

Chiral Liquid Crystal Polymers

1. Synthesis and Properties of Glycidyl Ethers Containing Anisotropic Groups

Gisbert Schleier[†], Giancarlo Galli¹ and Emo Chiellini^{1,2*}

¹ Istituto di Chimica Organica Industriale, Centro CNR Macromolecole
Stereordinate Otticamente Attive, Università di Pisa, Via Risorgimento 35,
I-56100 Pisa, Italy

² Istituto Chimica Generale, Università di Pisa, Via Diotisalvi 2, I-56100 Pisa, Italy

SUMMARY

Chiral glycidyl ethers containing biphenyl side groups have been synthesized starting from optically active isopropylidene glycidol. The anisotropic moiety can be bound to the oxirane ring either directly or through flexible spacers of varying length. Details relevant to the above reactions and to the reaction sequences adopted to get the corresponding glycidyl ethers are presented.

INTRODUCTION

The synthesis of functional stereordered polymers for potential application in catalysis (CHIELLINI et al. 1981) and biomedicine (CHIELLINI et al. 1978; CHIELLINI et al. 1980; GALLI et al. 1981) has attracted since a few years our attention. In connection with this investigation, a research was undertaken which intended to apply hydroxy-terminated optically active oligo(oxirane)s for the preparation of a) precursors for the synthesis of intrinsically dissymmetric crown ethers b) segmented polycondensation polymers with hard and soft blocks of well defined hydrophilic character.

Oxirane monomers suitably functionalized can be used for the preparation of side chain liquid crystal polymers and a study on their polymerizability has been undertaken. There is, in fact, a great variety of side chain liquid crystal polymers already known (BLUMSTEIN and HSU 1978), but no liquid crystal poly(oxirane)s have been so far described in the literature.

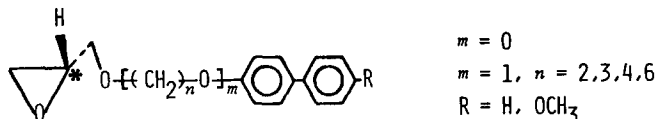
The trend recently approached in the above field is addressed to achieve a high backbone flexibility to allow the onset of thermotropic behaviour at reasonably low temperatures (FINKELMANN and REHAGE 1980; FINKELMANN et al. 1981). Poly(oxirane)s are known to exhibit pretty low glass transition temperatures (LAL and TRICK 1970) and therefore they appear capable to fulfill the requested structural requirements. Furthermore, the presence of a chiral center in the polymer backbone for such systems may provide a unique insight into the interactions between main chain and anisotropic si-

[†] Present address: BASF Aktiengesellschaft, D-6700 Ludwigshafen, Federal Republic of Germany

* To whom correspondence should be addressed

de groups, also as a function of the distance from the backbone.

The biphenyl unit seemed to us to be a suitable side group as it is known to give rise to different mesomorphic polymers (MAGNINI et al. 1980; FINKELMANN et al. 1978) and because it should be inert under various polymerization conditions. Accordingly, a series of optically active glycidyl ethers of the following general structure has been prepared and data relevant to their synthesis and properties are here reported.

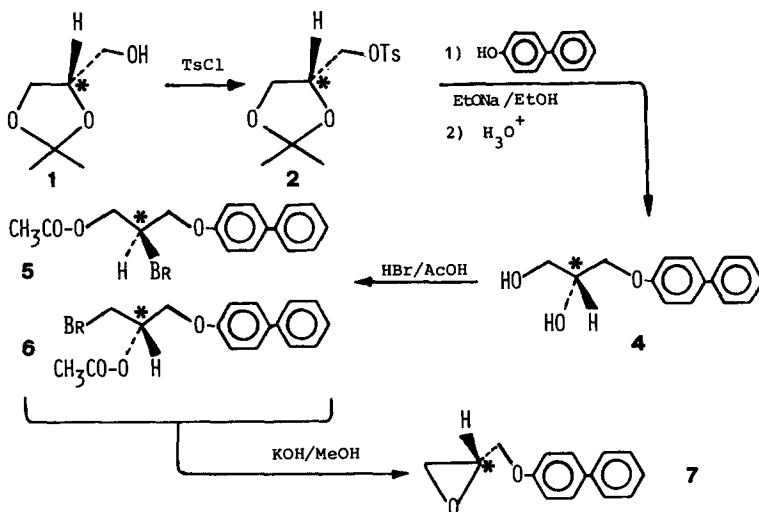


RESULTS AND DISCUSSION

All the preparations of optically active oxirane derivatives were based on the utilization of (S)-|(2,2-dimethyl-1,3-dioxolane-4-yl)|methanol (**1**), prepared from (D)-mannitol (LE COCQ and BALLON 1963), as starting material. The side groups were generally inserted on **1** by a Williamson type reaction. Subsequent acid hydrolysis yielded deprotected optically active diols, which could be easily converted to the corresponding chiral oxiranes by means of reaction sequences able to guarantee for a controlled chemical and stereochemical pathway.

