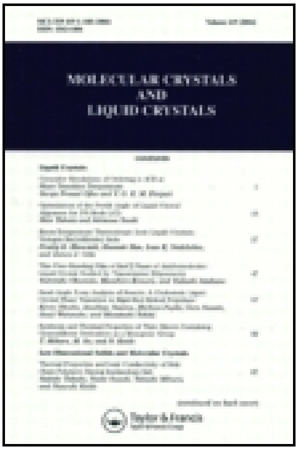


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Liquid Crystalline Side Chain Polymers with Fluorene as Mesogenic Group

G. Kossmehl[a], M. Schulz[a], H.-M. Vieth[b] & A. Van Der Est[b]

[a] Institut für Organische Chemie. Freie Universität, Berlin Takustr. 3, D-1000, Berlin, 33, FRG

[b] Institut für Atom- und Festkörperphysik, Freie Universität, Berlin Arnimallee 14 D-1000, Berlin, 33, FRG

To cite this article: G. Kossmehl, M. Schulz, H.-M. Vieth & A. Van Der Est (1990): Liquid Crystalline Side Chain Polymers with Fluorene as Mesogenic Group, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 193:1, 171-175

To link to this article: http://dx.doi.org/10.1080/00268949008031822

Mol. Cryst. Liq. Cryst. 1990, Vol. 193, pp. 171–175
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

LIQUID CRYSTALLINE SIDE CHAIN POLYMERS WITH FLUORENE AS MESOGENIC GROUP

GERHARD KOSSMEHL, MICHAEL SCHULZ, Institut für Organische Chemie, Freie Universität Berlin Takustr.3, D-1000 Berlin 33, FRG

HANS-MARTIN VIETH, ARTHUR VAN DER EST, Institut für Atom- und Festkörperphysik, Freie Universität Berlin Arnimallee 14, D-1000 Berlin 33, FRG

Abstract The properties of some liquid crystalline side chain polysiloxanes with 2,7-disubstituted fluorene as mesogenic unit are reported. The polymers exhibit smectic A and smectic E like textures. Beside DSC and polarizing microscopy ^{2}H NMR spectroscopy was used to characterize the phase transitions. Anthracene-d$_{10}$ was used as a solute probe molecule and its order parameters were calculated in the liquid crystalline polymer phases. Two other low molecular weight liquid crystals (8CB, MPNOF) were studied by the same method. The general use of anthracene-d$_{10}$ for ^{2}H NMR spectroscopy as probe molecule for liquid crystalline polymers is discussed.

Low molecular weight liquid crystals with a 2,7-disubstituted fluorene unit are well known and have been thoroughly investigated[1]. We wish to report on the characterization of some liquid crystalline polysiloxanes with 2,7-disubstituted fluorene as mesogenic unit in the side chains (see *Fig.1.*).

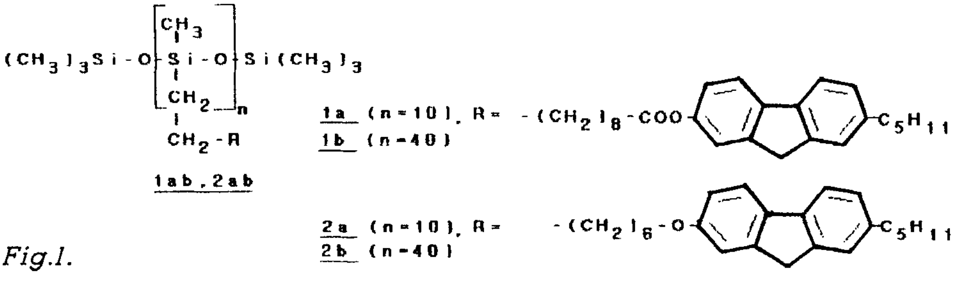


Fig.1.

The use of solute molecules as probes for the study of orientational ordering in low molecular weight liquid crystals is a well established method[2-5]. The NMR spectra of such solutes yield only an indirect measure of the ordering of the liquid crystalline soluent. However, they are much easier to interpret than the spectra of liquid crystal molecules themselves. This is particulary true for polymeric liquid crystals where the motions of mesogenic units are often only partially averaged on the NMR time scale. Details of the preparation and characterization of the polymers by usual spectroscopical methods and elemental analysis will be given in another paper.

Phase behaviour of the polymers

Tab.1. Thermal transitions* (°C) of the polymers

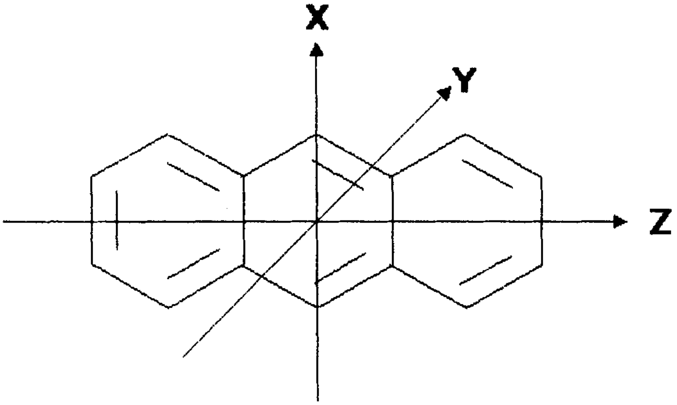
Nr.	cycle	transition temperature
1a	h	g 130-140 S 170-191 I
1a	c	I 180-157 S_A 142-138 S_E 135-116 g
1b	h	g 137-143 S_A 174-194 I
1b	c	I 192-166 S_A 139-130 g
2a	h	g 141-153 S_E 153-158 S_A 168-186 I
2a	c	I 177-155 S_A 154-147 S_E 143-133 g
2b	h	g 97-133 S_E 152-163 S_A 168-194 I
2b	c	I 182-163 S_A 153-141 S_E 121- 80 g

* =DSC, polarizing microscopy; S=smectic like (A,E) I=isotropic state, g=glassy, h=heating cycle, c=cooling cycle

As may be seen in *Tab.1.* the polymers exhibit only smectic mesophases. The S_A-like mesophase exhibits a conical fan texture and the S_E-like phase has a conical fan texture with concentric rings. The S_E-like texture freezes to a glassy state with decreasing temperature. A crystallization was not detectable by further cooling.

