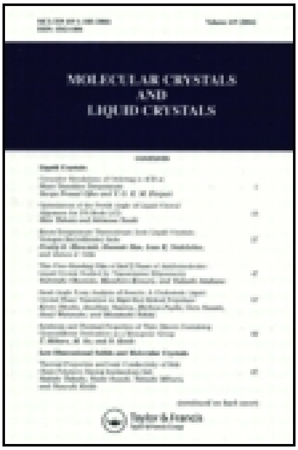


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Thermotropic Hydrocarbon Side Chain Liquid Crystalline Polymers

Joseph J. Mallon [a] & Simon W. Kantor [a]
[a] Polymer Science and Engineering Department, University of Massachusetts, Amherst, Ma., 01003, U.S.A.

Version of record first published: 19 Dec 2006.

To cite this article: Joseph J. Mallon & Simon W. Kantor (1988): Thermotropic Hydrocarbon Side Chain Liquid Crystalline Polymers, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 157:1, 43-56

To link to this article: http://dx.doi.org/10.1080/00268948808080224

Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt., 1988, Vol. 157, pp. 43-56
Reprints available directly from the publisher.
Photocopying permitted by license only.

Printed in the United States of America

THERMOTROPIC HYDROCARBON SIDE CHAIN LIQUID CRYSTALLINE POLYMERS

JOSEPH J. MALLON and SIMON W. KANTOR
Polymer Science and Engineering Department
University of Massachusetts, Amherst, Ma. 01003 U.S.A.

ABSTRACT Virtually all known liquid crystalline polymers contain heteroatoms that can increase mesophase stability through anisotropic intermolecular attractions such as dipolar interactions or hydrogen bonds. In the present work the syntheses of all-hydrocarbon polymers with a mesogenic group in the side chain are discussed. Five high molecular weight polymers have been prepared by Ziegler-Natta polymerizations of liquid crystalline biphenyl-containing monomers. Three of the polymers display a smectic structure as indicated by fiber X-ray diffraction patterns. The results of the variations of the lengths of the spacer and terminal groups and data from polarized light optical microscopy and differential scanning calorimetry are discussed.

INTRODUCTION

A large number of side chain liquid crystalline polymers have been prepared in recent years.[1-3] Poly(acrylate), poly(methacrylate) and poly(siloxane) derivatives seem to be the most prevalent, due at least in part to the relative ease with which they can be prepared. Many of the mesogens that have been utilized contain ester, biphenyl, Schiff base and azoxy groups. Nitrile, alkyl and alkoxy tails are also quite common. In fact, nearly all side chain liquid crystalline polymers contain heteroatoms such as N, O or Si in their structures. These heteroatoms are useful because they allow simple, versatile synthetic methods to be used for their preparation and they may stabilize the mesophase through polar attractions or hydrogen bonds.

However, these attractive forces are not believed to be necessary for the formation of the liquid crystalline phase, as predicted by Flory in 1956[4]. In this view, the existence of a mesophase is governed by shape anisotropy alone. Other theories[5] have attempted to include the effects of anisotropic interactions that are present in real molecules, but the estimation of the magnitude of these interactions is complicated. Conventional mesogens contain a variety of polarizable groups whose mutual interaction is difficult to predict from the molecular structure. It has been suggested[5] that 4,4'-di-n-alkyl-bis-bicyclo[2.2.2]octanes would be useful to test theories because of their simple structure and weak intermolecular interactions.

To investigate these ideas, we have synthesized a series of hydrocarbon side chain liquid crystalline polymers. These polymers contain only carbon and hydrogen atoms and have no strong dipoles or hydrogen bonds. The use of a biphenyl mesogen with polarizable electrons results in increased dispersion attractions in these polymers. To our knowledge, this is the first report in which a mesogen has been incorporated into an all-hydrocarbon side chain liquid crystalline polymer. An additional benefit of the selection of the appropriate monomers is the use of Ziegler-Natta polymerization catalysts to synthesize the polymers, which allow control of tacticity over a wide range. Thus, the effect of tacticity on the nature and stability of liquid crystalline phases may be investigated.

In this report the synthesis and preliminary characterization of the polymers by a variety of techniques is described. A companion paper describes the monomer synthesis and properties. Detailed X-ray and thermal experiments are in progress and these results will be reported in a future communication.

