesogenic cores from the polymer backbone and so allow for the core units to interact with little or no constraint. The typical length of the spacer group to achieve this is 7-12 methylene units[7].

In order to obtain polymers with low Tg values, a flexible polymer backbone is required, and it has been shown that polysiloxanes[8] give the most flexible backbones. In this respect they are superior to polyoxyethylene, polyacrylate and polymethacrylate backbones. Polymers derived from oxetanes are a less widely studied class of polymer although such polymers which incorporate two rings in the mesogenic group have been reported[9,10]. These polymers gave liquid-crystalline phases from room temperature up to 100 °C.

In this article we report the synthesis of oxetanes of type **I** in order to generate a flexible backbone in the derived polymers. The pendant groups in these polymers are spaced out more thinly along the backbone and are attached at every fourth atom. As the side chains are well separated from one another along the polymer backbone, it is possible that shorter length spacer groups (*e.g.*, only 6 methylene units long) can be used to give liquid crystalline mesophases.



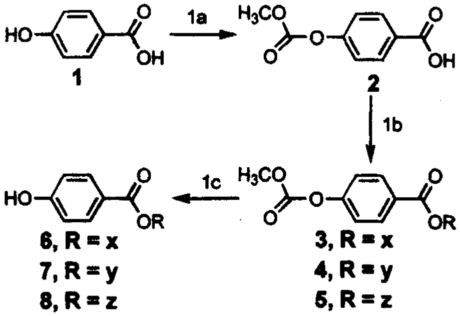
I

Some of the monomers prepared are also of interest as low molecular weight materials for ferroelectric applications, and our study of those properties will be reported in a further paper.

RESULTS AND DISCUSSION

Synthesis

Scheme 1 shows the route to the alkyl 4-hydroxybenzoates (**6-8**) utilizing methyl chloroformate as a protecting group for 4-hydroxybenzoic acid.

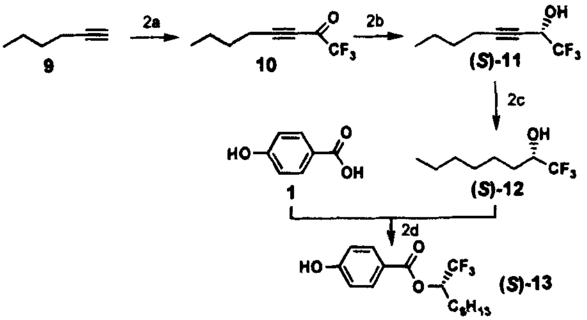


Where: x = (*R*)-1-methylheptyl
y = (*R*)-2-methylbutyl
z = 1-propylbutyl

Reagents: 1a...i) 1M NaOH, H_2O, $ClCO_2CH_3$; ii) HCl; 1b...DEAD, PPh_3, ROH, THF; 1c...ethanol, NH_3.

Scheme 1

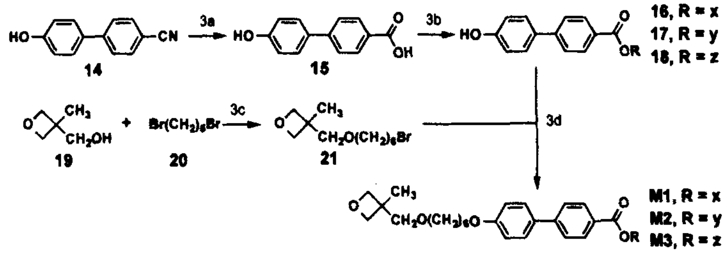
Scheme 2 gives the route to (*S*)-(-)-1-(trifluoromethyl)heptyl 4-hydroxybenzoate (**13**). The synthesis of (*S*)-(-)-1,1,1-trifluorooctan-2-ol (**12**) was carried out according to R. Lindermann *et al.*[11] and P. Ramachandran *et al.*[12] The final step in the synthesis is an acid-catalysed esterification, with the retention of configuration of the chiral group, as described by T. Kitazume *et al.*[13]



Reagents: 2a...i) 2.5M BuLi, THF; ii) $CF_3CO_2CH_2CH_3$; 2b...(-)-DIP-chloride, diethanolamine, ether; 2c...10% Pd-C, H_2, THF; 2d...toluene-*p*-sulfonic acid, *p*-xylene.

