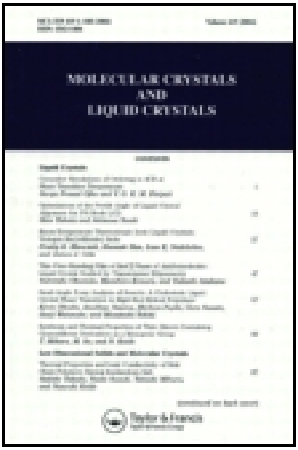


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Synthesis and Properties of Liquid Crystalline Side Chain Polysiloxanes of Negative Dielectric Anisotropy

V. Surendranath [a] & D. L. Johnson [a]

[a] Department of Physics, Liquid Crystal Institute, Kent State University, Kent, OH, 44242

Version of record first published: 22 Sep 2006.

To cite this article: V. Surendranath & D. L. Johnson (1989): Synthesis and Properties of Liquid Crystalline Side Chain Polysiloxanes of Negative Dielectric Anisotropy, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 167:1, 207-212

To link to this article: http://dx.doi.org/10.1080/00268948908037177

Mol. Cryst. Liq. Cryst., 1989, Vol. 167, pp. 207–212
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Synthesis and Properties of Liquid Crystalline Side Chain Polysiloxanes of Negative Dielectric Anisotropy

V. SURENDRANATH and D. L. JOHNSON
Liquid Crystal Institute and Department of Physics, Kent State University, Kent, OH 44242

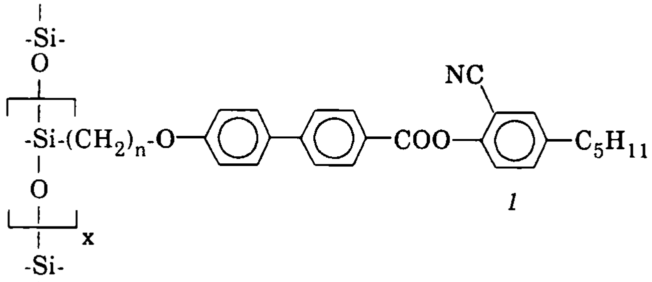
(*Received April 8, 1988*)

A series of alkenyl substituted biphenyl benzoates having a lateral cyano substituent have been prepared. These liquid crystalline monomers were hydrosylylated with polymethylhydrosiloxane. The monomers have wide nematic range, and the polymers show wide range liquid crystallinity.

Keywords: liquid crystals, polysiloxanes, synthesis

INTRODUCTION

A large number of polymers containing a mesogenic pendant group and a polysiloxane backbone have been prepared and characterized.[1–5] Many liquid crystalline side chain polysiloxanes with pendant groups having a terminal cyano substituent have also been prepared.[6] These polymers with positive dielectric anisotropy have potential application in electrooptic display in the twisted nematic mode. Polymeric liquid crystal materials with negative dielectric anisotropy also have potential application in display devices operating in the dynamic scattering mode. Very few liquid crystalline side chain polysiloxanes with negative dielectric anisotropy have been prepared.[7] This paper reports the synthesis of new alkene substituted biphenyl benzoates with a lateral cyano substituent. These new liquid crystalline molecules were attached to a polysiloxane backbone to give the polymers 1 which would be expected to have negative dielectric anisotropy.

