This article was downloaded by: [Tomsk State University of Control Systems and Radio]
On: 18 February 2013, At: 13:44
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954
Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

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

On the Phase Behaviour of a Liquid-Crystalline Polymer Containing Diaza-18-Crown-6-Ether Units

H. Fischer [a]

[a] H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Royal Fort, Bristol, BS8-1L, U.K.

Version of record first published: 04 Oct 2006.

To cite this article: H. Fischer (1994): On the Phase Behaviour of a Liquid-Crystalline Polymer Containing Diaza-18-Crown-6-Ether Units, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 238:1, 249-253

To link to this article: http://dx.doi.org/10.1080/10587259408046932

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.tandfonline.com/page/terms-and-conditions

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Mol. Cryst. Liq. Cryst., 1994, Vol. 238, pp. 249–253
Reprints available directly from the publisher
Photocopying permitted by license only
© 1994 Gordon and Breach Science Publishers S.A.
Printed in the United States of America

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:44 18 February 2013

On the Phase Behaviour of a Liquid-Crystalline Polymer Containing Diaza-18-Crown-6-Ether Units

H. FISCHER

H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Royal Fort, Bristol, BS8-1L, U.K.

(Received September 16, 1992; in final form January 13, 1993)

A new synthetic route for a crown ether containing liquid crystalline polymer will be presented. The polymer has been prepared using 1,4,10,13-tetraoxy-7,16-diazacyclooctadecene (diaza-18-crown-6-ether) and terephthaloyl-bis-(4-oxybenzoic) chloride. The mesogenic properties of the polymer have been examined using DSC, polarization microscopy and x-ray diffraction methods.

Keywords: liquid crystals, polymer, crown ether

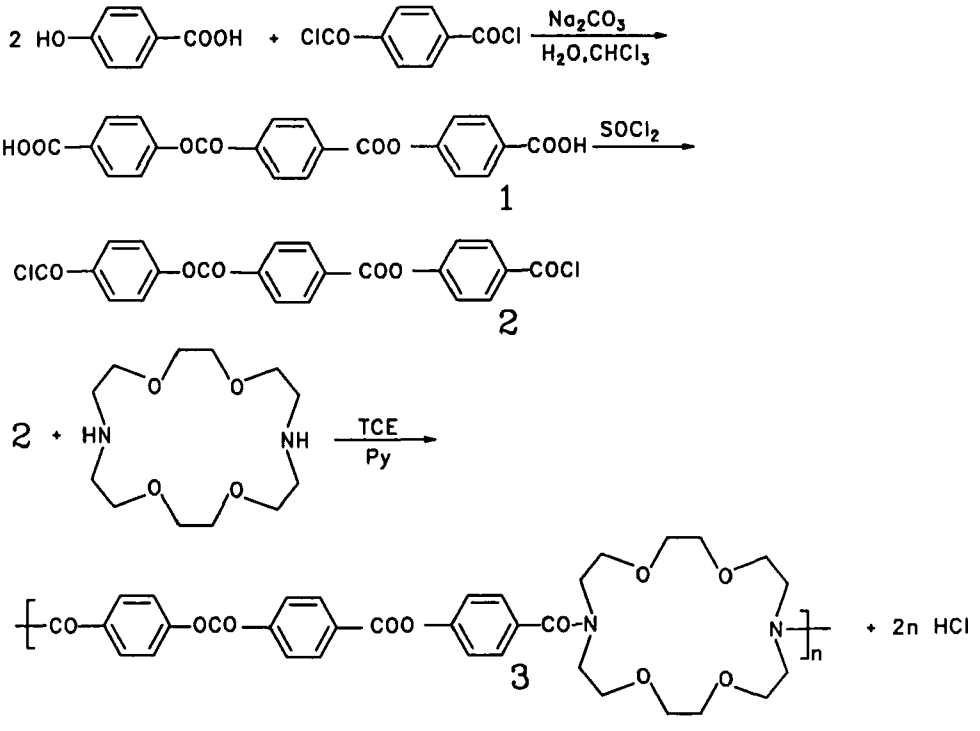
INTRODUCTION

Liquid crystalline polymers can contain a wide variety of different monomeric units and different functional groups in the mesogens. Only a few examples are known in which crown ether units are used as the mesogenic element to form liquid crystalline phases.[1,2] Prompted by the general goal of functionalizing mesogenic polymers, we synthesized by a new route a main-chain liquid-crystalline polyamide containing diaza-18-crown-6-ether units[2] and investigated its mesomorphic properties by DSC, polarization microscopy and x-ray diffraction methods.

