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Ralf Ruhmann[a]; Thomas Thiele[a]; Dietmar Wolff[b]; Dietrich Prescher[c]; Jürgen Springer[b]
[a] Institut für Angewandte Chemie Berlin-Adlershof e.V., Berlin, Germany [b] Technische Universität Berlin, Institut für Technische Chemie, Berlin, Germany [c] Universität Potsdam, Institut für Festkörperphysik, Berlin, Germany

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Liquid crystalline side group polymers with azo-chromophores and fluorinated tails of varying length

by RALF RUHMANN*†, THOMAS THIELE†, DIETMAR WOLFF‡,
DIETRICH PRESCHER§ and JÜRGEN SPRINGER‡

†Institut für Angewandte Chemie Berlin-Adlershof e.V., Rudower Chaussee 5,
Haus 12.5, D-12484 Berlin, Germany
‡Technische Universität Berlin, Institut für Technische Chemie,
Straße des 17. Juni 35, D-10623 Berlin, Germany
§Universität Potsdam, Institut für Festkörperphysik, Rudower Chaussee 5,
Haus 12.5, D-12484 Berlin, Germany

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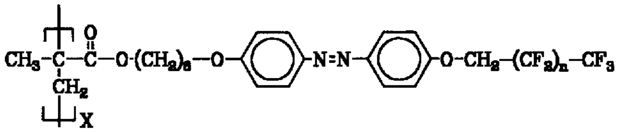
A series of side group liquid crystalline polymethacrylates with 4′-(1H,1H-perfluoroalkoxy)-azobenzene mesogenic units was synthesized and characterized by differential scanning calorimetry, polarizing optical microscopy and X-ray diffraction methods depending on the tail length. The phase behaviour is discussed as a function of the length of the tail groups. Very high clearing temperatures up to 290°C were observed for the polymers with long tail groups.

1. Introduction

The syntheses and structural investigations of side group liquid crystalline polymers (SGLCPs) are of increasing interest due to a broad range of possible applications [1]. Especially, 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, it is known from the field of low molecular mass liquid crystals that fluorinated materials often show several advantageous properties for LCD applications, such as favourable mesophase behaviour, low viscosity, high thermal stability and high polarity [3]. Therefore, a combination of both these features in one system has been the subject of recent work.

Different synthetic routes to the introduction of fluorine containing moieties into polymers have been developed. Thus, Perčec *et al.* studied the effect of fluorinated spacers on the mesophase behaviour of a comb-like polyether [4]. Interesting effects like microphase separation were obtained with copolymers of 1H,1H-perfluoroalkyl methacrylates with monomers with mesogenic side groups [5, 6]. Other authors used the strong electron withdrawing effect of fluorine or of the trifluoromethyl group as a polar substituent in ferroelectric side group polymers [7] or in other side group liquid crystalline polymers [8–10].

We decided on the latter method: the introduction of a fluorine containing tail in the mesogenic side group of polymethacrylates. Our comparison of the phase behaviour of polymethacrylates with 4′-trifluoromethoxy-azobenzene mesogenic groups and that of corresponding non-fluorinated analogues in relation to the spacer length confirmed the strong influence of fluorination on the liquid crystalline properties of side group polymers [11–13]. These interesting results led us to continue the investigations by varying the length of the fluorinated tail of the azobenzene mesogenic unit in side group polymethacrylates:



PM_{n+2} (n = 0 .. 6)

The paper presented here reports on the synthesis and phase behaviour of side group liquid crystalline polymethacrylates carrying 4′-(1H,1H-perfluoroalkoxy)azobenzene mesogenic groups with varying lengths of the tail group. The liquid crystalline behaviour of these compounds was studied by differential scanning calorimetry (DSC), by polarizing optical microscopy and by X-ray diffraction methods.

2. Experimental

2.1. *Monomers*

The synthesis of the monomers starting from the corresponding 1H,1H-perfluoroalkanols will be

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*Author for correspondence.