Scheme 2

Scheme 3 shows the synthesis of the simple biphenyl ester containing monomers (**M1-M3**). Reaction step 3c is a phase-transfer reaction described by M. Matoi *et al.*[14] which gives **21** in 70% yield. The final step in the synthesis of monomers **M1-M3** gave good yields (80-90 %).

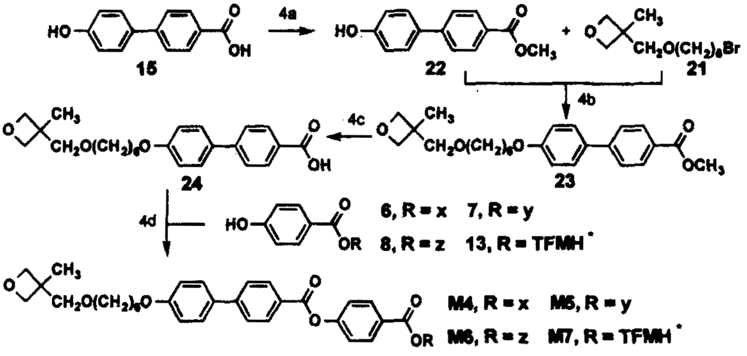


Where: x = (*R*)-1-methylheptyl
y = (*R*)-2-methylbutyl
z = 1-propylbutyl

Reagents: 3a...CH_3CO_2H, 11M H_2SO_4; 3b...DEAD, PPh_3, ROH, THF; 3c...50% NaOH, hexane, TBAB; 3d...K_2CO_3, butanone.

Scheme 3

In order to synthesise polymers with broad smectic phase temperature ranges, it was clear, from the results for the polymers **P1-P3**, that monomers with three rings in the mesogenic group would be required, and scheme 4 shows the synthesis of such monomers. The etherification step 4b gives excellent yields >85%. The key step in this synthesis is the hydrolysis of the methyl ester (**23**) to give the carboxylic acid (**24**). Oxetanes are prone to ring opening in the presence of strong acids and this can lead to problems on acidification of the sodium salt to yield the carboxylic acid. Acidification was achieved by careful addition of hydrochloric acid to a stirred suspension of the sodium salt in ethanol at pH 5. The mixture was left to stir for several hours and the acid was filtered off and washed with copious amounts of cold water. Esterification with *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) gave the monomers (**M4-M7**) in good yields (70-80%).

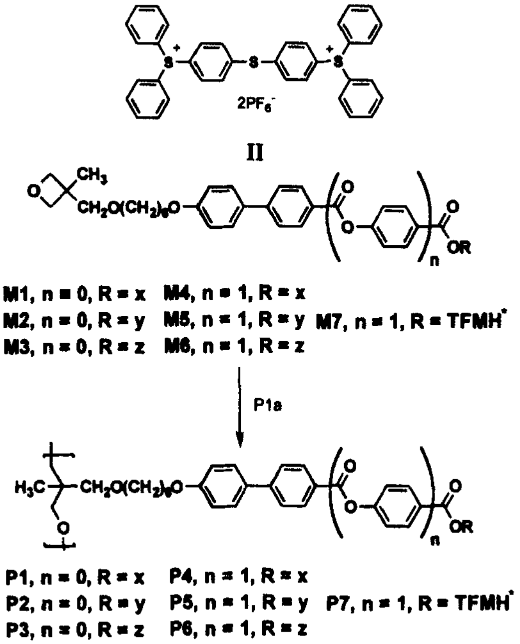


Where: **x** = (*R*)-1-methylheptyl
y = (*R*)-2-methylbutyl
z = 1-propylbutyl
TFMH* = (*S*)-1-(trifluoromethyl)heptyl

Reagents: 4a...CH_3OH, 11M H_2SO_4; 4b...K_2CO_3, butanone; 4c...i) 11M NaOH, ethanol, ii) 1M HCl; 4d...DCC, DMAP, CH_2Cl_2.

Scheme 4

Initially, the standard boron trifluoride-ether initiator in various organic solvents was used to attempt the polymerisations. Unfortunately even after one week this method only yielded a mixture of dimer, trimer and tetramer. However, photoinitiator, SARCAT KI 85™, (II) at 2 mol% gave polymerisation in good yield with 70-80% conversion. The polymerisation process was then optimised for **M6** using various reaction times and different pre- and post-irradiation conditions, the results are displayed in Table II.



