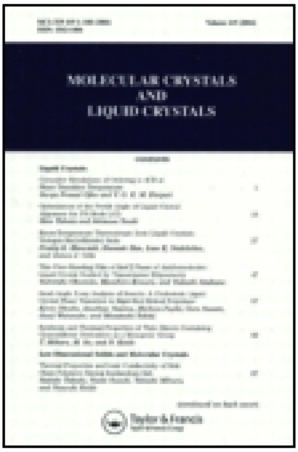

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Thermotropic Perfluoroalkyl Azobenzoates. Studies of Low Molar Mass Compounds and Side Chain Polymer Derivatives

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Thermotropic Perfluoroalkyl Azobenzoates. Studies of Low Molar Mass Compounds and Side Chain Polymer Derivatives

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A series of 4'-[(carbonyloxy-1,1,2,2-Tetrahydrofluorodecyl)]-4-(ω-bromo-alkenyloxy) azobenzenes, 4'-[(carbonyloxy-1,1,2,2-Tetrahydrofluorodecyl)]-4-(alk-1-enyloxy) azobenzenes have been synthesised. Also, a polyacrylate has been formed by phase transfer catalysed reaction between one of the ω-bromo-alkenyloxy compounds and sodium polyacrylate as well as two polysiloxanes formed by hydrosilylation of the alkenyloxy compounds and a polyhydrosilane. All of the low molar mass compounds show the S_A phase on heating and an increase in perfluoroalkyl chain length results in an increase in clearing temperature whilst an increase in the hydrocarbon chain length shows a decrease in clearing temperature. Upon grafting these low molar mass units to a polymer backbone, the resulting materials also show smectic mesophases despite having quite low clearing entropies ($\Delta S/R \sim 0.2 - 0.6$). The precursor polymers are of low molar mass (Mw 1200–1800 g mol^{-1}) and this may be the reason why the polymers do not show glass transition temperatures.

Keywords: Perfluoroalkylated liquid crystals; Thermotropic Azobenzene compounds; Side chain liquid crystal polymers

INTRODUCTION

Azobenzene compounds do play an important part in the "toolkit" of molecules available for research on photoactive materials[1]. It is well known that certain azobenzene dyes exhibit non-linear optical behaviour and that the azobenzene group is able to undergo cis-trans isomerism on exposure to light of certain frequency thus altering the refractive index of functionalised polymers[2] and disrupting liquid crystallinity in mesogenic derivatives[3]. There has also been recent

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interest in liquid crystalline molecules (and polymers) which have a perfluoroalkylated chain acting as part of the mesogenic core of the molecule. It has also been demonstrated that a perfluoroalkyl chain enhances the thermal stability of mesomorphic phases exhibited by certain molecules relative to the corresponding molecules containing a hydrocarbon chain[4]. This is probably because of the extended configuration of the perfluoroalkyl chain caused by its relatively rigid nature and the very marked phase separation between the former and the hydrocarbon constituents of the molecules. Recently there have been many studies of thermotropic compounds and polymers containing perfluoroalkyl chains. Some of these are compounds[5,6] and polymers[7] containing a single aromatic unit, side chain polymers with laterally attached mesogens[8] and low molar mass aromatic esters[4]. The latter work illustrates that when the perfluoroalkyl chain replaces a hydrocarbon chain it surpresses nematic phase formation and encourages the formation of stable smectic phases.

In this study, we have prepared a number of compounds and polymers bearing both an azobenzene unit and a perfluoroalkyl chain in order to obtain liquid crystalline materials with stable smectic mesophases and the photoactive azobenzene unit. The high polarity and thermal stability of perfluoroalkylated compounds coupled with the special properties of the azobenzene group make these materials worthy of study.

