Pergamon

0014-3057(95)00141-7

Eur. Polym. J. Vol. 32, No. 3, pp. 295–298, 1996

0014-3057/96 $15.00 + 0.00

COMB-BRANCH CHIRAL LIQUID CRYSTALLINE POLYMERS—IV. COPOLYMERS OF (S)-2-[2-(4′-METHOXY-4-BIPHENYLOXY)-1-METHYL ETHOXY] ETHYL METHACRYLATE AND A NON CHIRAL MESOGEN BASED ON ITACONIC ACID

J. M. G. COWIE* and H. W. HUNTER
Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, Scotland

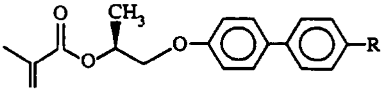
(Received 31 January 1995; accepted in final form 7 March 1995)

Abstract—An optically active monomer (S)-2-[2-(4′-methoxy-4-biphenyloxy)-methyl ethoxy] ethyl methacrylate (**3**) with a chiral centre located in the spacer unit has been copolymerized with di-[6-(4′-methyl-4-biphenyloxy)hexyl]-2-methylene butane-1,4-dioate (**2**) to give a range of copolymers displaying either both smectic and chiral nematic or only chiral nematic, liquid crystal phases. These samples displayed selective reflection of visible light, the wavelength of which tended to shorten as the amount of chiral monomer in the copolymer increased. There was also evidence to suggest that the homopolymer of **3** reflects in the UV region.

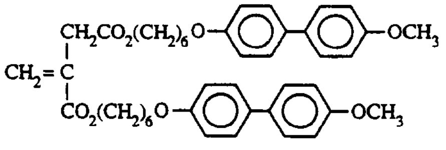
INTRODUCTION

Comb–branch liquid crystal polymers containing a chiral centre tend to exhibit interesting optical properties, such as selective reflection of electromagnetic radiation arising from the helical structure that is generated in the chiral nematic phase [1–3]. Most of these polymers have the chiral unit located in the terminal group of the pendant mesogen [4], but an alternative approach is to incorporate the chiral centre in the spacer unit, lying between the backbone of the polymer and the mesogen [5]. This is a more flexible approach as it leaves the terminal group free for further modification. The nature of the terminal unit of a mesogen in a side chain liquid crystal polymer can have an influence on the nature and thermal stability of the liquid crystal phase formed and it is of interest to examine these effects, particularly when copolymerization can also provide an added dimension to these systems.

In a previous paper [6] we examined a series of copolymers prepared by reacting (S)-2-[2-(4′-cyano-4-biphenyloxy)-1-methyl ethoxy] ethyl methacrylate (**1**) with a non chiral mesogen di-[6-(4′-methyoxy-4-biphenyloxy)hexyl]-2-methylene butane-1,4-dioate (**2**) derived from itaconic acid. In this paper work extending this study is described in which the terminal of **1** is altered to a methoxy unit and the monomer (S)-2-[2-(4′-methoxy-4-biphenyloxy)-1-methyl ethoxy] ethyl methacrylate (**3**) is copolymerized with **2** to give a series of copolymers that exhibit liquid crystalline behaviour that is different from that observed for copolymers of **1** and **2**.



1: R = CN
3: R = OCH$_3$



2

EXPERIMENTAL

The synthesis if the itaconic acid derivative, monomer **2**, has been described elsewhere [6]. The chiral monomer **3** was prepared according to reaction Scheme 1. Compound **4** was prepared from (S)-ethyl lactate as described previously [5].