M1, n = 0, R = x **M4, n = 1, R = x**
M2, n = 0, R = y **M5, n = 1, R = y** **M7, n = 1, R = TFMH***
M3, n = 0, R = z **M6, n = 1, R = z**

P1, n = 0, R = x **P4, n = 1, R = x**
P2, n = 0, R = y **P5, n = 1, R = y** **P7, n = 1, R = TFMH***
P3, n = 0, R = z **P6, n = 1, R = z**

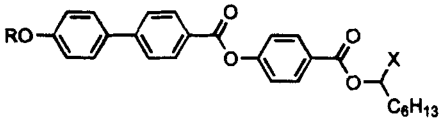
Where: **x** = (*R*)-1-methylheptyl
y = (*R*)-2-methylbutyl
z = 1-propylbutyl
TFMH* = (*S*)-1-(trifluoromethyl)heptyl

Reagents: P1a...2 mol% SARCAT KI 85™, UV irradiation.

Scheme 5

Monomers - Transition Temperatures and Phase Morphologies

The phase morphologies and the transition temperatures of the monomers (**M1**-**M7**) were determined by a combination of microscopy and DSC, the results of these studies are given in table I. Monomers **M1**-**M3** for the two-ring systems were not mesogenic; monomer **M2** melted at 25.0 °C but **M1** and **M3** were liquids at room temperature and did not freeze on cooling to -70 °C. All the monomers with three aromatic rings in the core of the mesogenic unit displayed liquid-crystalline phases; monomers **M4**-**M6** all melted close to 35 °C but did not recrystallize on DSC analysis until the samples had been maintained at -70 °C for 30 minutes. The melting points of the monomers can be compared with several examples from the MHPOBC series[15]. For example, monomer **M4** is similar to **III**, but more closely related to **IV**[16] on the basis of the length of the terminal chain. Compared to these compounds, **M4** shows a reduced melting point (39.0, 32.5 °C; leading to a room temperature smectic C phase), clearing point (45.6, 35.9 °C) and smectic C stability (64.3, 63.7 °C) because of the bulky end group on the terminal chain. In addition, a variety of smectic C subphases has been suppressed by the presence of the bulky unit which probably causes a disruption in the interaction of the head / tail groups in the packing of the mesophases. The comparison of compound **V**[17] and **M7** (trifluoromethyl compounds) is equivalent to the comparison of **III** and **M4** for the methyl analogues. The pair of trifluoromethyl compounds shows that the bulky oxetane unit causes an extremely large depression of melting point (>150 °C) but the clearing point and smectic C depressions (61.7 and 65.5 °C) are similar to those seen for **M4** and **III**.



III, $R = C_8H_{17}$, $X = CH_3$ C 73.5 (SmI^*_A 62.2) SmC^*_A 118.8 SmC^*_{ferri} 119.8 SmC^* 121.6 SmC^*_{alpha} 122.6 SmA^* 147.7 I

IV, $R = C_{10}H_{21}$, $X = CH_3$ C 67.0 SmC^*_A 115.0 SmC^* 122.0 SmA^* 138.0 I

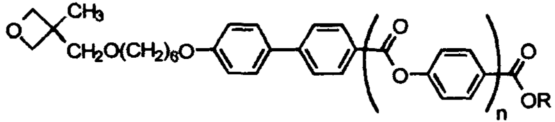
V, $R = C_8H_{17}$, $X = CF_3$ C 84.5 SmC^*_A 108.0 SmC^* 109.0 SmA^* 121.0 I

Polymers - Transition Temperatures and Phase Morphologies

The polymerisations were carried out using a thin film of a mixture of the monomer and photoinitiator. The two-ring monomers (**M1-M3**) polymerised readily to give polymers with high DP values in the range of ≈ 60-80 (see Table III) but with a fairly high polydispersity (up to 3.4). Only **P2** showed liquid crystalline behaviour, having a smectic A phase from 80 °C until the Tg at -2.6 °C. The Tg of **P2** can be compared to the values for its polysiloxane analogue[18] which occur at 30-50 °C for a range of molecular weights. The percentage conversion of the two-ring monomers into the polymers was high, being 80% or higher. Polymerisation of the three-ring monomers was more sluggish and **M4-M7** gave polymers with a much lower DP than the two-ring monomers but the products have liquid-crystalline properties that occur over a broad temperature range. Polymers **P4-P6** gave consistent DP values of 19-23 repeat units but **P7** has a much lower DP of 11. All the three-ring polymers show smectic A and smectic C mesophases and have Tg values below 20 °C. The percentage conversion of these monomers was lower than for the two-ring materials, but was typically higher than 60%.