Determination of the orientational ordering

Here, we have chosen anthracene-d_{10} as a probe of the temperature dependence of the orientational ordering in the liquid crystalline polymer 2b and in two low molecular weight liquid crystals, 4-cyano-4'-octylbiphenyl (8CB, K 21.5 S_A 33.5 N 40.5 I) and 2-(4-methylpentyl)-7-nonanoylfluorene[8] (MPNOF, K 80.5 S_A 105 I). 2% w/w anthracene-d_{10} were dissolved in the isotropic phase of the matrix. This low concentration had little effect on the measured transition temperatures and no effect on the observed textures of the solvents. ^{2}H NMR spectra were taken with descending temperature from the isotropic phase down to the solid respectively glassy state. The quadrupolar splittings were directly obtained from the spectra . The order matrix of the solute was then calculated from these splitting using literature values of the molecular structure and electric field gradient tensor at the site of the deuteron[6,7].



Anthracene with symmetry axes

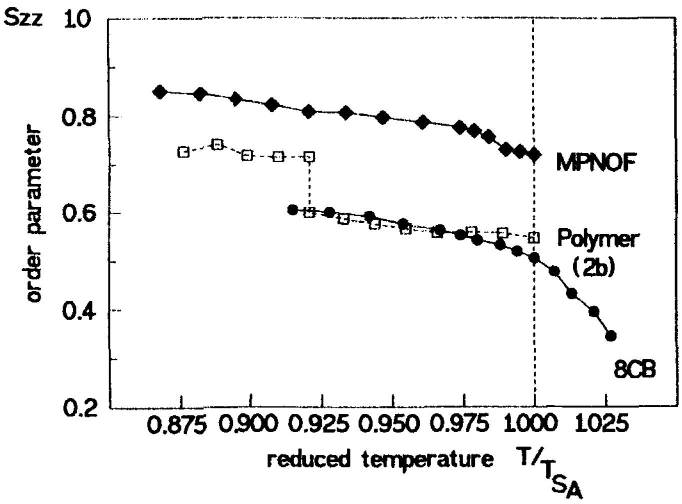


Fig.2.

In *Fig.2* the order parameter S_{zz} of the long axis of the anthracene molecule is plotted against reduced temperature (T/T_{SA},T_{SA}= transition to smectic A phase) in the three solvents. As can be seen, in 8CB a typical Maier-Saupe[9] dependence is observed in the nematic phase. Note also that the temperature dependence is much weaker in the smectic A phase than in the nematic phase. The central aromatic core of MPNOF is also a 2,7-disubstituted fluorene unit and hence this liquid crystal can be seen as a low molecular weight analogue of polymer 2b. Here, the weak temperature dependence of S_{zz} typical of a smectic phase is observed.

In the synthesized liquid crystalline polymer 2b the measured orientational behaviour closely corresponds to the phase transitions given in *Tab.1* . On cooling, a weakly ordered phase (smectic A like, S_{zz}= 0.55-0.60) appears which then converts at T = 140°C (see *Tab.1.*) in a sharp step to a higher ordered phase (smectic E like, S_{zz}=0.70-0.73). Likewise , the order parameter (S_{xx}-S_{yy}) changes in all cases in a consistent manner with the mesophase transitions of the studied matrix . It is interesting to note that S_{zz} for anthracene is considerably larger in MPNOF than in the other two solvents. This indicates that anthracene molecule experiences a different orienting potential in this liquid crystal. It is possible that this is due to an inherent difference in the structures of the smectic phases of the low molecular weight (MPNOF) and polymeric (2b) 2,7-disubstituted fluorene liquid crystals.

Summary

We have shown that the existence of partially ordered mesophases can be easily demonstrated from the ^2H NMR spectrum of solute molecules dissolved in liquid crystalline polymers . This provides a simple method for the characterization of such systems.

REFERENCES

1. D. Demus, H. Demus, H. Zaschke, Flüssige Kristalle in Tabellen, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1976.
   D. Demus, H. Zaschke, Flüssige Kristalle in Tabellen II, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1984.
2. P. Diehl, C. L. Khetrapa, NMR Basic Principles and Progress, 1, 1 (1969).
3. J. W. Emsley and J. C. Lindon, NMR Spectroscopy using liquid crystal solvents, Pergamon Press, Oxford (1975).
4. C. L. Khetrapal, A. C. Kunwar, Adv. Liq. Cryst., 6, 173 (1983).
5. J. Lounila and J. Jokisarri, Progr. NMR Spectrosc., 15, 249 (1982).
6. J. W. Emsley, R. Hasim, G. R. Luckhurst, G. N. Gilstone, Liquid Crystals, 1, 437 (1986).
7. D. Catalano, C. Forte, C. A. Veracini, J. W. Emsley, G. N. Shilstone, Liquid Crystals, 2, 357 (1987).
8. J.Canceill, C. Gros, J. Billard, J. Jaques, Pramana Suppl., 1, 397 (1975).
9. W. Maier, A. Saupe, Z. Naturforsch., 13, 564 (1958); 14a, 882 (1959); 15a, 287 (1960).