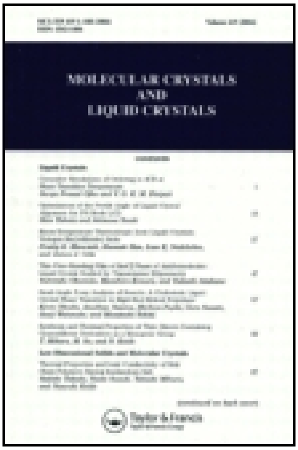


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Orientation Ability of Thermotropic Liquid Crystalline Comb-Like Siloxane Polymers as Studied by NMR Spectroscopy

H. Roth [a] & B. Krücke [b]

[a] WB Polymerphysik, Karl-Marx-Universität, Linnéstr. 5, Leipzig, DDR - 7010, GDR

[b] Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, Weinbergweg 16., Halle, DDR - 4050, GDR

Version of record first published: 22 Sep 2006.

To cite this article: H. Roth & B. Krücke (1990): Orientation Ability of Thermotropic Liquid Crystalline Comb-Like Siloxane Polymers as Studied by NMR Spectroscopy, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 193:1, 223-227

To link to this article: http://dx.doi.org/10.1080/00268949008031830

Mol. Cryst. Liq. Cryst. 1990, Vol. 193, pp. 223–227
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ORIENTATION ABILITY OF THERMOTROPIC LIQUID CRYSTALLINE COMB-LIKE SILOXANE POLYMERS AS STUDIED BY NMR SPECTROSCOPY

HANNA ROTH [1], BERND KRÜCKE [2]
1) WB Polymerphysik, Karl-Marx-Universität, Linnéstr. 5, Leipzig, DDR - 7010, GDR
2) Sektion Chemie, Martin-Luther-Universität Halle-Wittenberg, Weinbergweg 16, Halle, DDR - 4050, GDR

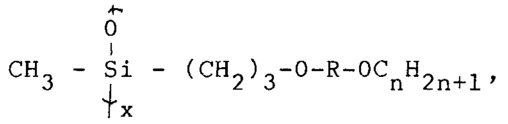
Abstract Smectically ordered samples of comb-like siloxane polymers were studied by FT-1H-NMR-method to get information about the macroscopic order parameter varying mainly the chain-end length of the mesogenic side group.

INTRODUCTION

Thermotropic liquid crystalline comb-like polymers having the mesogenic groups in the side chains have been the subject of a great number of scientific publications in the last years (for example [1-3], for reviews see Finkelmann, Shibaev in [4]). In [5] we gave a detailled account of results on comb-like siloxane polymers, e. g., with regard to the mesophase and its temperature stability, obtained by FT wide-line NMR and in [6] we presented micrographs of nematic and smectic textures of these polymers. In [7] we discussed questions which arose from the research work on these lc-polymers. The present paper continues this with proton-NMR measurements and their discussion with regard to the influence of mobile chemical groups in the side-chains on the orientation ability of the polymeric system.

EXPERIMENTS

The synthesis and X-ray characterization of the comb-like siloxane polymers are described in [8]. They had the following structures:



$$CH_3 - \overset{\overset{\uparrow}{O}}{\underset{\downarrow x}{Si}} - (CH_2)_3{-}O{-}R{-}OC_nH_{2n+1},$$

where x - 36, R = -phenyl-OCO-phenyl-, with n = 3 - 12. FT-^{1}H-NMR spectra were taken of the oriented comb-like siloxane polymers at magnetic fields of 1.4 T. The substances were oriented in normal NMR tubes (diameter 5 mm, inner surfaces untreated) in magnetic fields of 2.1 T at definite temperature/time-cooling down programs, i. e., T/t = 0,025 K/min.

RESULTS

We have obtained interesting results for polymers of this type by variation of the alkyl end group of the mesogenic side chain: -phenyl-OCO-phenyl-OC$_n$H$_{2n+1}$ up to n = 12. NMR measurements of this homologous series unambiguously show that with growing length of the alkyl chain end (up to a certain n) the order parameter S [9] increases (Fig. 1, b). The chain end should not be important for the macroscopic order parameter, because this parameter covers the orientation of the domains, of the molecules already ordered in microscopic regions. On the other hand we have to consider that the viscosity changes in non-ordered regions as the molecules increase and the moment on the oriented regions (in consequence of the anisotropic susceptibility) does not only depend on the magnetic but also on the elastic and viscous moments.

