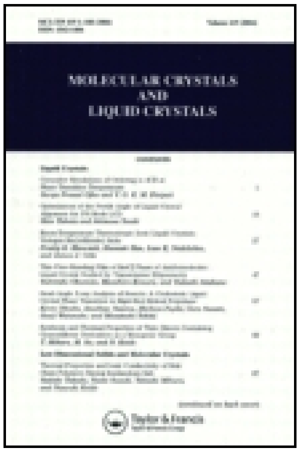

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis and Evaluation of Novel Side Chain Liquid Crystal Polymers with a Single Aromatic Unit

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Version of record first published: 04 Oct 2006

To cite this article: Xujin Bao & Leslie R. Dix (1997): Synthesis and Evaluation of Novel Side Chain Liquid Crystal Polymers with a Single Aromatic Unit, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 304:1, 41-46

To link to this article: http://dx.doi.org/10.1080/10587259708046941

Mol. Cryst. Liq. Cryst., 1997, Vol. 304, pp. 41–46
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SYNTHESIS AND EVALUATION OF NOVEL SIDE CHAIN LIQUID CRYSTAL POLYMERS WITH A SINGLE AROMATIC UNIT

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Abstract Polyacrylates with a 3-nitro-4-(1,1,2,2- tetrahydroperfluroalkyl) benzoate unit as a side chain substituent have been synthesised. These materials form rare examples of side chain thermotropic polymers containing a single aromatic unit. These polymers form smectic phases only.The phase behaviour has been investigated by optical microscopy and d.s.c.

INTRODUCTION

It has been demonstrated that perfluoroalkyl chains can act as an integral part of the mesogenic core of a molecule by virtue of their stiffness which, in turn, is a consequence of the large size of the fluorine atom that prevents free rotation around the carbon backbone. Takenaka[1,2] has shown that (1,1,2,2-tetrahydroperfluroalkyl) benzoates can form stable smectic phases even if there is only one aromatic unit present. In the latter case, a very polar substituent such a nitro group is required in the 3 or 4-position relative to the ester functionality.[2,3] We felt that it would be of interest to prepare side chain liquid crystal polymers containing a (1,1,2,2- tetrahydroperfluroalkyl) benzoate unit since examples of side chain liquid crystal polymers with only one aromatic unit are rare. At this point we wish to draw the attention of the reader to the work of Wilson[4] who has prepared thermotropic polyesters with (1,1,2,2- tetrahydroperfluroalkyl) benzoate units incorporated as side chain units.

SYNTHESIS

The poly(acrylates) were synthesised by grafting of 3-nitro-(4-ω-bromoalkoxy)-(1,1,2,2- tetrahydroperfluroalkyl) benzoates on to the sodium salt of polyacrylic acid using phase transfer catalysis as shown in scheme 1.

Synthesis of the series of compounds (1):

In a 100 ml round-bottomed flask, 3-nitro-4-hydroxybenzoic acid 3.67g (0.02 mol), 1,1,2,2-tetrahydroperfluorodecan-1-ol 9.75g (0.021 mol), DCC (Dicyclohexylcarbodiimide) 4.12g (0.02 mol), 4-pyrrolidino pyridine 0.30g (0.002 mol) and fresh dried THF 60 ml were stirred under N_2 at room temperature for 1 h, then refluxed overnight. The solution was filtered and the THF was removed by rotary evaporator. Then, CH_2Cl_2 was added. The solution was washed with 10 per cent HCl (aq), 5 per cent $NaHCO_3$ (aq) and water. The organic layer was dried with $MgSO_4$. The filtrate was evaporated to get a crudely yellow solid. The product was purified by column chromatography on silica gel with dichloromethane as eluent. Yield: 75-85 %. m.p.:87-89°C. ^1H NMR ($CDCl_3$, TMS): δ: 8.5 (s, 1H, aromatic), 8.2 and 7.1 (2d, 2H, aromatic), 4.6 (t,2H, $CH_2OC(O)$), 2.3-2.8 (m, 2H, CH_2R_f).

