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Liquid Crystals

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PRELIMINARY COMMUNICATION

Density measurements on liquid-crystalline side-chain polysiloxanes

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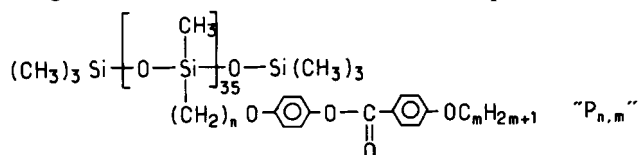
We have studied the behaviour of the density, ρ , as a function of temperature for a number of side-chain liquid-crystalline polymers. The polymers have a polysiloxane backbone and a benzoate ester side group with different tails or flexible spacers. From the values of ρ in the smectic A phase and from the layer thickness obtained from X-ray experiments we have determined a molecular area in the plane of the layers. The evolution of this parameter shows clearly the asymmetrical role of the tail and the spacer.

We report here an exploratory study of the temperature dependence of the density in the mesomorphic range of a number of liquid-crystalline side-chain polysiloxanes recently described [1]. The experiments were carried out with an Anton Paar Density Meter (DMA 60-DMA 602). The sample is introduced into a U-shaped tube which is supported rigidly at its open ends. The same tube is excited electronically to vibrate at its natural frequency. From the frequency change caused by a sample inside the tube, the density ρ of this material can be determined

$$\rho = A(T^2 - B),$$

where T is the period of oscillation of the sample tube while A and B are two apparatus constants which were determined as a function of temperature ($20^\circ\text{C} \rightarrow 150^\circ\text{C}$) using glycerol and styrene as standards. During the measurements the thermal stability is better than $\pm 0.05^\circ\text{C}$. The maximum error on the absolute value of the measured density is estimated to be $1 \times 10^{-3} \text{ g cm}^{-3}$. We note that the oscillating part of the sample tube has to be filled completely and homogeneously with the polymer without any entrapped gas; before introducing the polymer at high temperature (the isotropic liquid or mesophase) all solvents and gases have to be removed.

The materials studied are members of a new series of polymethylsiloxanes with the same mesogenic rigid core but different tails or flexible spacers



The transition temperatures listed in the table, were determined by microscopic observations. They correspond to the first appearance of the liquid-crystalline phase on decreasing the temperature from the isotropic state. Since the polymers present a

distribution of molecular weights, the range of temperature for the isotropic-mesophase transition is about 10°C .

Figure 1 shows the temperature dependences of the densities in the homologous series $P_{n,1}$ with variable length of the spacer ($n = 3$ to 10) and constant OCH_3 tail. We note a significant decrease of the density as the spacer length increases. Moreover we

Phase transition temperatures.

Polymer index	S_A	$T/^{\circ}\text{C}$		I
			N	
$P_{3,1}$	—	119	—	—
$P_{4,1}$	—	74	—	104
$P_{5,1}$	—	122	—	—
$P_{6,1}$	—	109	—	—
$P_{10,1}$	—	133	—	—
$P_{5,2}$	—	149	—	—
$P_{5,4}$	—	163	—	—
$P_{5,6}$	—	170	—	—
$P_{5,8}$	—	165	—	—

