Diamagnetic Anisotropy of Liquid Crystalline Side Chain Polysiloxanes in the Nematic and Smectic Phases

M. F. Achard [a], G. Sigaud [a], F. Hardouin [a], C. Weill [b] & H. Finkelmann [c]

[a] Centre de Recherche Paul Pascal, Université Bordeaux I, 33405, Talence Cédex, France

[b] Laboratoire de Physique de la Matière Condensée, Collège de France, 75231, Paris Cédex 05, France

[c] Institut fü Physikalische Chemie, 3392, Clausthat, Zellerfeld, West Germany
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DIAMAGNETIC ANISOTROPY OF LIQUID CRYSTALLINE SIDE CHAIN
POLYSILOXANES IN THE NEMATIC AND SMECTIC PHASES

M.F. Achard, G. Sigaud, F. Hardouin
Centre de Recherche Paul Pascal, Université Bordeaux I
33405 Talence Cédex - France

C. Weill
Laboratoire de Physique de la Matière Condensée,
Collège de France, 75231 Paris Cédex 05 - France

H. Finkelmann
Institut für Physikalische Chemie
3392 Clausthal-Zellerfeld-West Germany

We report here the first results on the diamagnetic ani-
sotropy $\Delta\chi$ of some thermotropic side chain polymers (polysi-
loxanes). Kinetic effects for the bulk orientation of the ne-
matic phase under a strong external field ($H = 15,25 \; 10^3$ Gauss)
are observed smaller than with linear polymers. The shorter
the flexible spacer between the mesogenic part and the back-
bone is the stronger these effects are. Concerning the tempe-
rature dependence, the saturated magnetic anisotropy increa-
ses regularly with decreasing temperature in the same extent
than for other nematic of L C monomers or linear polymers.

INTRODUCTION

Recently the effect of a magnetic field on some linear
semiflexible polymers with thermotropic nematic phase has
been investigated through the measurement of the apparent
diamagnetic anisotropy[1-3]. This paper reports new results on
the magnetic orientation of the nematic and smectic phases of
side chain polysiloxanes.

The studied polymers (P_4 and P_6) were synthetized by H.
Finkelmann et coll.[4,5]. These are poly-methyl-siloxanes with
phenyl benzoate side chains connected by flexible spacers
(4 and 6 methylene groups) to the main chain. These compounds
have two convenient features : the degree of polymerization
is well defined (95) and the clearing temperatures are lower
than those of polymers with only hydrocarbon backbones. At
last, the compound P_6 presents a monotropic nematic-smectic
transition.

The accurate DSC analysis of these polymers as compared to low molecular weight mesogens provides some preliminary remarks :

- The ratio of the molar entropies for the N-I transitions $\frac{\Delta S_{NI}(P_4)}{\Delta S_{NI}(P_6)}$ is closer to the ratio of the weights of the side group moieties than to the ratio of the weights including the backbone. Probably the polymer main chain tends to adopt a statistical conformation in the nematic phase while the only mesogenic side groups participate to the orientational order at the isotropic-nematic transition.

- For both polymers an endotherm peak corresponding to the melting is observed during the first heating (about 330K). But no crystallization peak is observed till the room temperature (at least) whatever the cooling rate conditions. This lack of recrystallization after a first melting and of course without any further annealing, makes the samples reliable with regard to reproducible studies of physical mesogenic properties.

EXPERIMENTAL RESULTS

The macroscopic magnetic anisotropy in the nematic phase is evaluated from the measurement, in the bulk, of the diamagnetic susceptibility in a direction parallel to the magnetic field : $\Delta\chi = \frac{3}{2}(\chi_{//H} - \overline{\chi})$.

For this purpose the Faraday balance technique is used as previously done for the linear nematic polymers[1-3].

The Figure 1 presents the evolution of $\Delta\chi$ versus time for the P_6 at different constant temperatures in the nematic phase. The applied magnetic field is 15,25 10^3 Gauss.