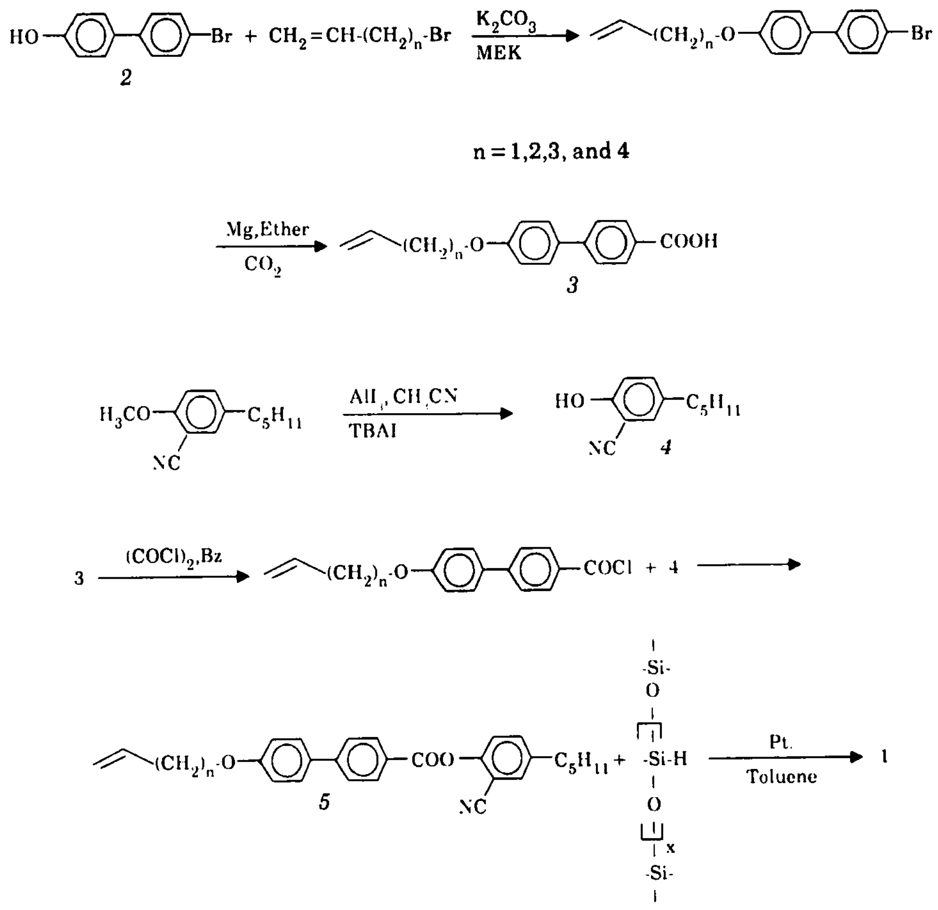


1

$x = \sim 35 \quad n = 3,4,5, \text{and } 6.$

SYNTHESIS

These mesogenic polysiloxane polymers were prepared by the platinum catalyzed alkylation of polymethylhydrosiloxane with mesogenic olefins. The mesogenic olefins *5* were synthesized according to the method given in Scheme 1. The acids *3* were prepared by alkylating 4′-hydroxy-4-bromobiphenyl with *n*-bromoalkene and the resulting bromo compound was coverted to the corresponding carboxylic acid *3* by the carbonation of the Grignard reagent prepared by the entrainment method. The details of the preparation will be published elsewhere. The phenol *4* required for the synthesis of the mesogenic olefins *5* was prepared by a modification of the procedure reported by Admaska *et al.*[8] Demethylation of 2-cyano-4-*n*-pentylanisole was accomplished in very high yields using aluminum triiodide in acetonitrile containing catalytic amounts of tetra-*n*-butylammonium iodide.[9] The mesogenic olefins *5* were obtained by condensing the acid chloride of *3* with phenol *4* in the presence of excess triethylamine.



SCHEME 1

MESOMORPHIC PROPERTIES

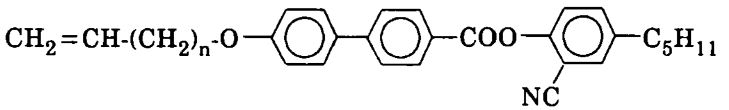
Transition temperatures for the mesogenic polymer precursors 5 are given in Table I. All four homologs are mesomorphic with wide nematic ranges. The homologs with n = 1 and 3 have higher N–I transitions as compared to those for the homologs with m = 2 and 4 indicating a substantial odd–even effect. Transition temperatures and enthalpies for the polymers 1 are given in Table II. The glass transition temperatures (T_g) decrease with increasing length of the spacer as expected. The clearing temperatures are appreciably higher than those for the corresponding olefinic precursors. The polymers on cooling from the isotropic phase form the nematic phase followed by a transition to a smectic phase which is thermally weak but clearly seen during cooling by DSC, which suggests this is a smectic A. However, no focal conic fan texture could be observed in microscopic studies even after annealing the sample for ~6 hours. The phases of these polymers are being further studied by x-ray.

EXPERIMENTAL

Transition temperatures were determined using a Perkin-Elmer DSC-4 or a DSC-2 instrument interfaced with a model 3600 data station. The DSC runs were carried out at 10° $\min^{-1}$; T_g values were taken at the mid-point of the transition indicated by DSC and the transition temperatures at the peak given by DSC. The microscopic

TABLE I

Transition Temperature (°C) and Heat of Transition ΔH (cal/g) for

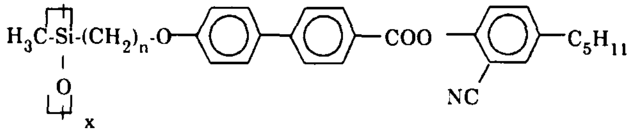


n	K-N	N-I
1	84.0	156.5
	[15.41]	[0.78]
2	75.5	125.5
	[14.80]	[0.44]
3	69.7	141.1
	[12.32]	[0.56]
4	70.8	122.5
	[13.87]	[0.41]

[ ] denotes ΔH values.

