Liquid Crystals
Publication details, including instructions for authors and subscription information:
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To cite this Article Wolff, Dietmar , Ruhmann, Ralf , Thiele, Thomas , Prescher, Dietrich and Springer, Jürgen(1996) 'Liquid crystalline side group polymers with fluorine-containing azo-chromophores', Liquid Crystals, 20: 5, 553 — 557
To link to this Article: DOI: 10.1080/02678299608031142
URL: http://dx.doi.org/10.1080/02678299608031142

LIQUID CRYSTALS, 1996, VOL. 20, NO. 5, 553-557

Liquid crystalline side group polymers with fluorine-containing azo-chromophores†

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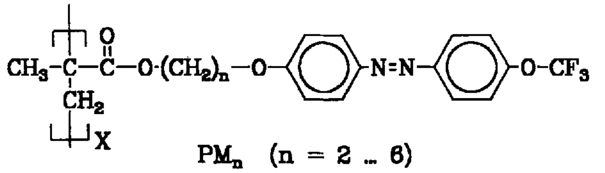
(*Received 31 October 1995; accepted 22 November 1995*)

A series of side group liquid crystalline polymethacrylates with 4′-trifluoromethoxyazobenzene mesogenic side groups was characterized by differential scanning calorimetry, polarizing microscopy and X-ray diffraction methods depending on the spacer length. The phase behaviour was compared with literature data for analogous non-fluorinated compounds. An unusual phase polymorphism N–S_{Ad}–I was observed for the polymers with spacer length $n=5$ and 6.

1. Introduction

The synthesis and structural investigations of side group liquid crystalline polymers (SGLCPs) are of increasing interest due to a broad range of possible applications [1]. Notably, the use of azobenzene containing polymers is predicted in the field of non-linear optics, in optical information storage and processing and in electro-optical displays [2]. Furthermore, studies of the application of low molecular weight liquid crystals and their mixtures have shown that fluorine-containing materials often combine several advantageous properties such as favourable mesophase behaviour for LCD applications, low viscosity, high thermal stability and high polarity [3]. Because only a few papers describe fluorine-containing SGLCPs [4–8], our work aimed to study the influence of fluorinated tail groups on the mesophase behaviour of such compounds.

This paper reports on the phase behaviour of side group liquid crystalline polymethacrylates with 4′-trifluoromethoxyazobenzene mesogenic side groups as a function of the spacer length:



$$-[CH_2-C(CH_3)(COO(CH_2)_n-O-C_6H_4-N{=}N-C_6H_4-O-CF_3)]_x-$$

PM_n (n = 2 ... 6)

The liquid crystalline behaviour of these compounds was studied by differential scanning calorimetry (DSC), by polarizing optical microscopy and by X-ray diffraction methods. The results are compared with literature data for the analogous non-fluorinated compounds [9, 10]. The synthesis and first results of the characterization of these polymers were described recently [11, 12].

2. Measurements

The molecular weights and the polydispersity indices (M_w/M_n) were obtained from size exclusion chromatography (SEC) using 2PL-gel columns (Fa. Knauer), tetrahydrofuran as eluent and polystyrene as standard.

The phase transition temperatures of the polymers were determined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC 7 apparatus at a scanning rate of 20 K min^{-1}. Indium was used for calibration. The maxima of the DSC enthalpy peaks of the second heating runs were taken as the phase transition temperatures. For phase assignment the samples were investigated using a polarizing microscope (Fa. Olympus) combined with a hot stage (Fa. Linkam THM 600).

X-ray diffraction was carried out in a home made temperature controlled ($\Delta T = \pm 0{\cdot}1$ K) vacuum chamber with a flat film camera at a distance of 81·5 mm from the sample. Monochromatic CuK_α radiation ($\lambda = 0{\cdot}15418$ nm, graphite monochromator) was focused by a glass capillary. The polymer samples PM_4, PM_5 and PM_6 were oriented inside the chamber in a magnetic field (2·4 T) perpendicular to the incident beam. For

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†Presented at the European Liquid Crystal Conference, Bovec, Slovenia, March 1995.

