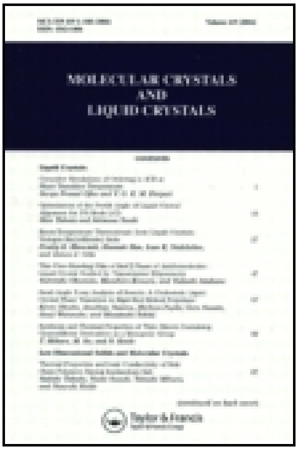

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Unusual Property in a Novel L-C Side Chain Polysiloxane Series

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UNUSUAL PROPERTY IN A NOVEL L-C SIDE CHAIN POLYSILOXANE SERIES

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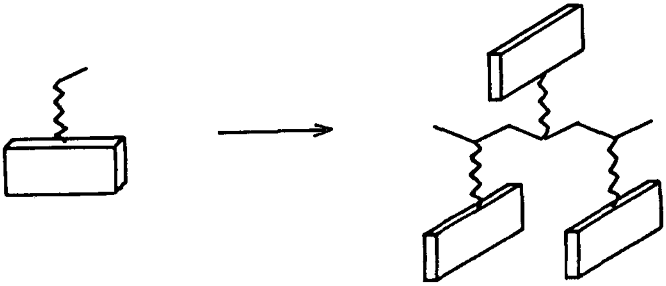
Abstract : A new series of polymethylsiloxanes with laterally grafted mesogens has been synthesized. For compounds with short spacers, the diamagnetic anisotropy variations in the nematic state present an anomaly which suggests a nematic-nematic transition.

1. INTRODUCTION

A new class of L.C. side chain polymers has been synthesized recently. In these compounds the mesogens cores are laterally attached to the main chain through a flexible spacer :



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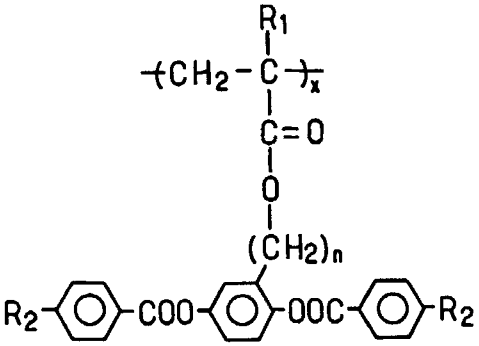
This new macromolecular structure primary tested in series of polymethacrylates[1] and polyacrylates[2] :



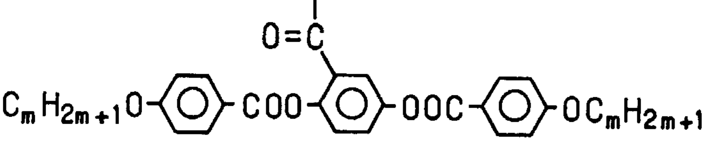
favours the existence of a nematic phase above the glassy state.

Subsequent studies of the optical properties of oriented samples suggest a biaxial character of this nematic phase for long spacers (n = 11)[3].

So far, only one thermotropic L.C., i.e : a low molecular weight compound[4] has been shown to exhibit a biaxial nematic.

This stimulating situation made us to undertake the synthesis of polymethylsiloxanes bearing laterally similar mesogenic cores.

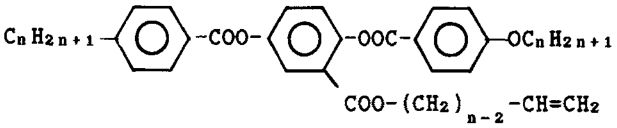
« $P_{n,m,m}$ »



2. EXPERIMENTAL PART

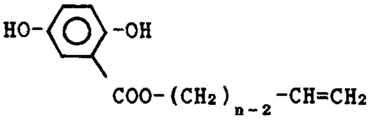
2.1 Synthesis

- Synthesis of 1-(ω-alkylene)2,5-bis-(4-alkyloxybenzoyloxy)--benzoates :



2 steps :

1- Synthesis of 1-(ω-alkylene)2,5-dihydroxybenzoates :



via "solid-liquid phase transfer" catalyzed reaction between potassium salt of 2,5-dihydroxybenzoic acid and the 1-bromo-alcenes with tetrabutylammonium bromide added as catalyst[5].

2- Synthesis of 1-(ω-alkylene)2,5-bis-(4-alkyloxybenzoyloxy)benzoates :
via esterification of 1-(ω-alkylene)2,5-dihydroxybenzoates by 4-alkyloxybenzoic acids with DCC and 4-pyrrolidino-pyridine as catalyst added[6].

- Addition of vinyl derivatives to the polysiloxane :
via hydrosilylation reaction[7], i.e., a 50% excess of vinyl derivative over a mole ratio of 1 : 1 based upon siloxane hydrogen. Hexachloroplatinic (IV) acid is used as catalyst.

The purities of all compounds are checked using ^{1}H-NMR (270 MHz).

2.2 Polymorphism

The mesomorphic properties are characterized by the usual methods (optical microscopy, DSC, X-ray diffraction). As yet observed on PMA$^{(1)}$ and PA$^{(2)}$, all these polysiloxanes are basically nematogenic.