TABLE II

Transition Temperature (°C) and Heats of Transition ΔH (cal/g^{-1}) for



n	I-N	N-S	T_g
3	172.0	112.0	28
	[0.32]	[0.35]	
4	181.0	94.5	22
	[0.50]	[0.5]	
5	162.5	115.5	9
	[0.34]	[0.35]	
6	164.7	94.5	8
	[0.40]	[0.25]	

[ ] denotes ΔH values.

studies were made using a Leitz polarizing microscope in conjunction with an FP-80 hot stage and FP-82 control unit or a Leitz ortholux polarizing microscope fitted with a modified and calibrated Mettler FP-2 heating stage. IR spectra were obtained using either a Perkin-Elmer 700 or a Pye Unicam 3-200 instrument. NMR spectra were determined using a Varian EM 360 (E) instrument in deuterated chloroform with TMS as the internal standard. Anal Tech silica gel GHLF 2.5 × 10 cm uniplates (250μ) and uv light were used for TLC. Silica gel Davisil grade 635 100 mesh 60 Å was used for column chromatography.

*2-Cyano-4-*n*-pentylphenol,* 4. To a cooled suspension of AlI_3 (19.35 g, 0.05 mol) in CH_3CN (100 ml) a solution of 2-cyano-4-*n*-pentylanisole (4 g, 0.05 mol) was added slowly. After adding tetra-*n*-butylammonium iodide (0.05 g) the mixture was refluxed for 12 hrs. The cooled reaction mixture was hydrolyzed with H_2O and extracted with Et_2O (3 × 50 ml). The combined organic extract was extracted with 10% NaOH (3 × 40 ml). The aqueous phase was separated, acidified with concd. HCl and extracted with Et_2O (3 × 30 ml). The organic layer was dried over anhyd Na_2SO_4, filtered and the filtrate evaporated to give the crude phenol *4*. This material was recrystallized from hexane–benzene (4:1) to give *4*:3.0 g (78.5%), of the phenol mp 80–81°. IR (Nujol) 3280 (OH,s) and 2240 cm^{-1} ($-C\equiv N$); NMR ($CDCl_3$), δ 0.9 (*t*,3,$-CH_3$) 1–2 (*m*,6,methylene H) 2.5 (*t*,2,CH_2Ar), 5.5 (OH, broad) and 6.8–7.5 (*m*,3,ArH).

*2-Cyano-4-*n*-pentylphenyl 4-[4-(allyloxy)phenyl]benzoate, 5 (n = 1).* The acid *3* (500 mg, 2 mmol) was stirred at RT with excess $(COCl)_2$ (0.5 ml) in dry benzene

(20 ml) containing a drop of DMF. The solvents were removed after 2 hrs *in vacuo* to give the crude acid chloride. This material was dissolved in CH_2Cl_2 (25 ml) and added dropwise to a cold solution of the phenol (410 mg, 2 mmol) containing excess Et_3N. The solution was stirred at room temperature and then washed with H_2O repeatedly and dried over anhyd Na_2SO_4. The residue obtained after solvent removal was purified by column chromatography on silica gel. The product was eluted with CH_2Cl_2 and recrystallized from abs. EtOH to give 0.61 g (78%) of the ester *5* ($n = 1$): TLC (CH_2Cl_2) $R_f = 0.6$. IR (Nujol) 2240 ($—C\equiv N$) and 1730 cm^{-1} (—COOR); NMR ($CDCl_3$), δ 0.9 (*t*,3,—CH_3), 1.0–1.8 (*m*,6,methylene H) 2.55 (*t*,2,CH_2Ar), 4.55 (*d*,2,OCH_2) 5.0–5.5 (*m*,2,vinyl H), 5.6–6.2 (*m*,1,vinyl H) and 6.8–8.4 (*m*,11,ArH).