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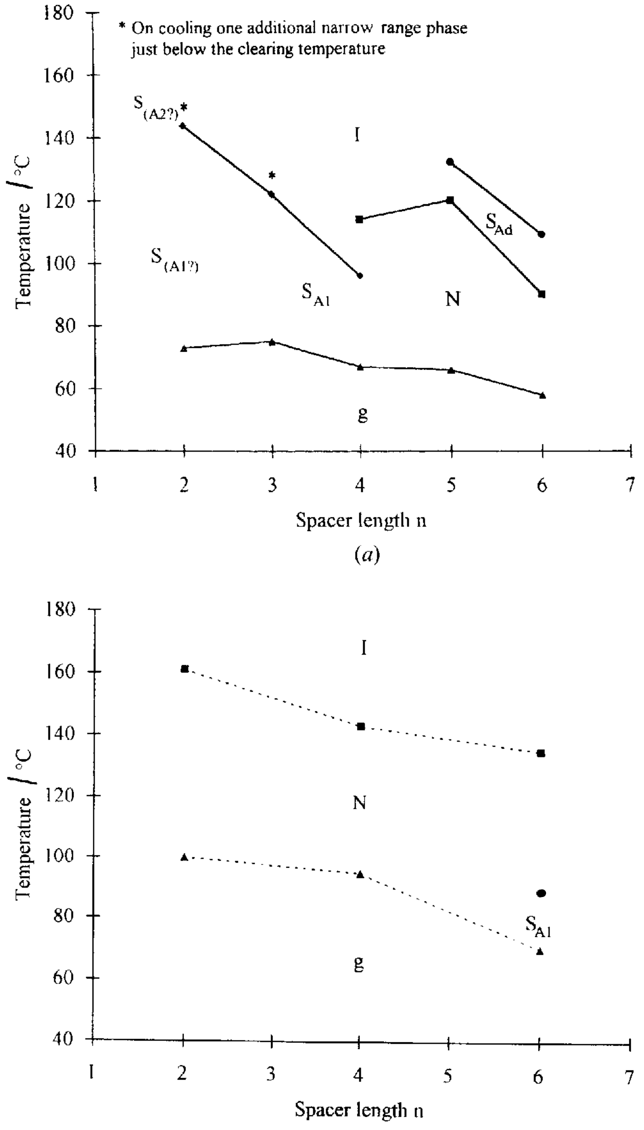
Table 1. Phase assignment of polymers PM_n ($n=2 \dots 6$).

Polymer	M_w/ $10^4 g\,mol^{-1}$	M_w/M_n	Phase behaviour[a]/°C						
PM_2	5·90	2·9	g	73	$S_{(A1?)}$			144	I[b]
PM_3	5·31	2·3	g	75	S_{A1}			122	I[b]
PM_4	7·21	2·5	g	67	S_{A1}	96	N	114	I
PM_5	3·93	2·4	g	66	N	120…125	S_{Ad}	132	I
PM_6	7·18	2·4	g	58	N	90	S_{Ad}	109	I

[a] g = glass; S_{Ad} = smectic A, where *d* denotes a layer period between the value of a monolayer and that of a bilayer; S = smectic; N = nematic; I = isotropic,

[b] On cooling only, one additional narrow range smetic (S_{A2}?) phase occurs just below the clearing temperature.



(*b*)

Figure 1. Phase diagram of polymers PM_n ($n=2 \dots 6$) (*a*) fluorinated and (*b*) non-fluorinated [9, 10] (abbrevations see table 1).

Table 2. Layer periods of polymers PM_n ($n=2 \dots 6$).

Polymer	Estimated length of one side group (plus backbone radius)/nm	Layer periods of smectic phases/nm	Orders of reflection
PM_2	1·8	3·55 HT[a] 1·77 LT[b]	3 1
PM_3	2·0	2·25 LT	1
PM_4	2·2	2·21 LT	1
PM_5	2·4	2·83 HT	2
PM_6	2·6	3·23 HT	2

[a] HT = high temperature phase.

[b] LT = low temperature phase.

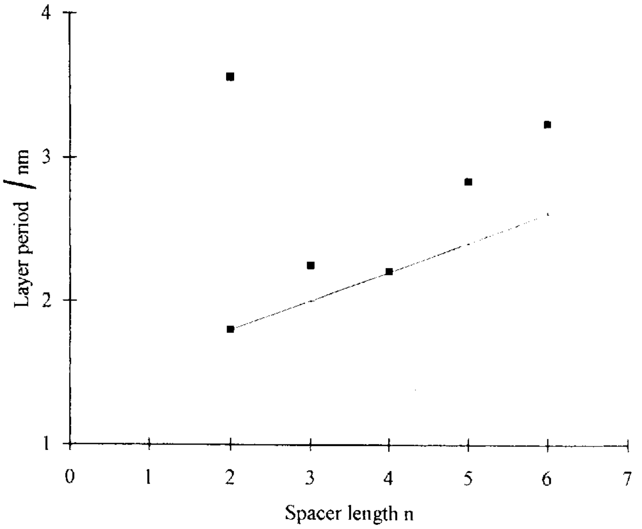


Figure 2. Layer periods (■) and estimated side group lenths (+) of polymers PM_n depending on spacer length.