The *p*-biphenyl glycidyl ether (**7**) was synthesized through direct nucleophilic displacement reaction performed on the corresponding tosylate **2** according to Scheme 1.

SCHEME 1 Synthesis of |(1,1'-biphenyl)-4-yloxy|methyl oxirane.



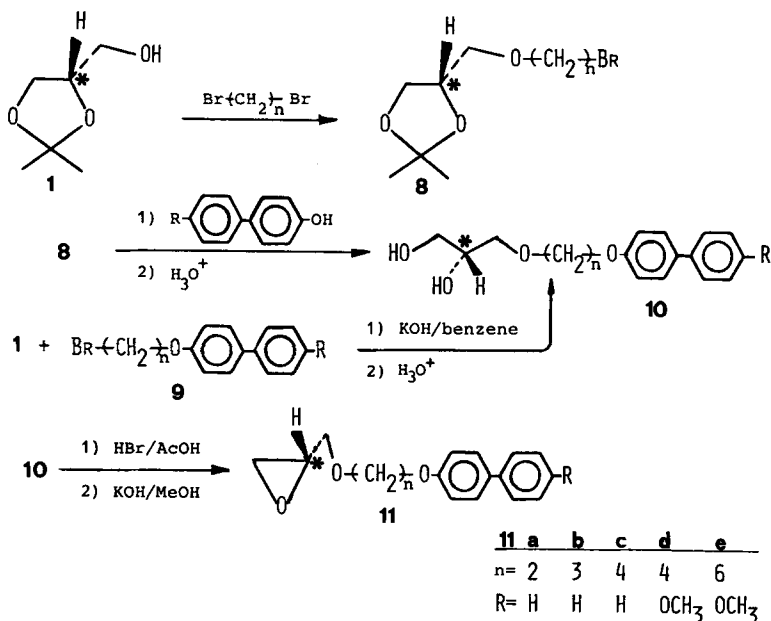
Two routes were on the contrary followed for the synthesis of glycidyl ethers with a variable number of methylene groups between the oxirane ring and the anisotropic moiety. Those procedures differ in the order by which the two ether linkages through the polymethylene spacer are formed (Scheme 2).

In the former case, **1** was preferentially O-alkylated with a large excess of a α,ω -alkyl dihalide under phase-transfer conditions in the presence of 50% NaOH and catalytic amounts of tetra *n*-butyl ammonium bromide. For the reaction of the bromide **8** with the appropriate 4-hydroxy-1,1'-biphenyl derivative the best results were obtained using dimethyl formamide and powdered KOH, especially for methoxy-biphenyl compounds. Subsequent acid hydrolysis yielded the optically active diol **10**.

According to the latter procedure, the 4-hydroxy-1,1'-biphenyl derivative was reacted with a α,ω -dihalide to the intermediate **9**, which was then reacted with **1** in refluxing benzene (or dimethyl formamide) to give the corresponding 1 O-alkylated product.

In all cases the glycols **10**, purified by column chromatography, were reacted with hydrobromic acid in acetic acid to give a mixture of acetoxy bromo derivatives, such as **5** and **6**, which were debromoacetylated with methanolic KOH. The crude product contained usually up to five components, from which the pure glycidyl ether **11** could be isolated, as the main product, by preparative thin layer chromatography on silica gel plates.

SCHEME 2 Synthesis of $\{\omega\text{-}[(1,1'\text{-biphenyl})\text{-4-yloxy}]\text{-alkyloxy}\}$ oxiranes



The physical data of all the compounds not reported in the literature are summarized in the Table.