EXPERIMENTAL

Synthesis

Terephthaloyl-bis-(4-oxybenzoic) acid, **1.** This acid was prepared following the procedure described by Bilibin *et al.*[3] A solution of 10.2 g (0.05 mol) terephthaloyl chloride in 100 ml chloroform was added, with rapid stirring, to a solution of 16.6 g (0.1 mol) 4-hydroxybenzoic acid in 250 ml of a 0.4 N aqueous solution of Na_2CO_3. Stirring was continued for 10 h. The precipitated white crystals were filtered, washed



SCHEME I

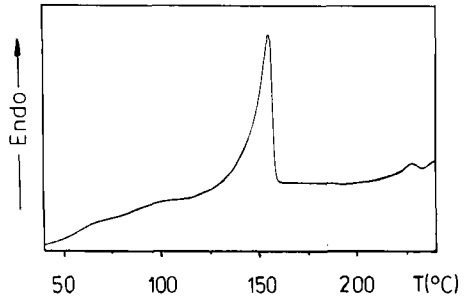


FIGURE 1 DSC heating curve of polymer **3**, scan rate 20 K/min.

with diluted hydrochloric acid and water and dried in vacuum. The yield was 18.5 g (87.6%).

Terephthaloyl-bis-(4-oxybenzoic)chloride, **2.** Five grams (0.011 mol) of **1** were refluxed in 100 ml thionyl chloride for 2 h. The solution was filtered and cooled to 0°C. The sediment was filtered, washed with petrol ether several times and dried in vacuum. The yield was 3 g (56%).
^{1}H-NMR: (200 MHz, DMSO-d_6): δ = 8.34 (s, 4 H, H arom, terephthalic acid), 8.07, 8.03 (d, 2 H, 2 H, H arom.), 7.50, 7.46 (d, 2 H, 2 H, H arom.)

Poly-diaza-18-crown-6-ether-terephthaloyl-bis-(4-oxybenzamide), **3.** Two and

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:44 18 February 2013

FIGURE 2 Polarized light micrograph of **3** at 200°C, nematic schlieren texture, 160×.

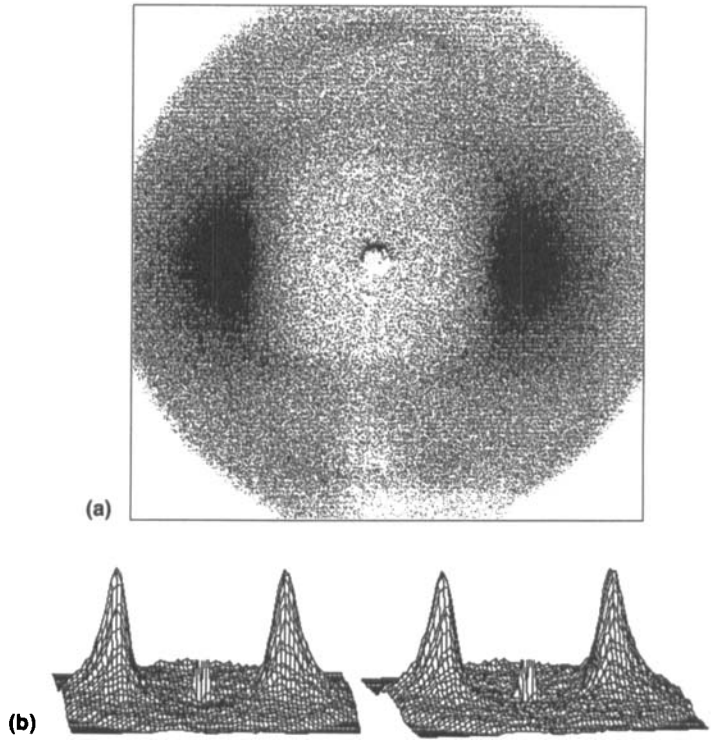


FIGURE 3 (a) 2D-plot and (b) 3D-plot (stereo view) of the x-ray diffraction pattern of an oriented sample of polymer **3** (fibre).