VINYL MOIETY							POLYMER					
n	m	K		N		I	T_g		N		I	ΔH_{NI}
4	4	.	100	.	113	.	.	35	.	119	.	1.6
4	6	.	108	.	(100)	.	.	23	.	99	.	1.5
10	4	.	60	.	84	.	.	17	.	88	.	1.0
10	6	.	47	.	85	.	.	13	.	91	.	0.7

( ) : monotropic transition
ΔH_{NI} : Jg^{-1}

Table 1

We can note in table 1 that the stability of the mesophase is only weakly improved from vinyl derivative to polymer in contrast with the usual comb-like linkage.

2.3 Diamagnetic anisotropy measurements

. 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 $\chi_{\parallel H}$ (Faraday balance[8])

$$\Delta\chi = \frac{3}{2}\left(\chi_{\parallel \bar{H}} - \bar{\chi}\right)$$

$\bar{\chi}$: average susceptibility measured in the isotropic state

H : 1.5 T

. For a long spacer (n = 10), the thermal variation of $\Delta\chi$ is continuous in the nematic phase and qualitatively comparable to the evolution of this parameter in LMW[9], in linear semi-flexible polymers[10,11] or in comb-like polymers[12,13] :

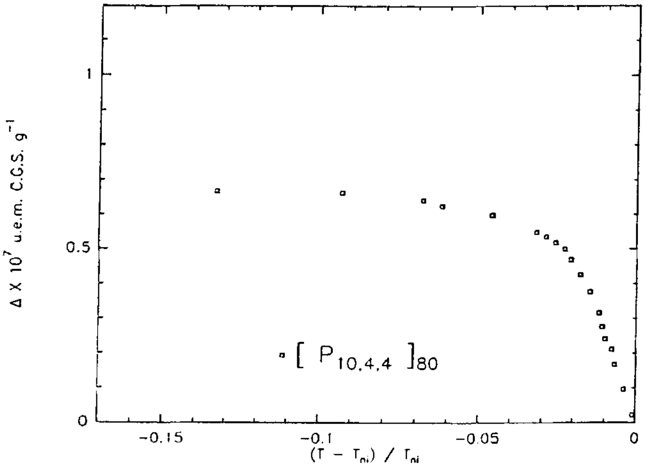
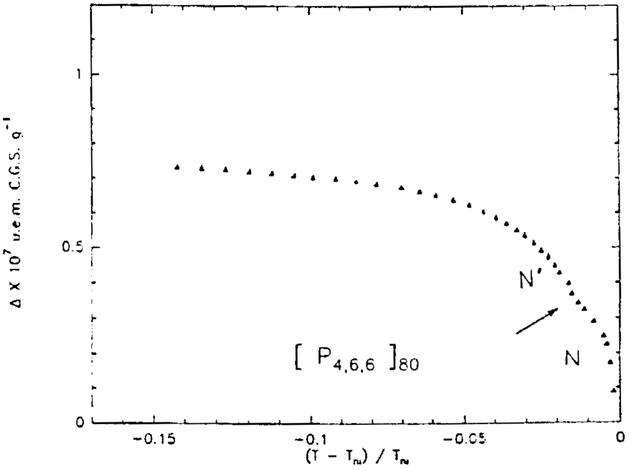
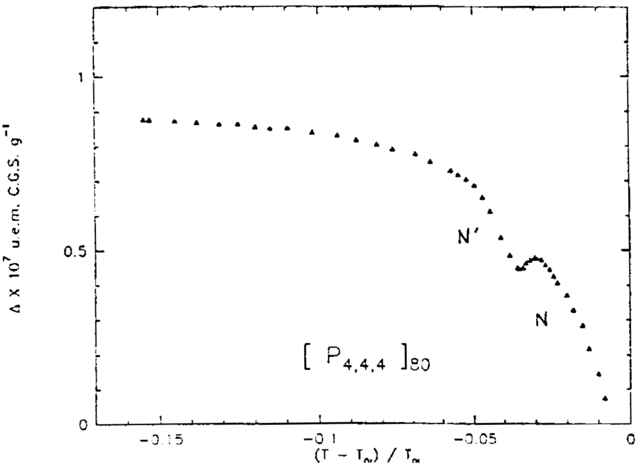


Figure 1

. A surprising result is observed for shorter spacer (n = 4) namely an anomaly more or less pronounced depending on the length of the aliphatic tails modifies the curves in the nematic range of temperature.





This behavior, never reported previously, suggests the occurence of a nematic-nematic transition : no other phase change can be considered since no Bragg spots are seen on the X-ray patterns and birefringent schlieren textures are observed throughout the mesomorphic domain.

Moreover a strong tendency to homeotropy of the nematic phase at low temperature would be consistent with an uniaxial medium. The optical characteristics of the N phase at high temperature have not been yet established. Nevertheless it is worth noting that $\Delta\chi$ is a macroscopic parameter : its thermal evolution is in direct ratio to the orientational order parameter for an uniaxial medium. We believe that the discrepancy to the classical Maier and Saupe[14] behavior which is the bump clearly evidenced in the figure 2b ($P_{4,4,4}$) could result from a biaxial character of the nematic at high temperature. We stress that a phase transition from a biaxial nematic to an uniaxial nematic with decreasing temperature looks possible since already reported for a low molecular weight system[4].

3. CONCLUSION

This result has to be confirmed through a systematic study of polymethylsiloxanes with different substituents laterally attached. Moreover the theoretical works which have been recently developped[15,16,17] to take in account the different couplings between the main chain and the mesogenic groups in comb-like polymers could be valuably extended to these novel chemical structures in order to explain our observations.

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