*2-Cyano-4-*n*-pentylphenyl 4-[4-(4-pentenyloxy)phenyl]benzoate,* 5 (*n = 3*). This compound was prepared in the same manner in a purified yield of 71.7%. TLC (CH_2Cl_2) $R_f = 0.62$; IR (Nujol) 2240 ($—C\equiv N$) and 1730 cm^{-1} (—COOR); NMR ($CDCl_3$) δ 0.9 (*t*,3,CH_3) 1.1–2.6 (*m*,10,methylene H) 2.7 (*t*,2,$ArCH_2$) 4.2 (*t*,2,OCH_2), 5.0–5.4 (*m*,2,vinyl H) 5.5–6.2 (*m*,1,vinyl H) and 6.9–8.6 (*m*,11,ArH).

*2-Cyano-4-*n*-pentylphenyl 4-[4-(5-hexenyloxy)phenyl]benzoate,* 5 (*n = 4*). This compound was prepared as before in a purified yield of 69.7%. TLC (CH_2Cl_2) $R_f = 0.62$, IR (Nujol) 2240 ($—C\equiv N$) and 1735 cm^{-1} (—COOR); NMR δ 0.9 (*t*,3,methyl H) 1.0–2.4 (*m*,12,methylene H) 2.7 (*t*, 2, $ArCH_2$) 4.1 (*t*,2,OCH_2) 5.0–5.4 (*m*,2,vinyl H) 5.5–6.2 (*m*,1,vinyl H) and 7.0–8.5 (*m*,12,ArH).

*2-Cyano-4-*n*-pentylphenyl 4-[4-(5-hexenyloxy)phenyl]benzoate,* 5 (*n = 4*). This compound was prepared as before in a purified yield of 69.7%. TLC (CH_2Cl_2) $R_f = 0.62$, IR (Nujol) 2240 ($—C\equiv N$) and 1735 cm^{-1} (—COOR); NMR δ 0.9 (*t*,3,methyl H) 1.0–2.4 (*m*,12,methylene H) 2.7 (*t*, 2, $ArCH_2$) 4.1 (*t*,2,OCH_2) 5.0–5.4 (*m*,2,vinyl H) 5.5–6.2 (*m*,1,vinyl H) and 7.0–8.5 (*m*,12,ArH).

PREPARATION OF THE POLYSILOXANES

Polymethylhydrosiloxane (Petrach, 2250 ave molecular weight) 52 mg (0.84 mmol of SiH) and 1 mmol of the olefinic ester *5* were dissolved in dry toluene (20 ml) and a few crystals of dicyclopentadienylplatinum (11) chloride[10] was added. The mixture was refluxed under nitrogen for 72 hr. After cooling most of the solvent was removed *in vacuo* at RT and then polymer precipitated by the addition of MeOH. The solvent was decanted and the residue was purified by dissolving in 1 ml of toluene and precipitating with 2 ml MeOH. This purification process was repeated several times and the remaining product dried *in vacuo*. Yields were ~55%. The melting characteristics of these polymers are given in Table II.

Acknowledgments

This material is based on work supported by the National Science Foundation Solid State Chemistry Grants DMR87-03524, DMR85-15221, and by DARPA/DNR #N00014-86-K-0072. We would like to thank the Chemistry Department for the use of the IR and NMR instruments. We would also like to thank Dr. M.E. Neubert for useful suggestions.

References

1. H. Finkelmann and G. Rehage, *Macromol. Chem. Rapid Commun.*, **1**, 31 (1980).
2. H. Finkelmann and G. Rehage, *Makromol. Chem. Rapid Commun.*, **2**, 317 (1981).
3. H. Ringsdorf and A. Schneller, *Makromol. Chem. Rapid Commun.*, **3**, 557 (1982).
4. H. Finkelmann and G. Rehage, *Macromol. Chem. Rapid Commun.*, **3**, 859 (1982).
5. B. A. Jones, J. S. Bradshaw, H. Nishioka, and M. L. Lee, *J. Org. Chem.*, **49**, 25, 4947 (1984).
6. P. A. Gemmel, G. W. Gray, and D. Lacey, *Mol. Cryst. Liq. Cryst.*, **122**, 205 (1985).
7. G. W. Gray, D. Lacey, K. J. Toyne, and M. S. White, *International Conference, Liquid Crystal Polymers,* Bordeaux, Abstract 13P1, July 20–24, 1987.
8. G. Adamska, R. Dabrowski, and J. Dziabuszek, *Mol. Cryst. Liq. Cryst.*, **76**, 93 (1981).
9. S. Anderson, *Synthesis*, 438 (1985).
10. M. A. Apfel, H. Finkelmann, G. M. Janini, R. J. Laub, B. H. Lichmann, A. Price, W. L. Roberts, T. J. Shaw, and C. A. Smith, *Anal. Chem.*, **57**, 651 (1985).