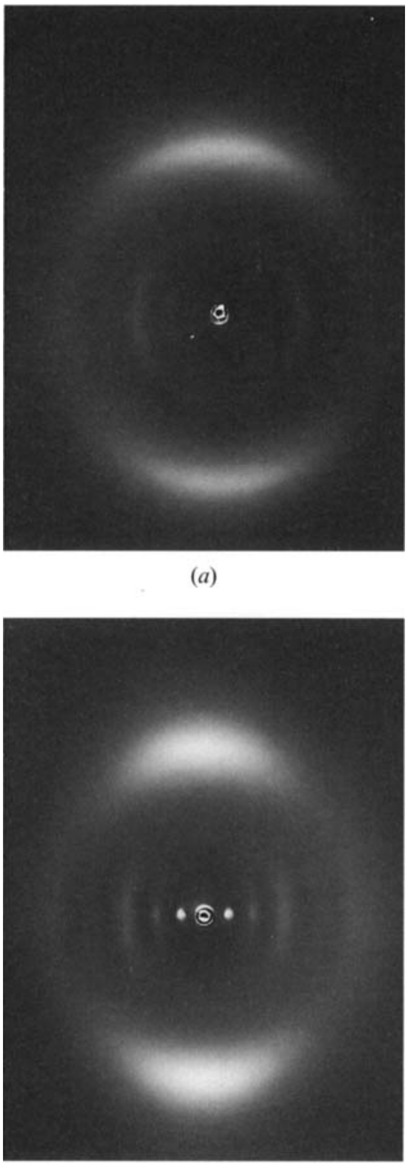
polymers PM_2 and PM_3, due to the high viscosity induced by the short spacers, no such orientation was possible, but for PM_3 a slight orientation was obtained by drawing a fibre from the anisotropic melt.

The results of the phase assignments are summarized in table 1.

3. Results and discussion

The synthesized polymethacrylates PM_n ($n=2 \dots 6$) show a phase polymorphism strongly dependent on the spacer length. The number-average degrees of polymerization allow us to neglect the dependence of the phase transition temperatures on the molecular weight. The phase transition temperatures obtained by DSC are given in table 1 in detail and in a phase diagram, figure 1 (*a*), as a function of the spacer length. In figure 1 (*b*), the phase transition temperatures [9] and the phase assignments [10] of the corresponding non-fluorinated compounds are given.

With increasing spacer length *n*, the glass transition temperatures of the polymers PM_n decrease slightly. This behaviour is well documented for side group liquid crystalline polymers [1]. In comparison with the non-fluorinated analogues, the glass transition temperatures are strongly decreased. For instance, polymer PM_2 shows a glass transition at a temperature of 73°C, whereas the glass transition of the corresponding non-fluorinated polymer is quoted as 100°C. Also the clearing temperatures of the polymethacrylates are decreased by the fluorine-substitution, but due to the simultaneous change of the glass transition in the same direction, the liquid crystalline temperature range is maintained.



(*a*)

(*b*)

Figure 3. X-ray diffraction patterns of magnetically oriented samples of fluorinated PM_6 at (*a*) 80°C (N phase) and (*b*) 97°C (S_{Ad} phase).