TABLE. Physical data of the prepared glycols and glycidyl ethers containing anisotropic biphenyl derivatives

General structure		Glycol ^a			Glycidyl ether ^a		
		yield (%)	mp. (°C)	$ \alpha _D^{25}$	yield (%)	mp. (°C)	$ \alpha _D^{25}$
<i>n</i>	R						
0	H	76	166	-2.3 ^b	60	98	- 9.7 ^c
2	H	22	103	-1.9 ^d	71	98	-16.3 ^c
3	H	45	101	-3.3 ^d	23	37	-15.1 ^c
4	H	48	100	-1.6 ^d	66	58	-13.1 ^c
4	OCH ₃	35	147	+1.6 ^b	55	107	-11.6 ^c
6	OCH ₃	60	142	-1.5 ^d	32	105	- 7.9 ^c

^a(R) absolute configuration. ^bIn THF. ^cIn benzene. ^dIn chloroform

At present no correlation can be given between optical rotatory power and optical purity for the oxiranes under investigation. Nevertheless, taking into account that the reactions involving the chiral center are known to occur without any appreciable racemization (GOLDING et al. 1973; SCHMIDT et al. 1980), it is plausible to assume the optical purity of the prepared glycidyl ethers to be very similar to that of the starting protected glycidol 1.

The prepared monomers **7**, **11a-11e** melted rather sharply with no indication of liquid crystal behaviour, despite the fact that a wide variety of biphenyl-containing low molecular weight compounds give rise to thermotropic mesophases (GRAY 1974).

All the monomers could be polymerized under mild conditions in the presence of PF₅ or AlEt₃/H₂O 5/1 (mol/mol) with rather good yields. The preparation and the physico-chemical characterization of the polymeric products will be the object of a forthcoming paper (SCHLEIER et al., in preparation).

EXPERIMENTAL PART

(*R*)-|(1,1'-biphenyl)-4-yloxy|methyl oxirane (**7**). To a solution of 0.20mol of sodium ethoxide in 200ml of ethanol was added a solution of 34g (0.20mol) of 4-hydroxybiphenyl in 150ml of ethanol. A solution of the tosylate **2** (NELSON et al. 1977) in 40ml of ethanol was then added. The mixture was refluxed for 4h, concentrated to half volume, treated with 400ml of water and extracted with diethyl ether. The organic layer was washed with 10% NaOH, water and dried on Na₂SO₄. Crystallization from ethanol gave 16.5g (yield 45%) of (*R*)-4-(1,1'-biphenyl-4-yloxy)methyl-2,2-dimethyl-1,3-dioxolane **3**.

9.3g (33mmol) of **3** were stirred with 100ml of 50% acetic acid at 100°C for 4h, then 100ml of water were added and the precipitate filtered off, dried and purified by elution on a silica gel column using chloroform and chloroform/methanol 1/1 as solvents. The collected product was crystallized from acetone/ethanol giving 6.1g (yield 76%) of **4** {mp. 166°C; $[\alpha]_D^{25}$ -2.3 (THF)}. 6.1g (25mmol) of **4** were suspended in 20ml of dichloromethane and 25ml (0.14mol) of a 33% solution of hydrobromic acid in acetic acid were added dropwise. The mixture was stirred for 2h at 0°C and then overnight at room temperature. Finally it was poured into 500ml of iced water and extracted with dichloromethane. The organic phase was washed with 5% Na₂CO₃, water, dried over Na₂SO₄ and then the solvent evaporated in vacuo. The solid residue was dissolved in 30ml of THF and 80ml of methanol and treated with a solution of 13.8g (25mmol) of KOH in 10ml of methanol. The reaction mixture was stirred for 2h at room temperature and the solvent evaporated. The crude product was crystallized several times from benzene giving 3.4g (yield 60%) of pure **7** {mp. 98°C; $[\alpha]_D^{25}$ -9.7 (benzene)}.

¹H-NMR (CDCl₃): δ (from TMS) = 7.5 (m, 7H, aromatic), 7.1 (m, 2H, aromatic), 4.2 (m, 2H, CH₂-O-Ø), 3.4 (m, 1H, CH-), and 2.9ppm (m, 2H, CH₂-). IR (KBr) = 3050, 1600, 1525, 1485, 1250, 1200, 1035, 900, 830, 760 and 600 cm⁻¹.

(*R*)-3-{ω-(1,1'-biphenyl)-4-yloxy|-alkyloxy}-propan-1,2-diols **10a**, **10c** and **10d** were synthesized according to the same procedure and the preparation of **10c** is reported here in detail as a typical case. A mixture of 19.4g (0.11mol) of powdered KOH and 120ml of acetone was heated for some minutes and then 108g (0.50mol) of 1,4-dibromo-butane were added. After refluxing for 3h, the acetone was distilled off and the residue diluted with chloroform and washed with 10% NaOH and water. Finally all the solvents were evaporated and the solid obtained was crystallized several times from *n*-heptane giving 23g (yield 66%) of **9c** having mp. 80°C. 3.3g (2.5mmol) of **1** and 1.4g (2.5mmol) of KOH were mixed with 150ml of benzene. After distillation of 50ml of benzene, 7.8g (2.5mmol) of **9c** in 30 ml of benzene were added. The reaction was protracted at reflux for 12h, then 250ml of water were added and the mixture extracted with diethyl ether. The crude product isolated was, without further purification, hydrolyzed to the corresponding diol (yield 48%) under the same reaction conditions given above for the synthesis of **4** starting from **3**.