one-half grams of **2** (0.0025 mol) and 1.31 g of 1,4,10,13-tetraoxy-7,16-diazacyclooctadecene (diaza-18-crown-6-ether) (0.0025 mol) were mixed and dissolved in a mixture of carefully dried tetrachloroethane (50 ml) and 1 g pyridine (0.012 mol). After stirring under nitrogen at room temperature for 24 h, the reaction mixture

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:44 18 February 2013

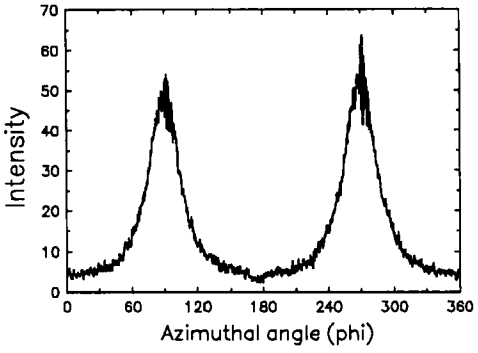


FIGURE 4 Azimuthal intensity plot versus phi of Figure 3 (2 theta = 19.73°).

was poured into 250 ml methanol. The precipitated polymer was washed several times with methanol, filtered and dried in vacuum. The yield was 2.7 g (78.5%). ^{1}H-NMR: (200 MHz, $CDCl_3$); δ = 8.33 (s, 4 H, H arom, terephthalic acid), 7.52, 7.49 (d, 2 H, 2 H, H arom.), 7.31, 7.27 (d, 2 H, 2 H, H arom.), 3.82 (m, 8 H, CH_2), 3.64 (m, 16 H, CH_2).

Characterization Methods

The thermal behaviour of the polymer was investigated with a Perkin-Elmer DSC 7; heating rate 20 K/min. Polarized light microscopy studies were performed on a Boetius hot stage attached to a Carl-Zeiss Jena microscope. X-ray diffraction data were obtained with a fine-focus x-ray tube (Cu-target) equipped with a graphite monochromator and a pinhole collimator (diameter 0.3 mm). The detection device was a Xentronics area detector X-100 from Nicolet/Siemens, coupled with a PCS system for collecting, storing and analyzing the x-ray images. Oriented samples were prepared by drawing fibres from a melt.

RESULTS AND DISCUSSION

A well known rigid bifunctional monomer **2**, which has frequently been used as a mesogen in liquid crystalline main-chain polymers, was synthesized according to Bilibin *et al.*[3] The polyamide was prepared from the diacid dichloride and the diaza-18-crown-6-ether in a low temperature condensation process as described in Scheme I.

The purity of the monomeric diacid dichloride of the stiff mesogen and of the polymer was ascertained by NMR spectroscopy. The molecular weight of the polymer **3** remains to be determined. DSC studies show two phase transitions, P_{cr} 155°C P_n 228°C P_{is}, dec (Figure 1).[4]

The very small heat connected with the phase transition at higher temperature hints at the existence of a nematic phase. Polarization microscopy at 200°C supports this conjecture; the observed schlieren texture is typical for a nematic phase (Figure 2).

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:44 18 February 2013

The x-ray pattern of a fibre sample obtained at room temperature is shown in Figure 3.

Two diffuse reflections in the wide angle range indicate the presence of a nematic phase. The lateral distance between the mesogens is about 4.5 Å. An analysis of the azimuthal intensity distribution as a function of Phi at a theta angle of 19.73° is shown in Figure 4. The order parameter was calculated by using a program developed by J. Gromcek, University of Connecticut, U.S.A. and is 0.6.

References

1. Y. S. Lipatov, V. V. Tsukruk, V. V. Shilov, V. N. Pastushak, A. I. Galatina and A. V. Bogatskij, *Dokl. Akad. Nauk SSSR*, **285**, 155 (1985).
2. J. M. G. Cowie and H. H. Wu, *Br. Polymer J.*, **20**, 515 (1988).
3. A. Y. Bilibin, A. V. Tenkovtsev, O. N. Piraner and S. S. Skorochodov, *Vysokomol. Soed.*, **A26**, 2570 (1984).
4. S. Diele, M. Naumann, F. Kuschel, B. Reck and H. Ringsdorf, *Liq. Cryst.*, **7**, 721 (1990).

Downloaded by [Tomsk State University of Control Systems and Radio] at 13:44 18 February 2013