A polyacrylate[5] closely related to polymers **P4-P6** had a similar phase sequence but the Tg for the polyacrylate was 56 °C. Upon increasing the spacer

TABLE I: Transition temperatures (°C) for monomers **M1-M7**.



Compound No.	n	R	mp[a] / °C	Iso		BP		SmA/SmA*		SmC/SmC*		recryst[b]
M1	0	1-MH*	—	•	—	—	—	—	—	—	—	<-70
M2	0	2-MB*	25.0	•	—	—	—	—	—	—	—	-21.7
M3	0	1-PB	—	•	—	—	—	—	—	—	—	<-70
M4	1	1-MH*	34.5	•	102.1	—	—	•	58.3	•	—	<-70
M5	1	2-MB*	36.6	•	134.1	•	130.7	•	90.6	•	13.3[c]	<-70
M6	1	1-PB	35.7	•	64.9	—	—	•	49.5	•	—	<-70
M7	1	TFMH*	<-70	•	59.3	—	—	•	43.5	•	—	<-70

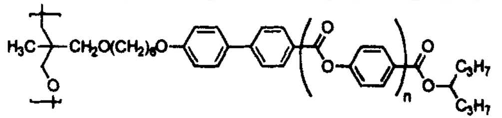
a .. determined by DSC after being maintained at -70 °C for 30 minutes.
b .. determined by DSC.
c .. transition at 13.3 °C to an unidentified phase.

1-MH* = (*R*)-1-methylheptyl
2-MB* = (*R*)-2-methylbutyl
1-PB = 1-propylbutyl
TFMH* = (*S*)-1-(trifluoromethyl)heptyl

length from 6 to 11 the Tg for the polyacrylate was reduced to 40 °C which is still 21-29 °C higher than for the polyoxetanes reported here.

Electrooptic studies are currently being carried out on all of the monomers and polymers reported here in order to assess their switching properties in the ferroelectric smectic C phase. Future work to be reported includes an investigation into the effect of introducing lateral fluoro substituents and of varying the length of the spacer groups.

TABLE II: Results for the polymerisation of monomer **M6** in various conditions.



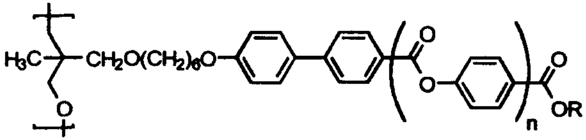
Time (min)	Mn	Mw	Mw/Mn	DP
30	8900	11400	1.3	14
60	9300	13349	1.4	15
90	7264	9885	1.4	12
120	7700	10154	1.3	12-13
180	7500	9954	1.3	12
640	7700	7740	1.3	12-13
60[a]	13200	18473	1.4	21
60[b]	10400	12481	1.2	17
60[c]	13700	20674	1.5	22

a .. pre-heated at 80 °C for 30 minutes and cooled to RT under N_2 in the dark.
b .. post-heated at 80 °C for 1 hour.
c .. pre-heated at 80 °C for 30 minutes and cooled to RT under N_2 in the dark and post-heated at 80 °C for 1 hour.

CONCLUSIONS

Several polymers derived from oxetanes have been produced which give broad smectic phase behaviour and have low Tg's, typically below room temperature. The polymers are extremely fluid as shown by their ability to give excellent

TABLE III: Transition temperatures (°C) and GPC data for polymers **P1-P7**.



Compound No.	n	R	Mn	Mw	Mw/ Mn	DP	Iso		SmA/SmA*		SmC/SmC*		Tg
P1	0	1-MH*	40617	82428	2.0	80	●	—	—	—	—	-5.7	●
P2	0	2-MB*	27521	79227	2.8	59	●	80.0	●	—	—	-2.6	●
P3	0	1-PB	51334	141607	3.4	83	●	—	—	—	—	-5.9	●
P4	1	1-MH*	14575	30449	2.0	23	●	167.8	●	150.2	●	11.8	●
P5	1	2-MB*	10998	71497	2.0	19	●	227.8	●	190.3	●	19.0	●
P6	1	1-PB	13700	20674	1.5	22	●	146.5	●	134.5	●	11.2	●
P7	1	TFMH*	7413	9889	1.3	11	●	108.7	●	88.4	●	14.9	●

1-MH* = (*R*)-1-methylheptyl
2-MB* = (*R*)-2-methylbutyl
1-PB = 1-propylbutyl
TFMH* = (*S*)-1-(trifluoromethyl)heptyl

textures for phase identification and classification by microscopy. The polymers anneal into smectic phases with well defined defect textures after only a few minutes (*e.g.* see Figure 1), and they do not give the sandy textures which are characteristic of SCLCP's.