The saturation of the nematic order, in the bulk, is rather rapidly reached ($t_S \simeq 5mn$) when the temperature is close to the I-N transition ($|T - T_{IN}| \simeq 10K$). On the other hand, farther from the isotropic phase the saturated order takes much longer time to be obtained ; e.g. $t_S \simeq 2$ hours for $|T-T_{IN}| \simeq 40K$.
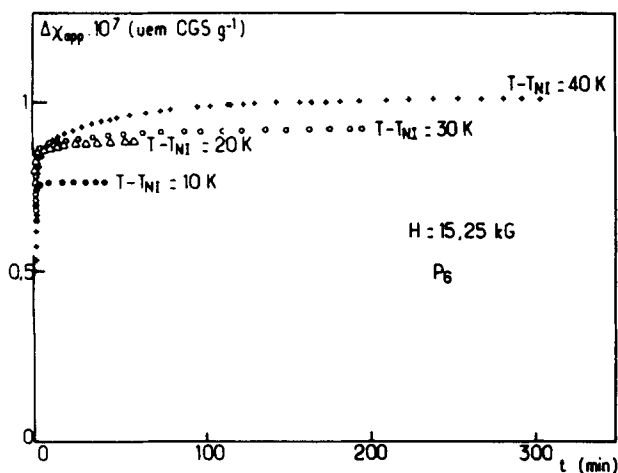
Figure 1 : Evolution of orientation (apparent anisotropy $\Delta\chi_{app}$) as a function of time at different temperatures in the nematic phase of P_6 ($H = 15.25 \ 10^3$ Gauss).

Though less pronounced than with linear polymers, an observable kinetic effect for the bulk orientation of the nematic phase of a side chain polymer is confirmed here. This effect is never observed for low molecular weight nematics within the time-scale of the experiment[6]. Following the remark in the introduction it seems consistent to compare the magnetic anisotropy for the two polymers with regard to the only mesogenic unit. In Figure 2 the temperature dependence of the saturated value of $\Delta\chi$ is shown for both polymers. Qualitatively the role of the flexible spacer appears quite comparable to the role of the aliphatic tail of a low molecular weight "free" mesogen or to a lesser extent to the role of the flexible part of a linear nematogenic polymer. Thus, with an increasing number of methylenes the macroscopic magnetic anisotropy decreases mainly because the molecular anisotropy of the mesogenic unit including the aliphatic spacer is modified. By comparison of the Figure 2 to the data for low molecular weight nematogens (the molecular structure of which
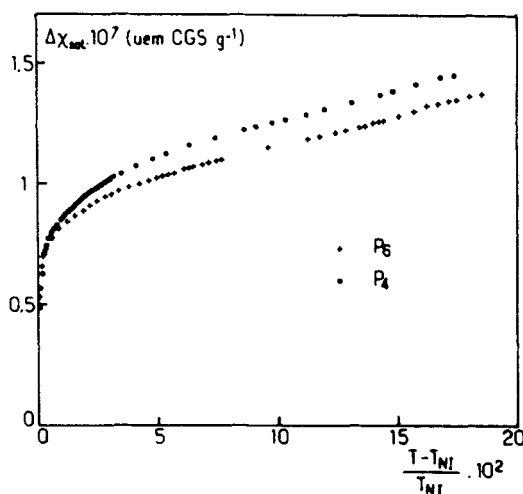
Figure 2 : Saturated diamagnetic anisotropy $\Delta\chi_{sat}$ (normalized per gram of mesogenic part) versus the reduced temperature for P_4 and P_6.

are similar to the side group of the polymers) it turns out that the degree of orientational order of the mesogenic side groups in the polymers is close to monomeric systems, in agreement with earlier measurements which indicate an order parameter only 10% smaller for the polymers than for the monomers[7]. However the connection between these magnetic measurements and an evaluation of the order parameter is not as straightforward as one could expect. In particular the computation of the molecular anisotropy $\Delta\chi_n$ of the repeat unit would be necessary. Unfortunately no data is available to take into account the microscopic anisotropy contribution of the part in the main chain. In no way it cannot be neglected in the evaluation of $\Delta\chi_0$ even though we consider that the backbone does not affect the nematic order parameter at long distance.