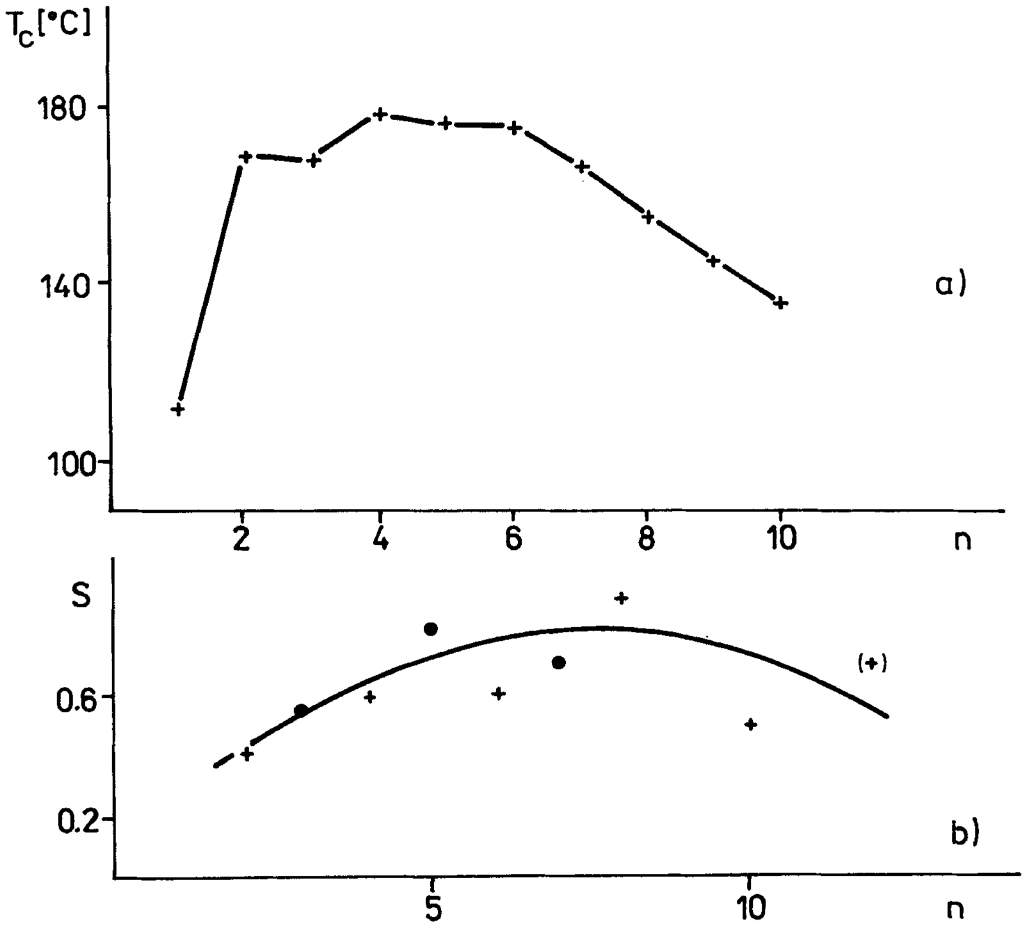


Fig. 1. Clearing temperature T_c (a) and order parameter S (b) as a function of the alkyl chain end n.
\+ even, ● odd chain end numbers.
S-values at $T = T_c - 100$ K.

We think that the increase of the macroscopic order parameter is due to a better alignment of the mesogenic molecules within the ordered regions.

Although a greater free volume is necessary for the rearrangement of molecules with longer chain ends and although the conformation possibilities increases with the mobility of the greater chain molecules the mobility of these alkyl groups (in connection with a higher axial ratio of the mesogenic side group) seems to be favourable for the formation of better-ordered structures, for the decrease of the entropy of the polymer system.

According to our experiment a chain end with 8 carbon atoms has the most favourable size for the formation of liquid crystalline phases in side chain polymers; the best orientation was measured (Fig. 1, b, experimental points, the error is omitted because only the tendency is important).

The continuous curve in Fig. 1, b should demonstrate the tendency of the order parameter change with growing length of the side chain end. This result corresponds to the behaviour of the clearing temperature (Fig. 1, a) of this homologous series. The clearing temperature (T_c) changes as the order parameter changes with growing side chain end n. Longer chain ends are adverse (because of their volume) to a maximum alignment of the mesogenic molecules. The entropy grows again beginning at a definite chain length, in our case n = 10.

It is even necessary to prove whether the result shown in Fig. 1, b is to be interpreted kinetically. If the longer alkyl chains indeed contribute to a better alignment of the mesogenic side chains, then it cannot be excluded that the mesogenic side chains with shorter alkyl ends could reach the same alignment. The process of the alignment could only take a comparatively longer time than with the favourable alkyl chain ends.

REFERENCES

1. F. Hessel and H. Finkelmann, Makromol. Chem., 189, 2275 (1988)
2. G. S. Attard, K. Araki et al., Liq. Cryst., 3, 6/7, 861 (1988)
3. S. U. Vallerien, F. Kremer and C. Boeffel, Liq. Cryst., 4, 1 79-86 (1989)
4. for example: H. Finkelmann, V. P. Shibaev in Adv. Polym. Sci., 60/61 (1984)
5. H. Roth and B. Krücke, Makromol. Chem., 187, 2655 (1986)
6. B. Krücke and H. Roth, Acta Polym., 39/4, 188 (1988)
7. H. Roth, Proc. of the 2nd Dresden Polym. Disc. (1989), TU and ITP Academy of Sciences, Dresden
8. B. Krücke, H. Zaschke et al., Acta Polym., 36, 639 (1985)
9. H. Schmiedel, B. Hillner et al., J. of Magn. Reson., 40 369 (1980)
   K. Müller, C. Eisenbach et al,, Progr. Colloid & Polym. Sci., 69, 127 (1984)