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described in detail elsewhere [14, 15]. The report will include the liquid crystalline behaviour of some intermediate products and monomers.

2.2. *Polymers*

Method A: about 2 g of the monomer was dissolved in 20 ml of *N*,*N*-dimethylformamide, and 2 mol % (based on monomer) of azobisisobutyronitrile (AIBN) was added. The monomer solution was degassed by passing nitrogen through it for 30 min and the monomer was polymerized at 70°C for 24 h.

Method B: about 2 g of the monomer was placed in a tube and heated slightly above its melting temperature. The molten monomer was stirred and degassed by passing nitrogen through for 30 min. Then 3 mol % (based on monomer) of AIBN or 1·5 mol % of 2,5-bis-(*t*-butylperoxy)-2,5-dimethylhexane was added and the monomer polymerized for one hour. After cooling, the mixture was dissolved in 20 ml of dichloromethane.

The polymers obtained were precipitated in ethanol and purified by reprecipitations from dichloromethane/ethanol. The purified polymers were dried *in vacuo* at 40°C for 48 h. For yield and properties of the polymers prepared see table 1.

2.3. *Measurements*

The molecular weights and the polydispersity indices (M_w/M_n) were obtained from size exclusion chromatography (SEC) using 2PL-gel columns (Knauer), tetrahydrofuran or chloroform 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 by polarizing optical microscopy (Olympus) combined with a hot stage (Linkam THM 600).

X-ray diffraction was carried out using a home made temperature controlled ($\Delta T = 1 \pm 0{\cdot}1$ K) vacuum chamber with a flat film camera at a distance of 81·5 mm and 84 mm from the sample. Nickel filtered Cu-K$_\alpha$ radiation ($\lambda = 0{\cdot}154$ nm) was focused by a glass capillary. PM$_2$ was oriented in a magnetic field of 2·4 T inside the chamber. The low temperature phases of polymers PM$_{n+2}$ (n = 3 … 6) were investigated using fibres drawn just below the $S_{C2} \rightarrow S_{A_d}$ transition temperature.

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

3. Results and discussion

The polymethacrylates PM$_{n+2}$ (n = 0 … 6) were synthesized by radical polymerization in solution or in the bulk. Despite a broad variation of the conditions, the polymerizations in solution gave products with very low molecular weights with increasing length of the fluorinated tail group. As shown in table 1 for the polymers PM$_2$ and PM$_3$ synthesized by polymerization in solution, samples with a degree of polymerization suitable for serious phase assignment could still be achieved. However, because of the strong dependence of the liquid crystalline properties on the degree of polymerization, the products of solution polymerization with a longer fluorinated tail group could not be used in the comparison of the behaviour over the series of polymethacrylates. According to experience from the literature [16, 17] polymerization of the monomers in the molten state was used to obtain polymers with satisfactory degrees of polymerization and in acceptable yields (table 1). For example, the polymer PM$_4$ synthesized by polymerization in solution (A) exhibited a number-average molecular weight M_n of 22000 g mol^{-1}. DSC of a

Table 1. Yields and properties of polymers PM$_{n+2}$ (n = 0 … 6).

Compound	n	Method[a]	Yield /%	M_n /10^4 g mol^{-1}	M_w/M_n	P_n	Phase behaviour[b] /°C
PM$_2$	0	A	83	2·7	2·7	58	g 91 S_B 101 S_{A1} 153 I
PM$_3$	1	A	73	2·0	2·4	39	g 90 S_{Ad} 141 I
PM$_4$	2	A	72	2·2	2·0	39	g 78 S 160 I
PM$_4$	2	B	67	4·6	4·7	82	g 115 S 184 I
PM$_5$	3	B	46	5·3	7·3	87	g 107 S_{C2} 177 S_{Ad} 200 I
PM$_6$	4	B	66	4·5	5·8	67	g 124 S_{C2} 196 S_{Ad} 243 I
PM$_7$	5	B	67	4·4	1·5	62	g 133 S_{C2} 206 S_{Ad} 276 I
PM$_8$	6	B	60	2·1[c]	2·0	28	g 113 S_{C2} 208 S_{Ad} 289 I

[a] A = polymerized in solution, B = polymerized in bulk.