Some other experimental observations of the polymer P_6 at low temperature are of interest :

- Starting from a sample in the nematic state with saturated orientation at 343K, the magnetic field is withdrawn. Fif-

teen hours later, in isothermal conditions, only a very weak
disorganization (< 5%) can be detected. Thus the relaxation
times are very high at low temperature, which has been re-
cently specified from measurements of visco-elastic cons-
tants performed by C. Casagrande et coll. on the same sys-
tems[8].

- Furthermore, the orientational order is kept in the smectic
  phase without any sharp discontinuity of $\Delta\chi$ at the nematic-
  smectic transition. From birefringence measurements a simi-
  lar behaviour has been also reported for copolymers of P_6
  inducing cholesteric phase[7]. These results usually charac-
  terize an uniaxial smectic A phase but it is also consistent
  with a smectic C phase for which the molecules remain ali-
  gned in the direction of the magnetic field. Let us note
  that this latter case is depicted in Figure 3 for a L.M.W.
  compound the chemical structure of which is closely related
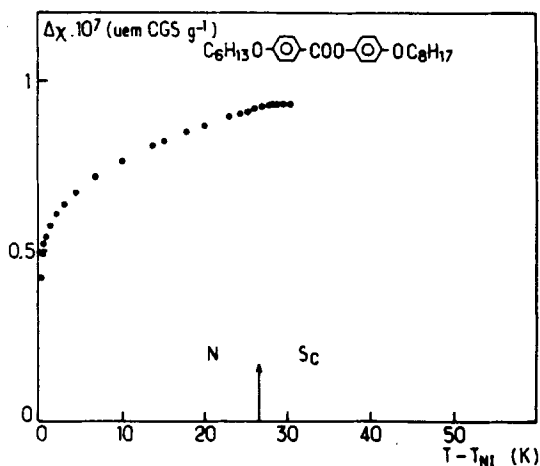 to that of the side group of the polymer P_6.

Figure 3 : Thermal variation of the diamagnetic anisotropy
for a low molecular weight model compound (without disconti-
nuity at the N-S_C transition).

Connected to the occurence of the biaxiality is the enthal-
py of transition ΔH_{NS_C} for this compound (≈ 265 mcalg^{-1})
and it must be compared to the weak heat peak of the poly-

mer ($\approx$ 70 mcalg^{-1}). Moreover the magnetic anisotropy of
the short molecule remains constant in the smectic C phase
while it increases further in the smectic phase of P_6
(Fig. 2). Thus, the polymer behaves like a typical uniaxial
medium going through a nematic-smectic A transition. Howe-
ver no characteristic texture of a smectic A phase can be
observed by optical microscopy within a reasonable scale of
time. Note that the cholesterylderivatives have been proved
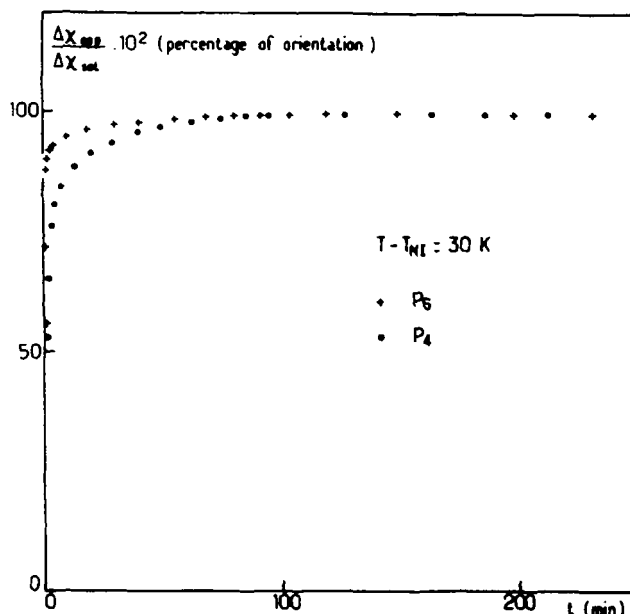to exhibit a smectic A phase by X-ray and polarizing-micros-
copy.