SYNTHESIS

The polymers prepared in this study were synthesized in chlorobenzene solution at room temperature with an $AlEt_3/TiCl_4$ catalyst. An Al/Ti mole ratio of 2.8/1 and a Ti/monomer mole ratio of 0.035/1 were employed.[6] Reaction times were generally 24-48 hours. The polymers were isolated by precipitation in EtOH. The synthetic scheme is shown in Figure 1. Satisfactory elemental analyses were obtained for all of the polymers. A future report will give detailed syntheses and analytical data.

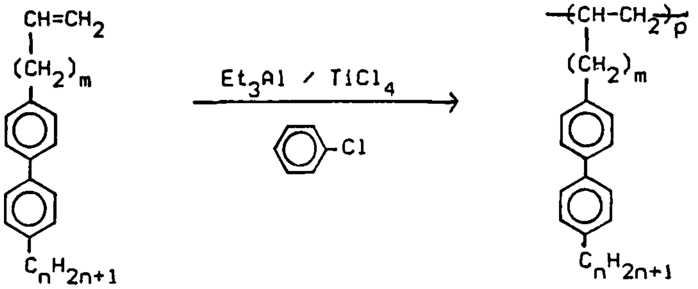


FIGURE 1

Polymer Synthesis

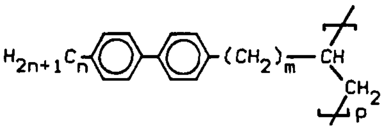
RESULTS AND DISCUSSION

The polymers prepared in this study were characterized by Differential Scanning Calorimetry, (DSC), Polarized Light Optical Microscopy (POM), X-ray diffraction of fiber samples and Gel Permeation Chromatography (GPC) in chloroform. All of the polymers were soluble in chlorobenzene, chloroform and hot (60°C) benzene. All of the polymers were fiber and film forming.

The polymer structures and GPC molecular weight data (relative to polystyrene standards) are given in Table I.

TABLE I

Polymer Structure



Code	n	m	M_n	M_w	M_w/M_n
PEBP04	0	4	49000	450000	9
PEBP06	0	6	43000	660000	15
PEBP26	2	6	90000	850000	9
PEBP44	4	4	14000	330000	24
PEBP46	4	6	70000	710000	10

While the molecular weights are generally high, the variability in molecular weight and molecular weight distribution between samples is due to the sensitivity of the heterogeneous catalyst. $AlEt_3/TiCl_4$ was selected as the catalyst since it has been reported to polymerize propylene to a 50/50 mixture of atactic and isotactic polymer.[7] Attempts were made to separate the polymers into atactic and isotactic fractions. Extraction with boiling hexane or cyclohexane was unsuccessful, as was recrystallization from benzene solution. Nuclear Magnetic Resonance (NMR) experiments are currently in progress to determine the degree of tacticity in selected samples.

The DSC, POM and X-ray data indicate that the polymers may be placed into two categories. PEBP04 and PEBP06 belong to the first category. The DSC heating and cooling scans for PEBP04 are shown in Figure 2 and are representative of both polymers. POM observations indicate that the one large peak present in each scan corresponds to polymer melting and recrystallization, respectively. Characteristic liquid crystalline textures were not observed by POM in either polymer. The X-ray diffraction pattern of a melt-drawn fiber of PEBP04 is shown in Figure 3. This fiber was annealed at 145°C for 2 hours, then cooled to 27°C before the X-ray photograph was taken. The fiber axis is vertical. The inner ring spacings correspond to a d-spacing of 28 Å, which is consistent with a layer structure with the side chains arranged on either side of the main chain and roughly perpendicular to the main chain. The wide angle equatorial reflections corresponding to 5.5 Å and 4.0 Å suggest that the main chains may be crystallizing. The rather diffuse ring corresponding to a