[b] G = glassy, S_{Ad} = smectic A (d denotes a layer periodicity between the value of a monolayer and that of a bilayer), S_{A1} = smectic A monolayer, S_B = smectic B, S_{C2} = smectic C bilayer, I = isotropic.

[c] Measurement of that part of the polymer soluble in tetrahydrofuran.

specimen of this polymer gave a glass transition temperature of 78°C and a clearing temperature of 160°C. The same polymer PM_4 produced by bulk polymerization (B) showed an increased molecular weight of $46000\,g\,mol^{-1}$. The higher degree of polymerization led to changed transition temperatures for PM_4 (B). The glass transition and the clearing temperature were found to be strongly increased for this polymer (table 1). Similar results were obtained for the polymers PM_7 and PM_8.

At present, bulk polymerization results in a broadening of the molecular weight distribution up to M_w/M_n-ratios from 4 to 7. However, in discussing the phase behaviour of the polymers this effect can be neglected.

The synthesized polymethacrylates PM_{n+2} ($n=0$ ... 6) show a phase polymorphism that is strongly dependent on the length of the fluorinated tail. The phase transition temperatures obtained by DSC are given in table 1 in detail and in a phase diagram (figure 1) relating to the length of the tail. With increasing length of the tail, the glass transition temperatures of the polymers PM_{n+2} increase slightly as already observed for the corresponding non-fluorinated polymers [17], and for polymethacrylates with 4′-trifluoromethoxyazobenzene mesogenic units as a function of the spacer length [13], where the decoupling of the mobility of the backbone from the mesogenic side groups increases with increasing spacer length. The behaviour of both non-fluorinated and fluorinated azobenzene containing polymethacrylates is in contrast to the usual behaviour of side group liquid crystalline polymers with non-fluorinated tail groups [1] and of polymethacrylates with perfluoroalkyl ester groups [18] and may be caused by the increased degree of order of the liquid crystalline phases appearing above the glass transition. This order diminishes the mobility of the polymer main chain and leads therefore to an increase of the glass transition temperatures.

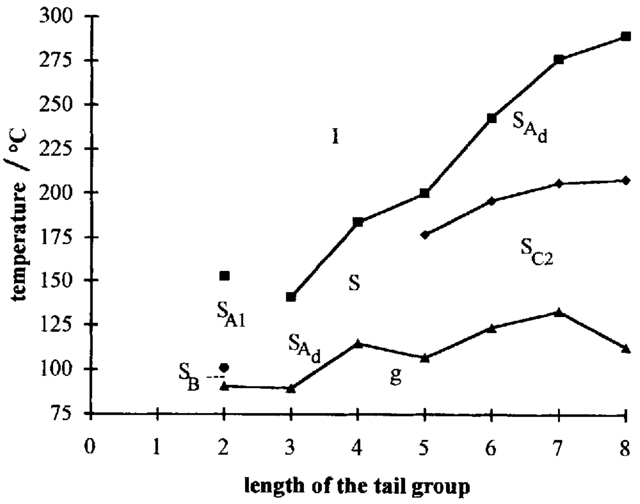


Figure 1. Phase diagram of polymers PM_{n+2} ($n=0$ ... 6) (abbreviations see table 1).

In addition, the clearing temperatures of the polymethacrylates are strongly increased by increasing the length of the fluorine-substituted tail group. A very broad temperature range of liquid crystalline properties develops up to 290°C for polymer PM_8 ($n=6$). The surprisingly high stability of the mesophases of the polymers with longer fluorinated tails can be attributed to the numerous possible dipolar interactions involving the fluorine atoms. The large C–F permanent dipoles can induce dipoles in the π-electron systems of the phenyl rings of lateral neighbouring side groups and generate the high thermal stability of the resulting liquid crystalline phases.