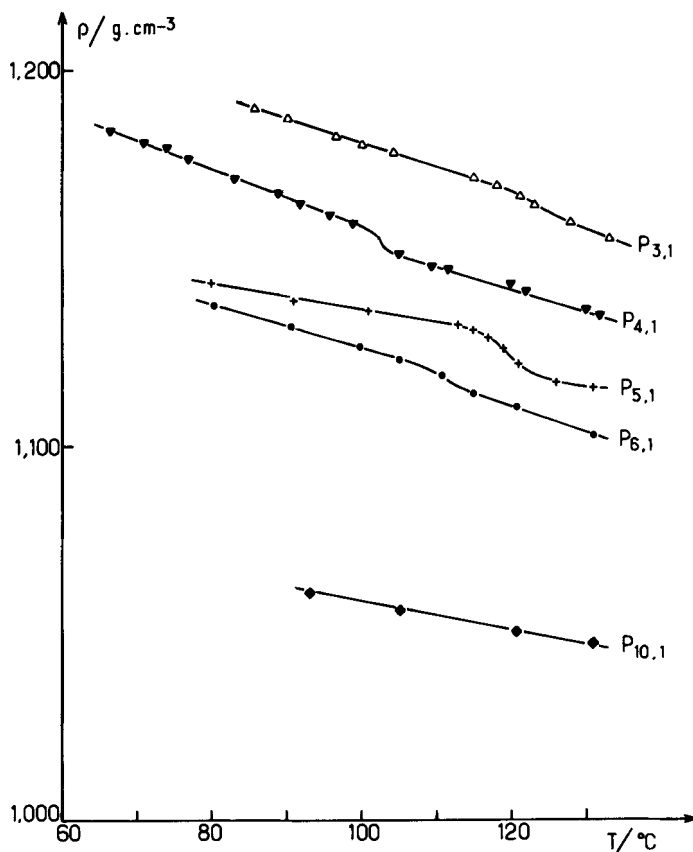


Figure 1. Densities (ρ) as a function of temperature for polysiloxane liquid crystals with different lengths of the spacer. Note that the change observed for $P_{4,1}$ corresponds to an isotropic to nematic transition. For $P_{3,1}$, $P_{5,1}$, $P_{6,1}$ the transition is isotropic to smectic A.

can remark that, as for a side-chain polymer studied previously [2], the density curves $\rho(T)$ are linear except for a jump near the clearing point (I-N or I-S_A). No discontinuity at the nematic-smectic A transition is observed for the P_{4,1} sample.

The effect of the tail length on the density appears in the homologous series P_{5,m} (cf. figure 2). The density reduces gradually as the chain length increases. Thus, the influence of the length of the spacer and the length of the tail on the density appear to be qualitatively the same at a given temperature (figure 3). In contrast, it has been

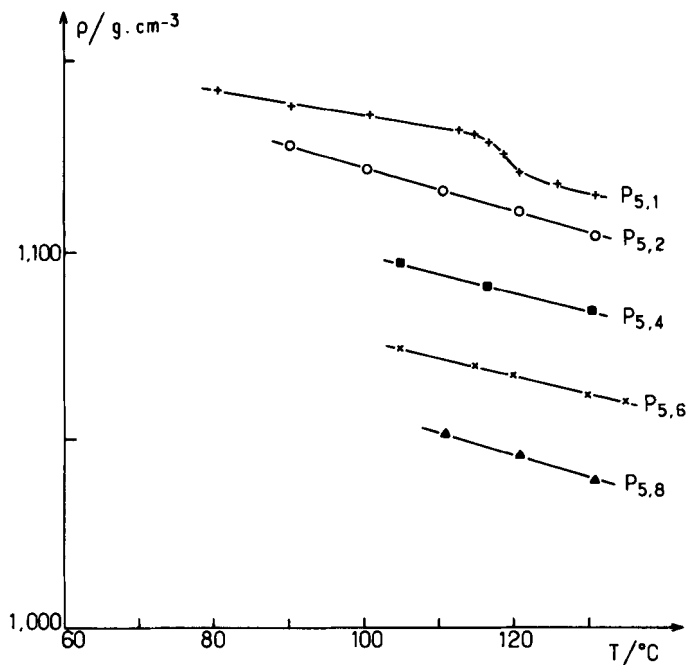


Figure 2. Densities (ρ) as a function of temperature for polysiloxane liquid crystals with different lengths of the aliphatic tail.