Synthesis of 3-nitro-(4-ω-bromoalkoxy)- (1,1,2,2- tetrahydroperfluroalkyl) benzoates (2a-g)

3.15g (0.005 mol) of 3-nitro-4-(1,1,2,2-tetrahydroperfluoroalkyl) benzoates **(1)** was dissolved in 60 ml of dry acetone; 0.03 mol of 1,5-dibromopentane, 2.07g of dry potassium carbonate, a few crystals of potassium iodide was added and the mixture heated under reflux for 48h. The mixture was cooled to room temperature, and the precipitate filtered off and washed with small amount of acetone. The filtrate was almost completely evaporated to dryness. Then, CH_2Cl_2 was added. The solution was washed with 10 per cent NaOH (aq),and water. The organic layer was dried with $MgSO_4$. The filtrate was evaporated to get a crudely yellow solid. The product was purified by column chromatograghy on silica gel with dichloromethane as eluent. Yield: 50-70 %. m.p.:76-78°C. ^1H NMR ($CDCl_3$, TMS): δ: 8.5 (s, 1H, aromatic), 8.2 and 7.1 (2d, 2H, aromatic), 4.6 (t,2H, $CH_2OC(O)$), 4.3 (t, 2H, CH_2O), 3.5 (t, 2H, $BrCH_2$), 2.3-2.8 (m, 2H, CH_2R_f), 1.9-2.1 (m, 6H, $CH_2CH_2CH_2$)

Acrylic polymers (3a-g)

Typical procedure modified from reference[5]. A mixture of 3-nitro-4-(1,1,2,2-tetrahydroperfluorodecyl)-4'-(5-bromopentoxy)benzoate **(2)** (1.56g, 0.002 mol), tetrabutylammonium bromide (0.13g, 0.0004 mol) in 10 ml of chloroform, and sodium polyacrylate solution (Aldrich, MW = 1200) (0.38g, 0.0018 mol, 45% water solution) were refluxed in an oil bath for 96h. The mixture was diluted with 70 ml of chloroform, washed with water (3 × 100 ml), and dried over sodium sulfate. The solvent was eveaporated and the solid dissolved in the minimum of chloroform (5 ml). The product was precipitated from a large excess of Methanol (80 ml) (0.40g). A ^1H n.m.r. spectrum of the polymeric product showed a broad resonance at δ 1.2-1.5 ppm due to the polymer backbone. There was no trace of the methylene bromide signal at δ 3.5 ppm, indicating that the polymer was free from the brominated precursor. Examination of the integrated spectrum indicates effectively quantitative substitution of the acrylate groups.

THERMAL ANALYSIS

Liquid crystalline phases were determined by examining the optical texture of samples under crossed polarised light. Phase transition temperatures were determined by differential scanning calorimetry (d.s.c.) always using a second heating scan at a rate of 10°C per second.