In low molecular mass liquid crystal materials, alkyl chain fluorination is found to suppress nematic character and enhance the formation of smectic phases [19]. Furthermore orthogonal smectic phases should be favoured with respect to tilted smectic phases by incorporating perfluoroalkoxy tail groups. In agreement with this behaviour, the series of polymers PM_{n+2} ($n=0$ ... 6) exhibits several phase transitions above the glass transition indicating the more pronounced occurrence of smectic phases.

For mesophase assignment, X-ray diffraction measurements were carried out on magnetically oriented and non-oriented samples and on fibres of the polymers at different temperatures. The layer periodicities are compared with the lengths of the side groups of the polymers PM_{n+2} estimated with *Hyperchem* (table 2).

Table 2. Layer periodicities of polymers PM_{n+2} ($n=0$ ... 6).

Compound	Estimated length of one side group (plus backbone radius) /nm	Layer periodicity of smectic phases /nm
PM_2	2·72	2·81 HT[a] 2·88 LT[b]
PM_3	2·86	4·32
PM_4	2·98	4·33
PM_5	3·10	5·13 HT 4·37 LT
PM_6	3·22	[c] 4·55 LT
PM_7	3·34	[c] 4·75 LT
PM_8	3·46	[c] 4·98 LT

[a] HT = high temperature phase.
[b] LT = low temperature phase.
[c] High temperature phase was not investigated because of possible thermal decomposition.

A sample of polymer PM_2 ($n=0$) could be magnetically oriented. The X-ray patterns at room temperature and at 130°C are displayed in figure 2. Because of the magnetic moment of the phenyl rings, the smectic layer reflections appear in the direction of the magnetic field. The smectic layer normals are thus preferentially disposed along the magnetic field direction. For the S_{A1} mesophase, layer reflections up to the second order and for the S_B mesophase, layer reflections up to the third order were detected in the originals. The wide angle halo of the S_{A1} phase still reflects the liquid-like lateral arrangement of the mesogenic groups, whereas for the S_B phase, a more ordered lateral organization of the mesogens can be concluded from the sharp wide angle reflection. In the high temperature phase, a layer periodicity of 2·81 nm was estimated, corresponding with the calculated van der Waals length of the side groups (plus backbone radius). In the low temperature phase, a slightly increased layer periodicity of 2·88 nm was detected for this polymer. Therefore smectic phases with monolayers appear in both cases.

For PM_3 ($n=1$) and PM_4 ($n=2$) no orientation was achieved due to the very high value of the phase transition enthalpy. Therefore the phases of these polymers, as well as the high temperature phases of PM_5–PM_8 were investigated using powder samples. In the small angle region layer reflections up to the third order appear for PM_3 and PM_4. In the wide angle region diffuse halos demonstrate the liquid-like lateral arrangement of the side groups within the layers. From the layer periodicity, it can be concluded that the phases have to be assigned as orthogonal smectic Ad or tilted smectic C2. It is not quite clear from the X-ray investigation of these non-oriented samples if the smectic phases are of the S_A or of the S_C type. However, additional observations by polarizing microscopy exhibited a fan-like texture, indicating the occurrence of an S_A phase for PM_3, figure 3(*a*). Since the layer periodicity of 4·32 nm corresponds to a partial overlapping of the side groups, this S_A phase is of the S_{Ad} type, where d denotes a layer periodicity between the value of a monolayer and that of a bilayer (table 2). For PM_4, the studies with polarizing microscopy revealed no clear textures. Therefore a detailed phase assignment is not possible for this polymer.