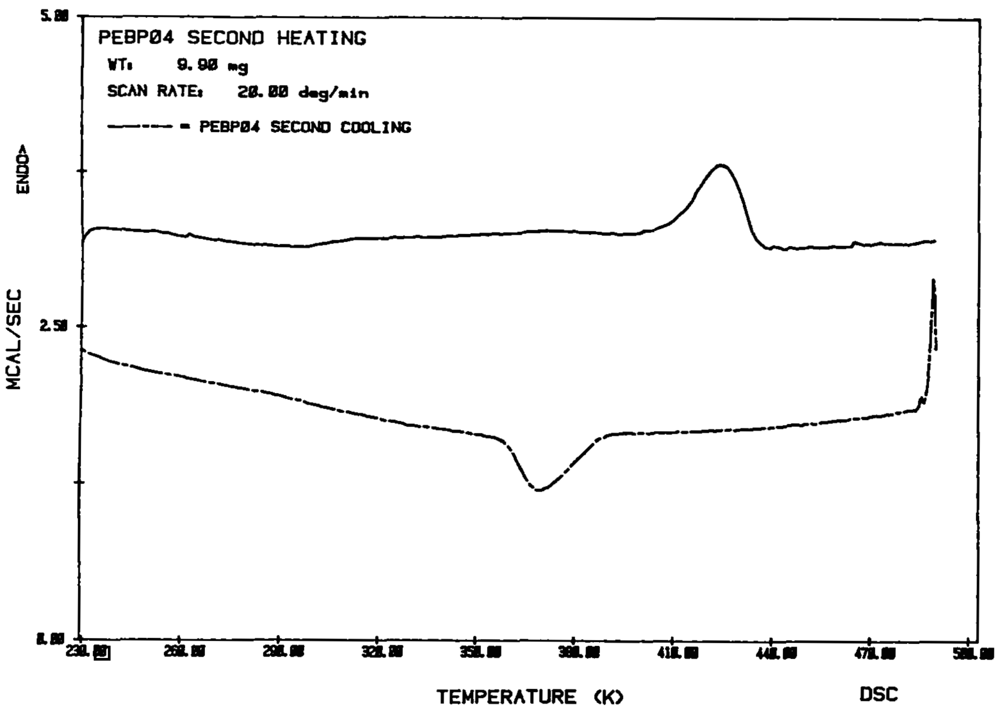


FIGURE 2. DSC heating and cooling scan for PEBP04

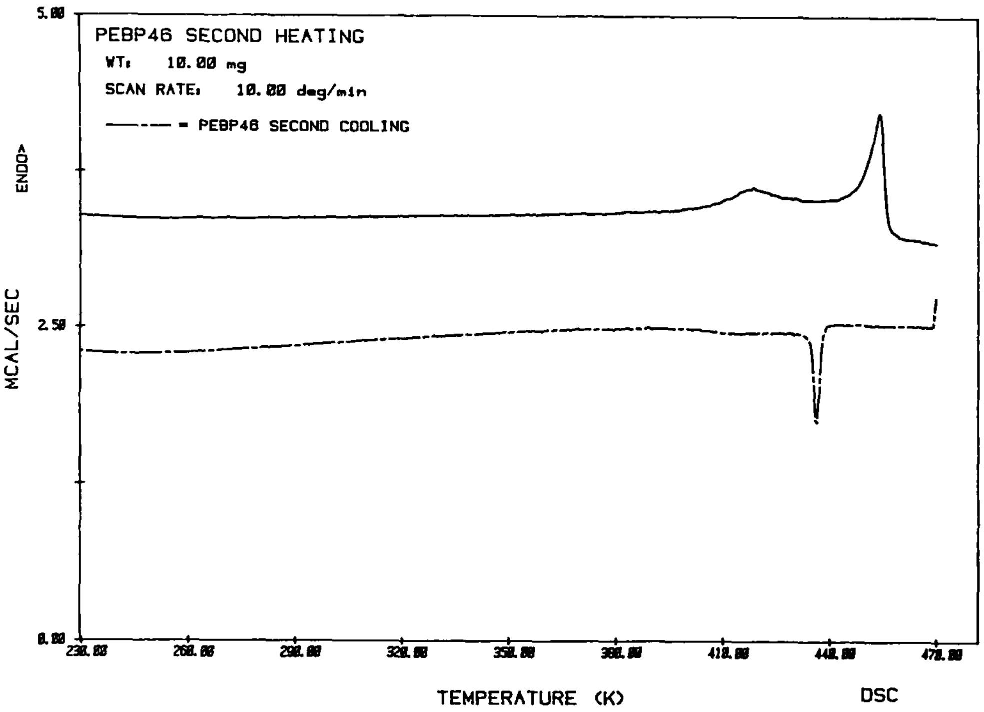


FIGURE 4. DSC heating and cooling scan for PEBP46

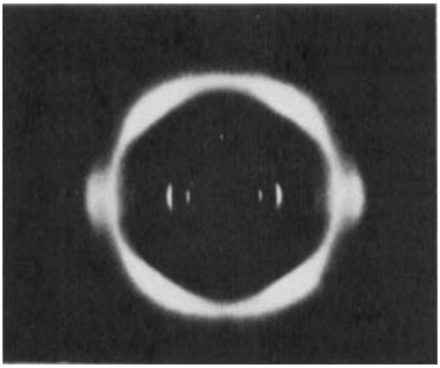


FIGURE 3

X-ray of PEBP04
Fiber axis vertical

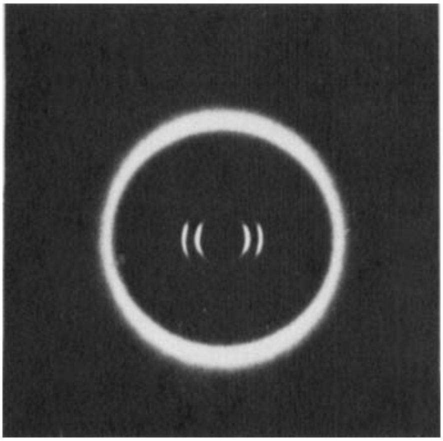


FIGURE 6

X-ray of PEBP46
Fiber axis vertical

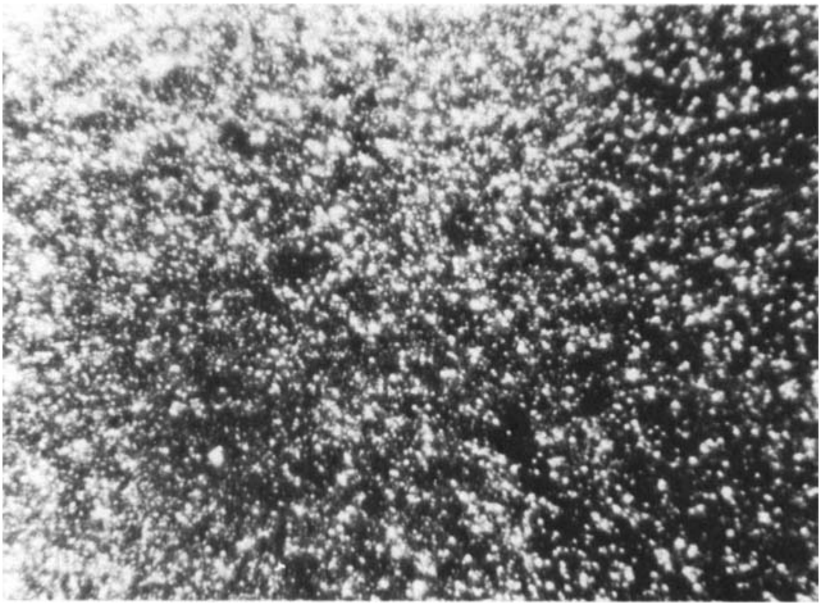


FIGURE 5

PEBP46 170°C 460X
Crossed polarizers

4.7 Å spacing is probably due to the intermolecular spacings of the side chains. The X-ray evidence, and the POM and DSC observations cited above confirm that PEBP04 and PEBP06 are crystalline and not liquid crystalline polymers.

PEBP26, PEBP44 and PEBP46 belong to the second category. The DSC trace of a representative polymer, PEBP46, is shown in Figure 4. These polymers display a broad, lower melting peak or shoulder and a sharp, higher melting peak. POM observations show that the polymers become isotropic when they are heated above the second DSC peak. Cooling the polymers from the isotropic melt results in recrystallization of the polymers at the temperatures indicated