Figure 4 : Evolution of the percentage of orientation as a
function of time in the nematic phase of P_4 and P_6 $(T-T_{NI}=30K)$

CONCLUSION

In the vicinity of the isotropic phase the magnetic be-
haviour of these side-chain polymers is rather close to that
of an usual nematic : especially the small kinetic effects
of orientation in the bulk under a strong external field.
This makes these polymers different from the linear nematic
polymers for which the times of orientation are much higher[2].
One can consider that an aliphatic segment little contributes
to the diamagnetic energy whatever the compound is. But, un-
like the side chain polymers these flexible parts certainly

affects strongly the nematic ordering in the linear polymers. In addition, the isotropic-nematic transition entropy for P_4 and P_6 are the same order of magnitude than for the corresponding monomers[9] which is rather different for semi-flexible linear polymers[3,10].

Farther from the isotropic phase, strong kinetic effects of orientation occur in the nematic phase of the side chain polymers too. The shorter the spacer is, the stronger the effects are (Fig. 4) as observed by C. Casagrande et coll.[8] using a quite different technique. In good agreement with the idea that a large flexible spacer makes the correlations in orientation of mesogenic side chains easier.

With regard to the thermal variation, the saturated magnetic anisotropy increases regularly with decreasing temperature in the same extent than for an usual nematic or for a nematic from a linear polymer as well. This seems to support the idea of a large universality of the thermal evolution of the order parameter in the nematic phase.

At last, the lack of crystallization (except annealing) for these systems keeps the mesogenic orientation at temperatures below the glass transition. This result has been previously reported for some linear polymers providing in this case an orientated fiber in the bulk[2,11,12].

REFERENCES

1. C. Noel, L. Monnerie, M.F. Achard, F. Hardouin, G. Sigaud, H. Gasparoux, Polymer, 22, 278 (1981)

2. F. Hardouin, M.F. Achard, H. Gasparoux, L. Liebert, L. Strzelecki, J. Polym. Sci. Polym. Phys. Ed. 20, 975 (1982)

3. G. Sigaud, D.Y. Yoon, A.C. Griffin, Macromolecules (to be published)

4. H. Finkelmann, G. Rehage, Macromol. Chem. Rapid Commun. 1, 31 (1980)

5. H. Finkelmann, G. Rehage, Macromol. Chem., Rapid Commun.
    1, 733 (1980)

6. See for example, F. Hardouin, M.F. Achard, G. Sigaud,
    H. Gasparoux, Mol. Cryst. Liq. Cryst. 39, 241 (1977)
    and the references therein

7. H. Finkelmann, H. Benthack, G. Rehage, Journ. Chimie Phys.
    80, 163 (1983)

8. C. Casagrande, M. Veyssie, C. Weill, H. Finkelmann,
    Mol. Cryst. Liq. Cryst. Lett. 92, 49 (1983)

9. H. Finkelmann, H.J. Kock, G. Rehage, Mol. Cryst. Liq.
    Cryst. 89, 23 (1982)

10. R.B. Blumstein, E.M. Stickles, A. Blumstein, Mol. Cryst.
    Liq. Cryst. Lett. 82, 205 (1982)

11. L. Liebert, L. Strzelecki, D. Van Luyen, A.M. Levelut,
    Eur. Polym. J. 17, 71 (1981)

12. G. Maret, A. Blumstein, Mol. Cryst. Liq. Cryst. 88, 295
    (1982)