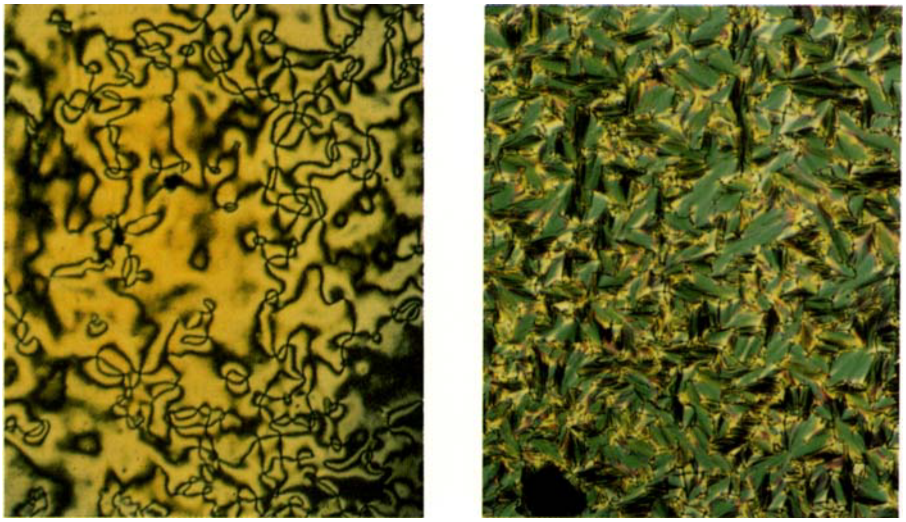
In low-molecular-weight liquid crystals, tail fluorination is found to suppress nematic character and enhance the formation of smectic phases [13]. Furthermore orthogonal smectic phases should be favoured over tilted smectic phases by incorporating perfluoroalkoxy tail groups. In agreement with this behaviour, the number of phase transitions is increased in the series of polymers PM_n ($n=2 \ldots 6$) in comparison with the non-fluorinated analogues, indicating the intensified appearance of smectic phases. For example, the polymethacrylates PM_n ($n=4 \ldots 6$) exhibit two phase transition temperatures above the glass transition, while only the non-fluorinated polymer with a spacer length $n=6$ shows a nematic–smectic phase transition.

For mesophase assignment, X-ray diffraction measurements on magnetically oriented fluorinated samples were carried out at different temperatures. The layer periods (*d*) are compared with the length of the side groups of the polymers PM_n, estimated by *hyperchem*, in table 2 and figure 2.

Surprisingly, below 90°C a nematic phase, figure 3 (*a*), and at higher temperatures between 90°C and 105°C a S_{Ad} phase (with a layer period between the value of a monolayer and that of a bilayer, indicating partial overlapping of the mesogenic side groups, figure 3 (*b*)) were found by investigating the fluorinated polymer PM_6. The nematic phase can be frozen in the glassy state. It is under investigation whether an additional nematic phase exists at any temperature between 105°C and the clearing temperature. If such a phase can be observed, the phase below 90°C must be assigned as a re-entrant nematic, as observed recently [14] for liquid crystalline polymers with other than polymethacrylate backbones.

A layer period of 3·23 nm was estimated for the S_{Ad} phase of PM_6, whereas for the non-fluorinated sample, a nematic phase at high temperatures and a S_{A1} phase with a layer period of 2·56 nm have been described [10]. The last value corresponds with the van der Waals length of the side groups (plus backbone radius) estimated by molecular modelling ($L=2{\cdot}6$ nm for both the fluorinated and the non-fluorinated polymers PM_6).

A total overlapping of the side groups of the non-fluorinated sample is possible only slightly above the glass transition, since this space filling arrangement requires decreased backbone mobility. The layer formation can be attributed to the interaction of the permanent dipoles of the oxygen atoms linking the spacer with the mesogenic group and the dipoles induced in the π-electron system of the phenyl ring of the lateral neighbouring side groups.



(*a*) (*b*)

Figure 4. (*a*) Schlieren texture of PM_4 at 114°C indicating a nematic phase; (*b*) fan-like texture of PM_5 at 125°C indicating a smectic A phase.