by the large DSC exothermic peak generated during the cooling cycle. A "fine grain" texture is exhibited by the polymer after it has recrystallized. A photomicrograph of this type of texture, characteristic of smectic polymer liquid crystals, is seen in Figure 5.

X-ray diffraction patterns obtained from fibers show only low angle equatorial reflections corresponding to the layer spacing and a diffuse wide angle ring characteristic of the intermolecular spacing of the side chains. A typical X-ray diffraction pattern for this second category is displayed by PEBP46 in Figure 6. A fiber sample was annealed at 175°C for one hour, then cooled to 27°C before its X-ray diffraction pattern was obtained. The layer spacing measured from the pattern was 39.9 Å and the intermolecular spacing was found to be 4.6 Å. The 39.9 Å layer spacing suggests the type of layer spacing ilustrated in Figure 7. The wide angle equatorial reflections present in Figure 3 are absent from Figure 6, indicating that the main

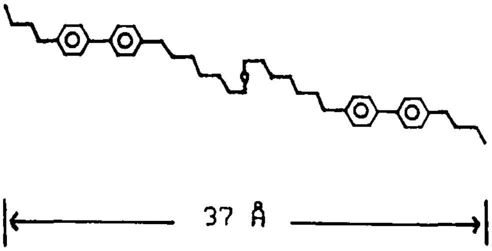


FIGURE 7

PEBP46 layer spacing

chains of PEBP46 do not crystallize, even after annealling.