(*R*)-3-{ω-(1,1'-biphenyl)-4-yloxy|-alkyloxy}-propan-1,2-diols **10b** and **10e** were synthesized according to the same procedure and the preparation of **10b** is reported here in detail as a typical case. A mixture of 21g (0.16mol) of **1**, 152g (0.75mol) of 1,3-dibromo-propane, 32g (0.40mol) of 50% NaOH and 2g of (*n*-Bu)₄NBr⁺ was vigorously stirred for 20h at room temperature, then 250ml of water were added and the mixture extracted with chloroform. The organic layer was

washed with water and dried over Na_2SO_4 . Fractional distillation gave 13.3g (yield 24%) of **8b** (bp.70-72°C/0.2mm). 1.4g (8mmol) of 4-hydroxybiphenyl, 2.8g (11mmol) of **8b**, 0.4g (10mmol) of 50% NaOH, 0.2g of $(n\text{-Bu})_4\text{NBr}$, 5ml of water and 40ml of dichloromethane were stirred for 24h at room temperature and for 12h at reflux. After cooling to room temperature, 50ml of water were added and the mixture extracted with diethyl ether. The ether extracts were washed with 10% NaOH and water, dried over Na_2SO_4 and evaporated in vacuo. The residue was dissolved in 20ml of acetone containing 2ml of 2N HCl and refluxed for 2h. The reaction product was precipitated in water, filtered, dried and crystallized twice from acetone and toluene respectively giving 1.1g (yield 45%) of **10b** {mp.101°C; $[\alpha]_D^{25}$ -3.3 (chloroform)}.

(R)- ω - $\{ (1,1'\text{-biphenyl})\text{-4-yloxy}\}$ -alkyloxy-oxiranes **11a-11e** were synthesized from the corresponding diols **10a-10e** under the same reaction conditions given above for the preparation of **7** from **4**.

ACKNOWLEDGEMENT

The authors are very grateful for a NATO Fellowship to G.S.

REFERENCES

- BLUMSTEIN A., HSU E.C. in "Liquid Crystalline Order in Polymers", A.Blumstein Ed., Academic Press, New York, 1978, p.105
- CHIELLINI E., GALLI G., CIARDELLI F., PALLA R., CARMASSI F. *Inf. Chim.* 176,221(1978)
- CHIELLINI E., LENZ R.W., OBER C. in "Polymer Blends", E.Martusceli et al. Eds., Plenum Press, New York, 1980, p.373
- CHIELLINI E., SOLARO R., D'ANTONE S. *Makromol.Chem., Suppl.* 5,82(1981)
- FINKELMANN H., HAPP M., PORTUGAL M., RINGSDORF H. *Makromol.Chem.* 179,2541(1978)
- FINKELMANN H., REHAGE G. *Makromol.Chem., Rapid Commun.* 1,31(1980)
- FINKELMANN H., KOCK H.J., REHAGE G. *Makromol.Chem., Rapid Commun.* 2,317(1981)
- GALLI G., BENEDETTI E., CHIELLINI E., OBER C., LENZ R.W. *Polymer Bull.* 5,497(1981)
- GOLDING B.T., HALL D.R., SAKRIKAR S. *J.Chem.Soc.Perkin I* 1973,1214
- GRAY G.W. in "Liquid Crystals Plastic Crystals", G.W.Gray and P.A. Winsor Eds., Ellis Horwood, Chichester, 1974, Vol.2, p.103
- LAL J., TRICK G.S. *J.Polym.Sci., A1* 8,2339(1970)
- LE COCQ J., BALLON C.E. *Biochemistry* 3,979(1963)
- MAGAGNINI P.L., FROSINI V., LUPINACCI D., BRESCI B. in "Advances in Liquid Crystal Research and Application", L.Bata Ed., Pergamon Press, Oxford, 1980, p.925
- SCHLEIER G., ANDRUZZI F., GALLI G., CHIELLINI E. in preparation
- SCHMIDT U., TALBIERSKY J., BARTKOWIAK F., WILD J. *Angew.Chem.Int. Ed.Engl.* 19,198(1980)