All the polymers PM_5–PM_8 exhibited a very similar phase sequence. The high temperature phase could only be studied by X-ray diffraction on non-oriented samples and with short exposure times, because the clearing temperatures have moved into a range where the thermal stability of the polymers is uncertain. Similar to the behaviour of PM_3, the results of the measurements on non-oriented samples indicate the appearance of a S_{Ad} or S_{C2} phase in the high temperature region. By the fan-like texture from polarizing microscopy, the type of phases could be more precisely specified to be S_{Ad}, figure 3(*b*). To avoid thermal decomposition, the polymers PM_5–PM_8 were oriented in the low temperature phase by drawing a fibre from the anisotropic melt. Layer reflections up to the fifth order appearing perpendicular to the fibre axis were obtained by X-ray diffraction. Between the maxima of these reflections and the fibre axis, a tilt angle could be detected. Furthermore, in the wide angle region, four diffuse crescents demonstrated the liquid-like lateral arrangement of the mesogenic units within the layers. Calculating the layer

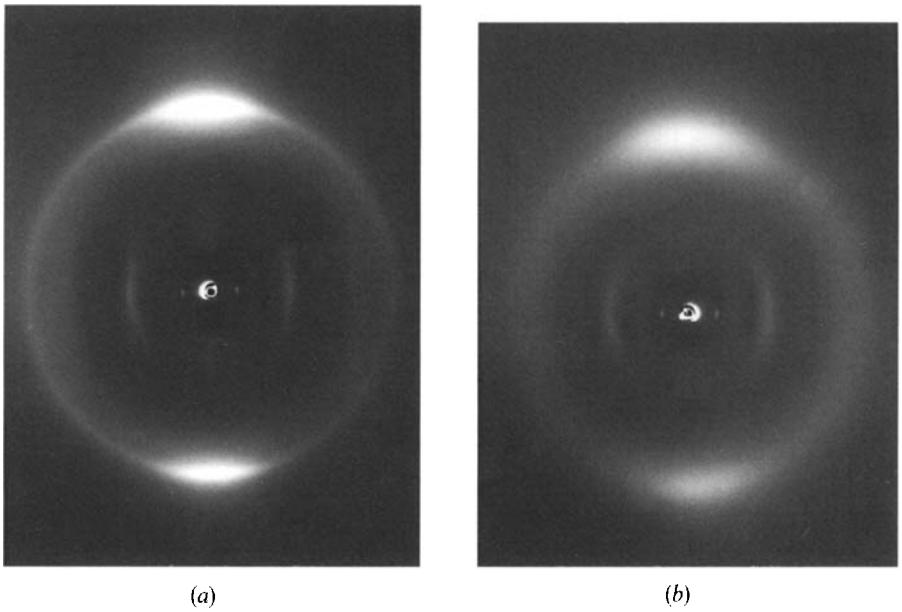
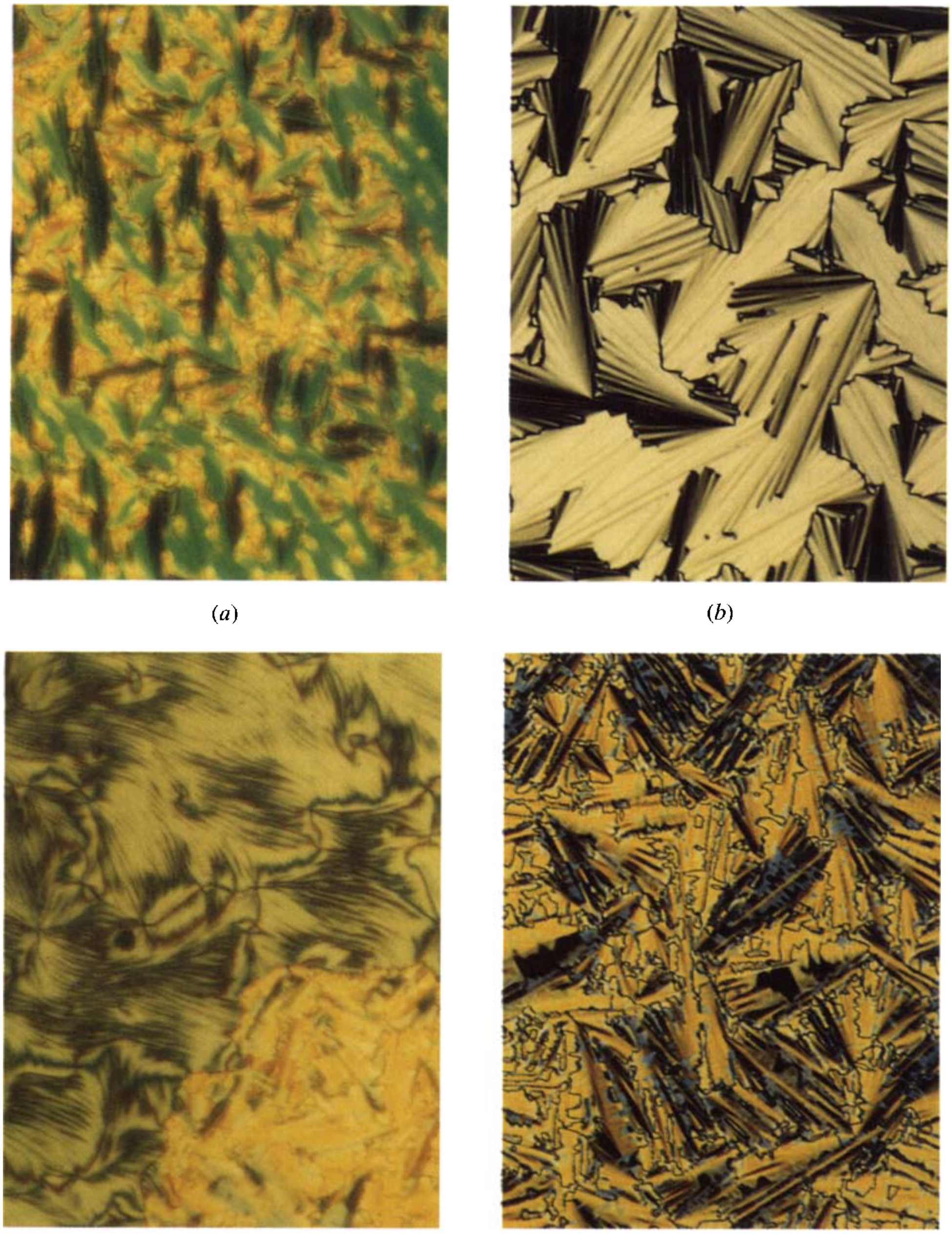