EXPERIMENTAL

Synthesis of (1,1,2,2-Tetrahydrofluorodecyl) 4-aminobenzoate (I)

A mixture of 4-nitrobenzoyl chloride (1.9g, 0.01 mol) and 1,1,2,2, tetrahydroperfluorodecan-1-ol (5.8g, 0.01 mol) was stirred in dry pyridine for 5h at 70°C. After cooling, the mixture was dissolved in dichloromethane and washed three times with dilute hydrochloric acid and then water. The organic layer was separated and dried over anhydrous magnesium sulphate, and the dichloromethane removed. The product was recrystallised from 3:1 hexane-ethanol mixture. The product (1,1,2,2-Tetrahydrofluorodecyl) 4-nitrobenzoate gave 85% yield. ^{1}H NMR δ_H ($CDCl_3$ standard TMS; 270 MHz): 2.62 (m, 2H), 4.76 (t, $J = 6$ Hz, 2H), 8.18 (d, J 8Hz, 2H), 8.32 (d, J 8 Hz 2H). Elemental analysis; gives 33.1% C (33.3% calc), 1.15% H (1.3% calc), 2.35% N (2.30 % calc).

The above product was reduced by metallic tin in acid solution to give (1,1,2,2-Tetrahydrofluorodecyl) 4-aminobenzoate (I). ^{1}H NMR δ_H ($CDCl_3$

standard TMS; 270 MHz): 2.62 (m, 2H), 4.02 (broad, 2H), 4.64 (t, *J* 6Hz, 2H), 6.63 (d, *J* 8Hz, 2H), 7.91 (d, *J* 8Hz, 2H).

Synthesis of 4'-[(carbonyloxy-1,1,2,2-Tetrahydrofluorodecyl)]-4-hydroxy azobenzene (II)

A solution of (I) (5.83g, 0.01 mol) in of 3 molar hydrochloric acid (12 cm^3) was cooled to 0–5°C and sodium nitrite (0.69g, 0.01 mol) in water (3 cm^3) was added dropwise. The reaction was kept below 5°C and urea added to destroy excess nitrite. The diazonium salt solution was then added to a cooled solution of phenol (0.94g, 0.01 mol) dissolved in of 2 molar sodium hydroxide solution(4 cm^3), keeping the reaction mixture below 5°C. After acidification with hydrochloric acid, the product was dissolved in chloroform and washed with water followed by drying over anhydrous magnesium sulphate and removal of solvent. The product was recrystallised from 2:1 cyclohexane:ethanol to give 45% yield of product. ^{1}H NMR δ_H ($CDCl_3$ standard TMS; 270 MHz): 2.62 (m, 2H), 4.64 (t, *J* 6Hz, 2H), 7.00 (d, *J* 8Hz 2H), 7.91 (overlapping d, *J* 8 Hz, 2H), 8.18 (d, *J* 8 Hz, 2H). IR (KBr): ν_{max} 1715 cm^{-1} (C=O): 3256 cm^{-1} (OH).

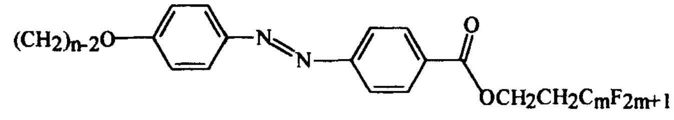
Synthesis of 4'-[(carbonyloxy-1,1,2,2-Tetrahydrofluorodecyl)]-4-(ω-bromo-pentyloxy) azobenzene (III a-l)