SCHEME 1; synthesis of acrylic polymers

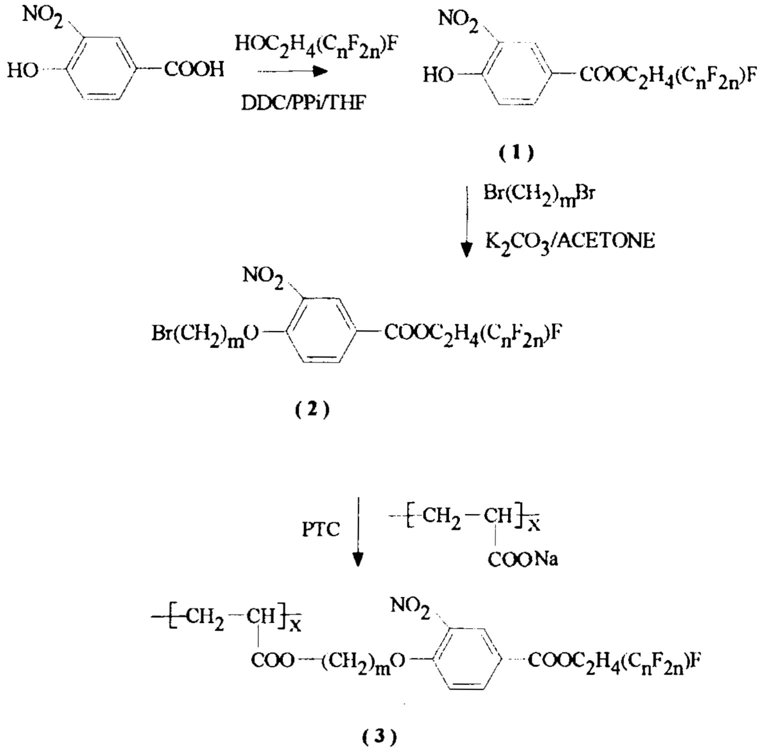

TABLE 1 Thermal properties of 3-nitro-(4-ω-bromoalkoxy)- (1,1,2,2- tetrahydroperfluroalkyl) benzoates

	n	m	C/°C	S_A	I/°C	$\Delta H_{C\text{-}SA}$ / Jg-1.	$\Delta H_{SA\text{-}I}$ / Jg-1.
2a	8	3	43	•	77	9.02	2.05
2b	8	4	53	•	84	9.81	1.72
2c	8	5	48	•	80	8.1	2.31
2d	8	6	48	•	74	7.49	2.59
2e	8	7	<25	•	50	-	2.03
2f	6	5	<25	•	85	-	3.5
2g	10	5	98	•	112	16.8	1.19

n = number of perfluorinated carbon atoms in the 1,1,2,2- tetrahydroperfluroalkyl chain. m = number of methylene units in 4-ω-bromoalkoxy chain. C = crystalline state. S_A = smectic A phase. I = isotropic state.

TABLE 2 Thermal properties of polyacrylates obtained from **2 a-g**

	n	m	g/°C	S_A	I/°C	$\Delta H_{C\text{-}SA}$ / Jg-1.	$\Delta H_{SA\text{-}I}$ / Jg-1.
3a	8	3	82	•	145	14.82	2.64
3b	8	4	106	•	144	19.7	2.56
3c	8	5	78	•	141	10.32	2.35
3d	8	6	96	•	134	17.8	2.48
3e	8	7	71	•	122	7.8	2.28
3f	6	5	61	•	121	4.76	2.31
3g	10	5	97	•	144	13.3	2.2

n = number of perfluorinated carbon atoms in the 1,1,2,2- tetrahydroperfluroalkyl chain. m = number of methylene units in alkoxy chain. g = glassy state. S_A = smectic A phase. I = isotropic state.

RESULTS & DISCUSSION

The liquid crystal phase behaviour of the 3-nitro-(4-ω-bromoalkoxy)- (1,1,2,2-tetrahydroperfluroalkyl) benzoates (**2a-g**) is summarised in table 1. All of these compounds showed the smectic A phase. Increase of the ω-bromoalkoxy chain length from 3 to 6 methylene units (**2a-d**) produces a gradual decrease in the phase transition temperatures, the compound with seven methylene units (**2e**) giving a smectic phase at ambient temperature. Increasing the perfluoroalkyl chain length from six to ten fluoroalkyl units (**2c,f,g**) raises the clearing temperature but appears to narrow the range over which the smectic A phase is stable.

The liquid crystalline phase behaviour of the corresponding polymers (**3a-g**) is summarised in table 2. The phase behaviour of the polymers tends to reflect that of the low molecular weight precursors; only the smectic A phase is observed and there is little change on increasing the length of the alkyl spacer unit except for a significant decrease in clearing temperature for the longest spacer. There is a significant increase in transition temperatures on increasing the length of the perfluoroalkyl chain. As expected, the transition temperatures for the polymers were significantly higher than for the low molecular weight precursors.

CONCLUSIONS

We have successfuly prepared a series of 3-nitro-(4-ω-bromoalkoxy)- (1,1,2,2-tetrahydroperfluroalkyl) benzoates (and acrylic polymers derived from these) and studied the effect of the length of both the alkoxy and perfluoroalkyl chains on the mesomorphic properties. Increasing the length of the alkoxyl group decreases transition temperatures but increasing the perfuoroalkyl chain length has an opposite effect. Much the same behaviour is observed for the acrylate polymers. These results are a direct consequence of the rigidity of the perfluoroalkyl chain. Increasing the length of the perfluoroalkyl chain is comparable to increasing the number of aromatic rings in a calamitic mesogen[6].

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