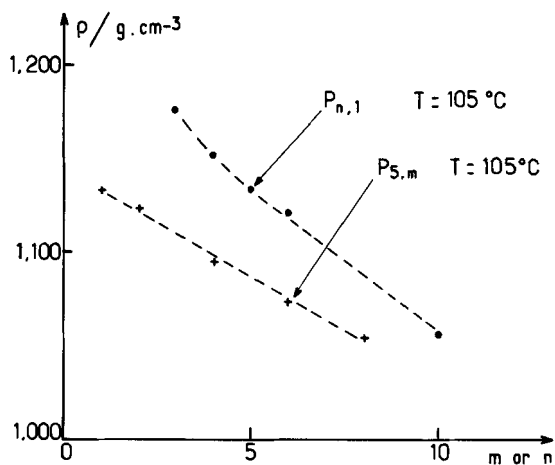


Figure 3. Isothermal density versus the spacer length and the tail length. The dotted line is a guide for the eye only.

found that these two parameters play a different role on the layer thickness, d , in the smectic A phase (figure 4). A molecular area in the plane of the layers can be calculated from the experimentally measured density and layer thickness [3].

In order to explain the partial bilayer structure of the smectic A phase in the $P_{n,1}$ series, the simplest model consists of local dimerisations of the mesogenic groups [3, 4]. Therefore the molecular area can be deduced as follows:

$$S = \frac{2M}{N_A \rho d},$$

where N_A is the Avogadro constant and M is the mass of the repeat unit. In addition to the two mesogenic groups extending in a direction perpendicular to the smectic planes, on average, we must take into account the contribution of one unit of syndiotactic backbone per layer.

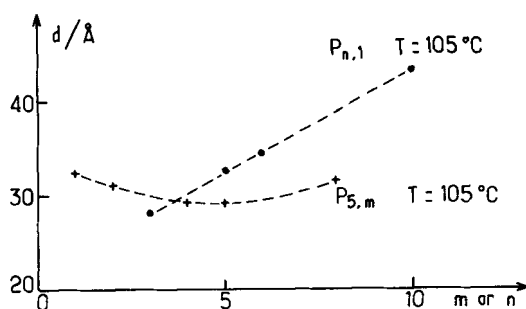


Figure 4. Isothermal layer spacing versus the spacer length and the tail length. The dotted line is a guide for the eye only.

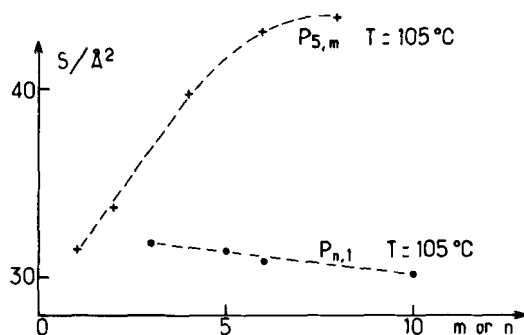


Figure 5. Unit area versus the spacer length and the tail length. The dotted line is a guide for the eye only.

Inspection of figure 5 reveals that the parameter S for the $P_{n,1}$ series is very close to that of low molar mass cyano derivatives ($\approx 32 \text{ Å}^2$) [3] in which the aromatic rigid cores must be efficiently packed forming smectic A layers of antiparallel pairings [4, 5]. On the other hand, for polymers with long aliphatic tails (e.g. $P_{5,8}$) S calculated from the same equation (cf. figure 5) is compatible with the area occupied by two free aromatic cores ($\sim 44 \text{ Å}^2$) [6]. In other words, the molecular area reduces now to $s = S/2$ ($\sim 22 \text{ Å}^2$) in complete agreement with the fact that the corresponding layer thickness is not larger than one mesogenic side-chain [1]. Thus, the asymmetrical role of the spacer and the tail, which was already noticeable in figure 4, is clearly depicted

in figure 5: only the length of the latter affects the degree of strong associations between mesogenic groups. Only the length of the former strongly affects the layer thickness in the smectic A phase.

Referring to these results, N.M.R. and neutron scattering experiments are in progress to specify the modifications to the molecular organization and dynamics in the smectic A phase of samples differing by their tail length or spacer length.

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