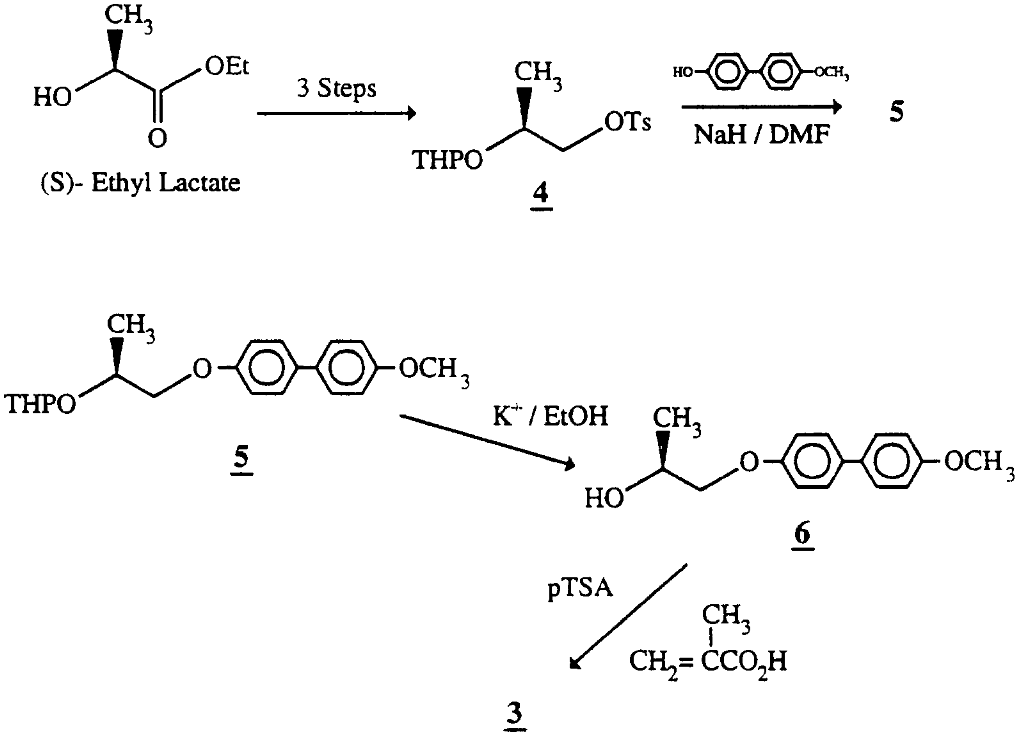
The chiral monomer (**3**) was prepared in three steps from the tosylate (**4**). The first step involved displacement of the tosyl group in (**4**) by the sodium salt of 4-methoxy-4′-hydroxy biphenyl in DMF, to give (**5**). Deprotection of the alcohol functionality in acidic ethanol gave the chiral alcohol (**6**) which was finally converted into the monomer (**3**) by esterification with methacrylic acid (Scheme 1).

1-(4′-methoxy-4-biphenyloxy)-2-(tetrahydro-2-pyranoxy) propane (5)

Sodium hydride (0.69 g, 29 mmol) was slurried in anhydrous DMF (15 ml) under a flow of nitrogen and a solution

---

*To whom all correspondence should be addressed.



Scheme 1.

of 4′-methoxy-4-hydroxybiphenyl (5.6 g, 28 mmol) in anhydrous DMF (50 ml) added slowly, dropwise. The mixture was stirred mechanically and heated to 50°C for *ca* 1 hr after the addition, during which time the phenoxide precipitated out of solution. A solution of the tosylate (**4**) (8 g, 25 mmol) in DMF (20 ml) was then added slowly, dropwise into the heterogeneous mixture whilst it was stirred vigorously. Stirring was continued for a further 12 hr at 50°C, by which time the mixture had become homogeneous. After cooling, DMF was removed from the reaction mixture by co-evaporation with xylene *in vacuo*, the last traces being removed by rotary vacuum pump. The crude mixture of product and starting material was separated by washing the solids with hot, 20% sodium hydroxide solution using a Buchner funnel (water-pump). Washing was continued until tlc analysis confirmed that only the desired product remained on the filter. After washing with water (120 ml) the product was dissolved in chloroform (100 ml) and the solution dried ($MgSO_4$). Filtration and evaporation afforded the title compound as a white solid, pure by tlc.