(*a*) (*b*)

Figure 2. X-ray diffraction patterns of magnetically oriented samples of PM_2 at (*a*) room temperature after annealing for several hours at 100°C (S_B phase) and (*b*) 130°C (S_{A1} phase).



(*a*) (*b*)

(*c*) (*d*)

Figure 3. (*a*) Fan-like texture of PM_3 at 138°C indicating an S_A phase. (*b*) Fan-like texture of PM_7 at 228°C indicating an S_A phase. (*c*) Broken fan-like and schlieren texture of PM_7 at 176°C indicating an S_C phase. (*d*) Broken fan-like texture of PM_7 at 47°C indicating an S_C phase.

periodicity (table 2) from the X-ray diffraction pattern of these fibres and taking into account the schlieren texture in areas aligned homeotropically in the high temperature phase and the broken fan-like texture obtained with polarizing microscopy (figures 3(*c*), 3(*d*)) for the polymethacrylates PM_5–PM_8, an S_{C2} phase could be assigned in all cases.

4. Conclusions

The phase behaviour of a series of side group liquid crystalline polymethacrylates with 4′-(1H,1H-perfluoroalkoxy)azobenzene mesogenic units has been studied by different methods. The introduction of fluorinated tail groups induces a strong dependence of the phase behaviour on the length of the tail group. Glass transition as well as clearing temperatures are increased with increased length of the fluorinated tail. As in low molecular mass liquid crystals, such fluorination is found to suppress totally the nematic character and enhance the formation of smectic phases.

Future work will focus on comparisons of the polymers described containing fluorinated groups with the corresponding non-fluorinated analogues, which have been reported recently [19].

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