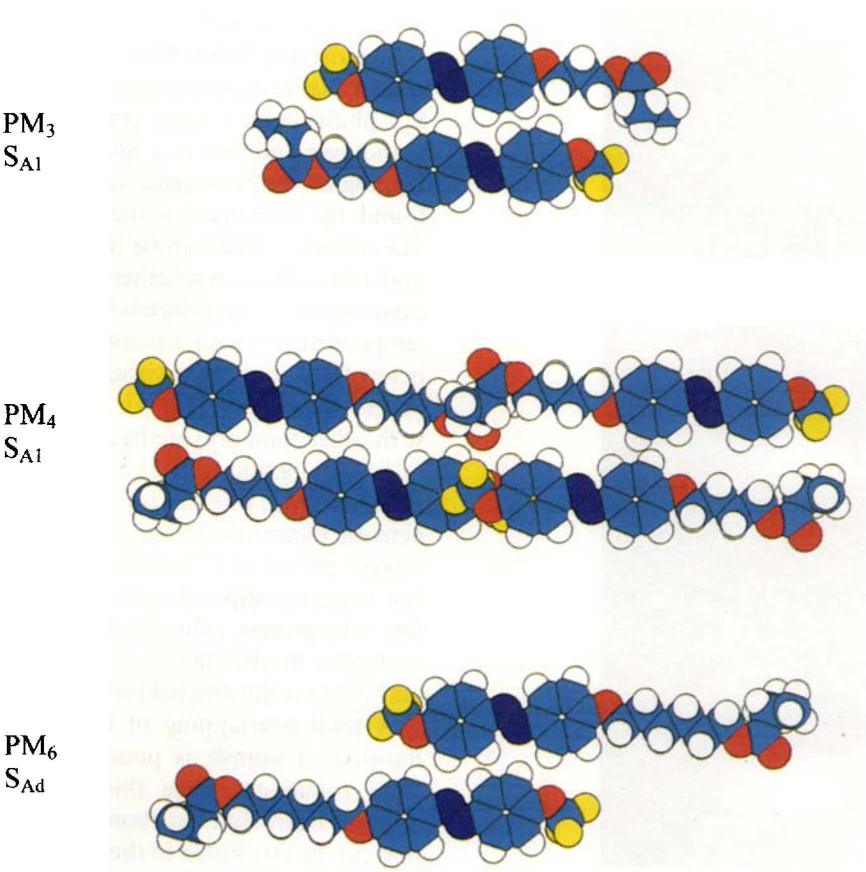


Figure 5. Side group overlapping of PM_3, PM_4 and PM_6 in the smectic phases.

The formation of the S_{Ad} phase by the fluorinated PM_6 polymer at higher temperatures cannot be attributed only to steric hindrance, since the van der Waals radii of the fluorinated and the non-fluorinated methyl groups are nearly identical. The higher dipole moment of the fluorine to carbon bonds should enhance an interaction of these dipoles and the dipoles induced in the π-electron system of the phenyl ring of the lateral neighbouring side groups. Therefore a smectic A phase with partial side group overlapping (S_{Ad}) could be assigned for the high temperature region of this polymer. The same argument holds for PM_5. Here a short range S_{Ad} phase just below the clearing temperature was found. The layer period was found to be 2·83 nm. At temperatures lower than 120°C, a nematic phase can also be observed for PM_5. Since on further cooling, a better space filling has to be achieved, the relatively stable 'dimers' have to shift along the length axis of the side groups resulting in the formation of a nematic phase.

The polymers PM_5 and PM_6 described here represent the first side group liquid crystalline polymethacrylates exhibiting a nematic phase below a smectic A phase.

For polymer PM_4, comparing the layer period with the calculated length of the side groups, a total overlapping of the side groups is observed. An arrangement of the mesogenic groups is proposed in which the F–C dipoles do not interact with the π-electron system of the phenyl rings of lateral neighbouring side groups, but with the phenyl rings of neighbouring mesogenic groups in the direction of the length axis of the side groups. Then 'strings' are formed which can shift along their lateral neighbours building a nematic phase at higher temperatures, see figure 4(*a*). This model agrees well with the observation that the smectic layer reflection is broadened perpendicular to the layer normal, indicating a very low coherence length in that direction. This coherence length of 2·1 nm (using the Debye-Scherrer equation) calculated from the half width of this reflection perpendicular to the magnetic field direction, corresponds to 4–5 side groups. So laterally, the S_{A1} layers are highly disturbed.

For PM_3, a S_{A1} phase is observed for which the space filling arrangement is possible without any steric hindrance, see figure 5.

For PM_2, no orientation was achieved. This is why it is not quite clear if the two smectic phases are of the S_A or of the S_C type. But since the layer period of 1·77 nm for the low temperature phase corresponds to the length of the side group, this phase seems to be S_{A1}, whereas the layer period of 3·55 nm for a high temperature phase observed only on cooling probably corresponds to a S_{A2} (bilayer) phase.

4. Conclusion

The phase behaviour of a series of side group liquid crystalline polymethacrylates with 4′-trifluoromethoxyazobenzene mesogenic side groups has been studied by different methods and compared with literature data for some analogous non-fluorinated compounds. The introduction of fluorinated tail groups induces a strong change in phase behaviour Glass transition as well as clearing temperatures are decreased. In agreement with low molecular weight liquid crystals, tail fluorination is found to suppress nematic character and enhance the formation of smectic phases. Future work will focus on related copolymer systems with fluorinated and non-fluorinated methoxy tail groups and on polymers with longer, partially fluorinated tail groups.

We acknowledge financial support by the Deutsche Forschungsgemeinschaft.

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