Yield: 6.67 g, 78%; mp 102–106°C; $[\alpha]_D^{20} = -18.02$°C ($CHCl_3$)
$C_{21}H_{26}O_4$ (342 gmol^{-1})
Calc: C 73.68% H 7.60%
Found: C 73.72% H 7.66%

(S)-1-(4′-methoxy-4-biphenyloxy)-2-hydroxypropane (6)

A suspension of the biphenyl (**5**) (5.1 g, 14.9 mmol) in acidified ethanol (100 ml) (prepared from a 1% solution of 0.1 M HCl in ethanol) was heated at reflux with stirring until complete solution had occurred. Reflux was continued for 15–20 min, by which time tlc analysis indicated the reaction had gone to completion. Water (25 ml) was added to the cooled mixture, the product collected by filtration and dried under vacuum. Careful recrystallisation from ethanol afforded the chiral alcohol (**6**) as a white crystalline solid;

Yield: 3.42 g, 89%; mp 152–154°C; $[\alpha]_D^{30} = +13.86$° (Acetone).
^{1}H Nmr: δ ppm (Acetone d-6, 90 MHz) 1.30 (d, 3H) methine C-CH_3; 2.37 (bs, 1H) ROH; 3.81 (s, 3H) $ArOCH_3$; 3.89 (t, 2H) -CH_2OAr; 4.18 (m, 1H) methine H; 6.90 (d, J = 9 Hz, 4H) Ar-H; 7.44 (d, J = 9 Hz, 4H) Ar-H.
Ir: $\tilde{\nu}$ (KBr) 3400, 1610, 1500, 1275, 1250, 1010, 820, 800 cm^{-1}
$C_{16}H_{18}O_3$ (258 gmol^{-1})
Calc: C 74.42% H 6.98%
Found: C 75.07% H 7.04%

(S)-2-[4′-methoxy-4-biphenyloxy-1-methyl ethoxy] ethyl methacrylate (3)

Methacrylic acid (8.6 g, 100 mmol), the chiral alcohol (**6**) (2 g, 7.75 mmol), p-toluene sulphonic acid (*ca* 0.1 g) and 2,6-di-t-butyl-4-methyl phenol (*ca* 0.5 g) were refluxed together in toluene (100 ml) for 12 hr using a Dean and Stark apparatus. After cooling, the toluene was evaporated *in vacuo* and chloroform (160 ml) and water (80 ml) added. After separating the layers, the organic layer was washed with 10% sodium hydroxide solution (3 x 30 ml) followed by water (30 ml), then dried ($MgSO_4$). After filtration the solution was concentrated and the crude product purified by column chromatography, using silica gel (Fisons) and chloroform as both the solvent and eluant.

Yield: 1.72 g, 68%; mp 78–80°C; $[\alpha]_D^{18} = -18.1$° ($CHCl_3$).
^{1}H Nmr: δ ppm ($CDCl_3$, 90 MHz) 1.41 (d, 3H) methine-C-CH_3; 1.95 (s, 3H) vinyl-CH_3; 3.77 (s, 3H) $ArOCH_3$; 4.02 (dd, 2H) -CH_2OAr; 5.30 (sex, 1H) methine-H; 5.5 (s (with fine structure), 1H) vinylic H trans to carbonyl; 6.09 *s, 1H) vinylic H cis to carbonyl; 6.90 (d, J = 9 Hz, 4H) Ar-H; 7.40 (d, J = 9 Hz, 4H) Ar-H.
$C_{20}H_{22}O_4$ (326 gmol^{-1})
Calc: C 73.62% H 6.75%
Found: C 74.07% H 6.97%

Table 1. Data for copolymerization of **2** with **3** in benzene at 70°C for feed ratios f_3, and copolymer compositions F_3, expressed in terms of monomer **3**

Copolymer number	f_3	F_3	Time (hr)	% Conversion	10^{-3} Mn
7a	0.15	0.32	23	6	—
7b	0.26	0.63	10	10	41.0
7c	0.34	0.70	14	11	29.0
7d	0.50	0.83	4	8	—
7e	0.75	0.95	8	8	185.0

Copolymerization. Copolymers of **2** and **3** were prepared in benzene using 2,2′-azobisisobutyronitrile (0.5 mol%) as the radical initiator. Monomers were degassed using freeze–thaw cycles and copolymerizations were carried out under vacuum at 70°C. All reactions were terminated at low % conversions to avoid composition drift and copolymers were recovered by precipitation in acetone or acetone/methanol mixtures (9:1). Samples were purified by repeated dissolution and reprecipitation then dried *in vacuo* at 60°C for several days. Results and reaction conditions are shown in Table 1.

Copolymer compositions were analysed by ^{1}H NMR, and by elemental analysis. Number average molar masses were measured by gel permeation chromatography and are expressed in polystyrene equivalents.