Figure 1: Photomicrograph of **P4** in a smectic A phase at 158.0 °C after annealing for 4 minutes.
(See Color Plate XII at the back of this issue)

Acknowledgements

The authors thank DERA (Malvern) for financial support for this work and also Total for the kind donation of the photoinitiator. This work is published with the permission of the Controller of Her Britannic Majesty's Stationery Office.

References

[1] J.-C. Dubois, P. le Barny, M. Mauzac, and C. Noel, in *"Handbook of Liquid Crystals"*, Vol 3, Ed., D. Demus, J. W. Goodby, G. W. Gray, H.-W. Spiess, and V. Vill, (Wiley-VCH, Weinheim), p. 207 (1998).

[2] T. Ikeda, O. Zushi, T. Sasaki, K. Ichimura, H. Takezoe, A. Fukuda, and K. A. W. Sharp, *Mol. Cryst. Liq.* Cryst., **225**, 67 (1993).

[3] K. Kuhnpast, J. Springer, G. Scherowsky, F. Giesselmann, and P. Zugenmaier, *Liq. Cryst.*, **14,** 861 (1993).

[4] P. le Barny, G. Ravaix, J. C. Dubois, J. P. Parneix, R. Njemo, C. Legrand, and P. M. Levelut, *SPIE*, **682,** 56 (1986).

[5] P. Davidson, K. Kuhnpast, J. Springer, and G. Scherowsky, *Liq. Cryst.*, **14,** 901 (1993).

[6] S. Pfeiffer, R. Shashidhar, J. Nacriri, and S. Mery, *SPIE,* **1665,** 166 (1992).

[7] G.-H. Hsiue, P.-J. Hsieh, S.-L. Wu, and C.-S. Hsu, *Polym. Bull.*, **33,** 159 (1994).

[8] S. Hachiya, K. Tomoike, K. Yuasa, S. Togawa, T. Sekiya, K. Takahashi, and K. Kawasaki, *J. SID,* **1,** 295 (1993).

[9] M. Motoi, K. Noguchi, A. Arano, S. Kanoh, and A. Ueyama, *Bull. Chem. Soc. Jpn.*, **66,** 1778 (1993).

[10] Y.-H. Lu and C.-S. Hsu, *Macromol.*, **28,** 1673 (1995).

[11] R. J. Lindermann and M. S. Lonikar, *J. Org. Chem.*, **53**, 6013 (1988).

[12] P. V. Ramachandran, B. Gong, A. V. Teodorovic, and H. C. Brown, *Tetrahedron: Asymmetry,* **5,** 1061 (1994).

[13] T. Kitazume, S. Kaneko, T. Yamazaki, and S. Watanabe, *J. Fluorine Chem.*, **60,** 135 (1993).

[14] M. Motoi, H. Suda, K. Shimamura, S. Nagahara, M. Takei, and S. Kanoh, *Bull. Chem. Soc. Jpn.*, **61,** 1653 (1988).

[15] A. D. L. Chandani, Y. Ouchi, H. Takezoe, and A. Fukuda, *Jpn. J. Appl. Phys.*, **28,** L1261 (1989).

[16] T. Kusumoto, K. Ogino, T. Hiyama, T. Isozaki, and Y. Suzuki, *Chem. Lett.*, p. 865 (1996).

[17] Y. Suzuki, T. Hagiwara, I. Kawamura, N. Okamura, T. Kitazume, M. Kakimoto, Y. Imai, Y. Ouchi, H. Takezoe, and A. Fukuda, *Liq. Cryst.*, **6,** 167 (1989).

[18] H. Endo, S. Hachiya, T. Sekiya, and K. Kawasaki, *Liq. Cryst.*, **12,** 147 (1992).