The evidence accumulated for polymers in the second category indicates that they are smectic liquid crystals. The low temperature peaks in the DSC scans have been designated as Tm, which represents a crystal to liquid crystal transition. The high temperature peaks have been designated as the clearing temperatures, Tcl, to form an isotropic melt. A liquid crystal to crystal transition on cooling is not indicated by DSC, so it is assumed that this transition is kinetically slow and takes place over a broad temperature range. It has been noted[8] previously that the hexagonal to orthorhombic transition in poly(1-octadecene) takes place over a broad temperature range and is not detectable by DSC. It is also possible that Tm represents the side chain melting of phase separated atactic material and Tcl is the side chain melting point of the isotactic material.[13] The isotactic and atactic phases of poly(1-octadecene) have been shown to melt separately[8-12], the atactic being the lower melting. Multiple temperature X-ray studies and annealling experiments are planned to elucidate the exact nature of Tm. We also plan to synthesize an isotactic version of PEBP26 with appropriate catalysts.

The Tm and Tcl transitions for the second category of polymers and the Tcl temperatures of the first category are listed in Table II. The peak temperatures have been reported for Tm and Tcl from the second heating DSC scans.

TABLE II

Polymer Transition Temperatures

Code	T_m °C	T_{cl} °C
PEBP04		151
PEBP06		126
PEBP26	shoulder	176
PEBP44	158	206
PEBP46	145	181

Based on these data, it appears that lengthening the flexible spacer causes a decrease in Tcl. This is the general behaviour associated with most side chain liquid crystalline polymers.[1] The presence or absence of a tail also seems to correlate with the presence or absence of a liquid crystalline phase. This correlation was also noted in the monomers and model compounds reported in a companion paper. Additional work is required to confirm this conclusion.

CONCLUSION

Hydrocarbon side chain liquid crystalline polymers containing biphenyl mesogens have been synthesized for the first time. Polymerization via Ziegler-Natta catalysis produced polymers with broad molecular weight distributions and weight average molecular weights from 330,000-850,000 as measured by GPC (polystyrene calibration). Polymers whose structures contain tails were found to be liquid crystalline by DSC, POM and fiber X-ray diffraction. Polymers whose structures lacked tails were found to be crystalline and did not exhibit liquid crystalline phases.

ACKNOWLEDGEMENT

This work was supported by the Materials Research Laboratory at the University of Massachusetts.

REFERENCES

1. H. Finkelmann, in "Polymer Liquid Crystals" ed. by A. Ciferri, W.R. Krigbaum and Robert B. Meyer, Academic Press, NY 1982 Chap. 2.
2. V.P. Shibayev and N.A. Plate, Polym. Sci. USSR, 19, 5 1065 (1977).
3. Gy. Hardy et al. Israel Journal of Chemistry, 25, 252-63 (1985).
4. Flory, P.J. Proc. R. Soc. London, Ser. A, 234, 73 (1956).
5. See H. Toriumi and E.T. Samulski, Mol. Cryst. Liq. Cryst., 101, 163-73 (1983) and references therein.
6. D.W. Aubrey and A. Barnatt, J. Polym. Sci. Pt. A1, 4, 1709-26 (1966).
7. John Boor, Jr. "Ziegler-Natta Catalysts and Polymerizations" Academic Press, New York. 1979 p. 111.
8. R.S. Porter, J. Wang and J.R. Knox, Polym. Journal, 10(6), 619-28 (1978).
9. P.L. Magagnini, F. Andruzzi and G.F. Benetti, Macromolecules, 13, 12-15 (1980).
10. P.L. Magagnini et al. Macromolecules, 14, 1845-1847 (1981).
11. P.L. Magagnini et al. Proceedings 28th Macromolecular Symposium, 1982 p. 802.
12. P.L. Magagnini et al. Polymer, 23, 277-80 (1982) and references therein.
13. Recent ^{13}C NMR experiments have shown that PEBP26 is isotactic. Thus, the shoulder on the DSC melting peak cannot be due to the melting of atactic polymer in this case.