Characterization of liquid crystal phases. The thermotropic mesomorphic behaviour of the copolymers was examined using both hot-stage polarizing microscopy and differential scanning calorimetry.

RESULTS AND DISCUSSION

The copolymerization of **2** with **3** shows a marked deviation from ideal behaviour with a strong tendency for the less bulky monomer **3** to be incorporated more rapidly into the copolymer at the expense of the sterically hindered monomer **2**. Figure 1 shows a plot of the copolymer composition F_3 against the composition of the feed f_3 and a non linear least squares curve fitting of the data gave monomer reactivity ratio values of $r_2 = 0.68$ and $r_3 = 8.94$. This could lead to blockiness in the copolymer structure but may not affect the mesomorphic behaviour significantly as the homopolymer of **3** displays only a chiral nematic phase and only at high contents of comonomer **2** does a smectic phase also develop.

The copolymers all exhibit enantiotropic behaviour, with those rich in non-chiral monomer tending to form both smectic and chiral nematic phases (N^*), whereas the copolymers rich in the chiral monomer **3** formed only the N^* phase. The data are summarized in Table 2.

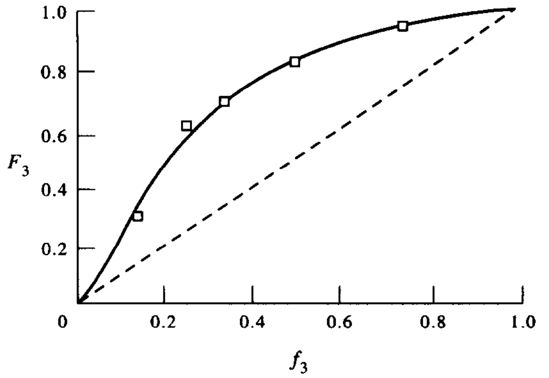


Fig. 1. Dependence of copolymer compositions F_3 and feed ratio f_3, expressed in mole fraction of **3**.

All copolymer samples displayed a chiral nematic phase typified by a planar structure, as viewed in the polarizing microscope, with the exception of sample **7a**. The latter sample showed a 'fingerprint' optical texture [7,8] rather than the more usual planar texture resulting from the Granjean plane structure of the chiral nematic phase. The 'fingerprint' is obtained when the helicoidal axes of the liquid crystal phase tend to lie parallel to the surface of the glass slides and can represent phases either with a long pitch length or a stable biaxial chiral nematic phase in which the rotation about the long molecular axes of the mesogens is hindered. In this case the dark lines characteristic of the fingerprint were replaced by coloured lines, indicating the latter explanation to be more likely, as observed by Finkelmann *et al.* [8].

On cooling from the isotropic melt, sample **7b** gave a blue-grey planar texture which changed through yellow to orange on further cooling, before changing into the smectic form. The reflection colours intensified when the sample was annealed, presumably because of the increase in time allowed for the molecular alignment to improve.

On further lowering of the temperatures of samples **7a** and **7b** a smectic-A phase (S_A) was formed, characterized by the focal–conic fanned texture which is typical of this phase.

The remaining copolymers, **7c–e**, displayed only the chiral nematic (N^*) phases and as the content of the chiral monomer **3** increased in the copolymers, the annealing times required to produce good planar textures became longer. It was also found that for sample **7e** and the homopolymer of **3** no reflection colours could be seen, suggesting that the helical pitch length was now very short and the samples were reflecting in the ultraviolet region.

Table 2. Phase transition temperatures for homopolymers and copolymers of **2** and **3**

Sample number	F_3	T_g(°C)	T_m(°C)	T_{S-N^*}(°C)	T_{N^*-I}(°C)	Reflected colour
2	0	64	125	(150)^a	—	—
7a	0.32	78	118	132	137	—
7b	0.63	67	—	108	117	**Blue-grey**
7c	0.70	68	—	—	91	**Blue**
7d	0.83	79	—	—	103	**Violet-blue**
7e	0.95	97	—	—	114	—
3	1.00	105	—	—	120	—

a—This is a smectic to isotropic transition.

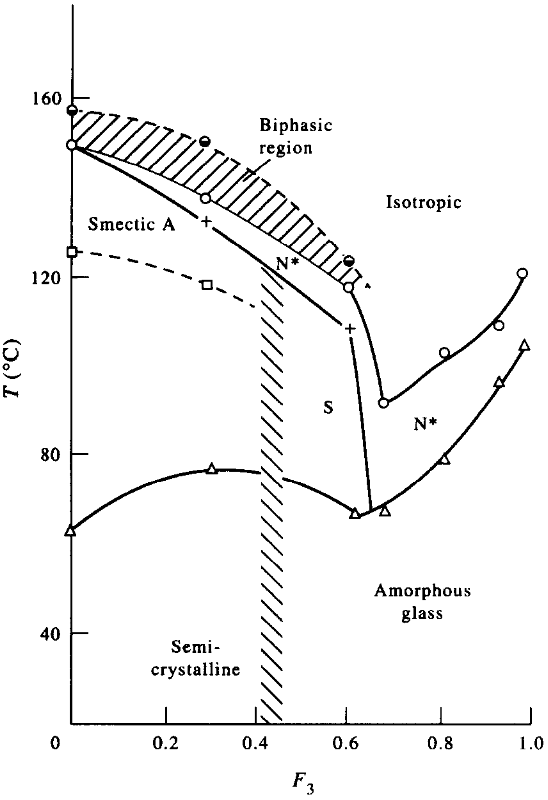


Fig. 2. Phase transition temperatures against composition (Δ): T_g; (□): T_m; (+): $T(S \rightarrow N^*)$; (○): T_I (DSC); (●): T_I microscopy.

The temperature dependence of the phase behaviour for the whole series is presented on Fig. 2. This shows the presence of a biphasic region where the chiral nematic phase co-existed with the isotropic phase over a narrow temperature range, as observed using the hot stage microscope. DSC measurements indicated a lower clearing temperature T_I but the endotherms were broad. This phenomenon is usually attributed to sample polydispersity. This diagram provides an overview of the series and allows an assessment of the changes brought about by changing the terminal unit from -CN to -OCH_3. The introduction of less polar methoxy unit leads to a decrease in the ordering of the copolymers. The range over which the smectic phase exists, and the crystallinity, is reduced and is detected only in copolymers having compositions with $\leqslant 0.4$ mole fraction of monomer **3** compared with a value of $\leqslant 0.55$ for monomer **1** [6]. The present system also has a chiral nematic region which extends over the whole range of composition including the homopolymer of **3**. This contrasts with copolymers containing **1**, where no liquid crystal phases were seen when the mole fraction of **1** exceeded 0.8, and only a very small region between 0.6 and 0.8 mole fraction composition where there was a stable nematic phase [6].

The results demonstrate that significant changes can be induced by minor structural changes in the mesogens. Also reinforced by this study is the conclusion that the itaconic acid derivative **2** also enhances ordering in the system, but that the different spacer lengths of the monomer reduce the regular packing of the mesogenic units in layers as reflected in the general decrease in the clearing temperature as the amount of **3** increases in the copolymer.

Acknowledgement—The authors wish to thank DSM for financial support (HWH) which enabled this work to be undertaken.

REFERENCES

1. H. Finkelmann and G. Rehage. *Adv. Polym. Sci.* **60/61**, 99 (1984).
2. V. P. Shibaev and N. A. Platé. *Adv. Polym. Sci.* **60/61**, 173 (1984).
3. Ya. S. Friedzon, N. I. Boiko, V. P. Shibaev and N. A. Platé. *Europ. Polym. J.* **22**, 13 (1986).
4. P. LeBarny and J. C. Dubois, In *Side Chain Liquid Crystal Polymers* (edited by C. B. McArdle). Blackie & Son Ltd, Glasgow (1989).
5. J. M. G. Cowie and H. W. Hunter. *Makromol. Chem.* **191**, 1393 (1990); J. M. G. Cowie and H. W. Hunter. *Makromol. Chem.* **192**, 143 (1991).
6. J. M. G. Cowie and H. W. Hunter. *J. Polym. Sci., Part A: Polym. Chem.* **31**, 1179 (1993).
7. P. G. DeGennes. *The Physics of Liquid Crystals.* Clarendon Press, Oxford (1974).
8. F. Hessel, R. P. Herr and H. Finkelmann. *Makromol. Chem.* **188**, 1597 (1987).