A mixture of II (3g, 4.35 mmol), 1,4-dibromobutane (4g, 0.018 mol) and potassium carbonate (2g) was refluxed overnight in acetone with a few crystals of potassium iodide. After filtration of the mixture and removal of acetone, the residue was dissolved in dichloromethane and washed with sodium hydroxide solution and with water. After drying and removal of the solvent, the product was purified on a silica gel column using dichloromethane as solvent. The yield of product was 30%. ^{1}H NMR δ_H ($CDCl_3$ standard TMS; 270 MHz): 1.64 (m, 2H), 1.94 (m, 2H), 1.84 (m, 2H), 2.62 (m, 2H), 3.50 (t, *J* 6Hz 2H), 4.08 (t, *J* 6Hz, 2H), 4.64 (t, *J* 6Hz, 2H), 6.99 (d, *J* 8Hz, 2H), 7.94 (overlapping d, *J* 8 Hz, 2H), 8.19 (d, *J* 8Hz, 2H). IR (KBr):): ν_{max} 1715 cm^{-1} (C=O). Elemental analysis (C,H,F) for $C_{27}H_{20}N_2O_3BrF_{17}$ gives 39.0% C (39.4% calc), 2.4%H (2.1% calc), 39.2% F (39.4% calc).

Synthesis of ω-alkenyloxy derivatives (IV a,b)

The hydroxyazobenzene compound (2 mmol), such as II, was mixed with an *n*-bromoalkene (4 mmol) and potassium carbonate (0.83g) with KI (a few crys-

X =



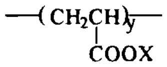
III a-l: RX where R = $BrCH_2CH_2$

m = 8	a	n = 2
	b	n = 3
	c	n = 4
	d	n = 5
	e	n = 6
	f	n = 7
m = 4	g	n = 3
	h	n = 5
m = 6	i	n = 3
	j	n = 5
m = 10	k	n = 3
	l	n = 5

IV a-b: RX where R = $[CH_2{=}CH\text{-}]$

m = 8	a	n = 3
	b	n = 5

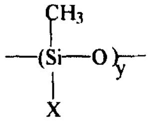
(V)



$-(CH_2\underset{COOX}{CH})_y-$

n = 7

(VI)



$-(\underset{X}{\overset{CH_3}{Si}}-O)_y-$

a (n = 5)
b (n = 7)

FIGURE 1

tals) and refluxed in acetone (50 cm^3) for 14 hrs. The hot reaction mixture was filtered and the residue washed with acetone. Dichloromethane was added to the residue and this solution was washed with aqueous sodium hydroxide twice, followed by water. The organic layer was dried over anhydrous $MgSO_4$ and the solvent removed. The product was purified by column chromatography on silica gel with dichloromethane as the eluent. Yield: 30–40%. ^1H NMR of 4'-[(carbonyloxy-1,1,2,2-Tetrahydrofluorodecyl)]-4-(Pent-1-enyloxy) azobenzene δ_H ($CDCl_3$ standard TMS; 270 MHz): 0.95 (m, 2H), 2.00 (m, 2H), 2.28 (m, 2H), 2.62 (m, 2H), 4.08 (t, *J* 6 Hz, 2H), 4.66 (t, *J* 6 Hz, 2H), 5.1 (m, 1H), 5.88 (m, 1H), 6.99 (d, *J* 8Hz, 2H), 7.94 (overlapping d, *J* 8 Hz, 2H), 8.19 (d, *J* 8Hz, 2H). IR (KBr) υ_{max} 1718 cm^{-1} (C=O); 994, 895 cm^{-1} ($CH{=}CH_2$).

Synthesis of acrylic polymer (V)

A mixture of IIId (1g, 2 mmol), tetrabutylammonium bromide (0.064g, 2 mmol) and sodium polyacrylate solution[14] (0.23g of polymer in 40% aqueous solution) with chloroform (6 cm^3) was refluxed for six days. The chloroform solution was washed with water and dried over magnesium sulphate before being precipitated into methanol. Yield; 25%. ^{1}H NMR of 4'-[(carbonyloxy-1,1,2,2-Tetrahydrofluorodecyl)]-4-(1-pentyloxyacrylate) azobenzene δ_H ($CDCl_3$ standard TMS; 270 MHz): 1.4–1.8 (broad, 6H), 2.71 (broad, 2H), 4.12 (t, 2H), 4.71 (broad, 2H), 7.04 (broad, 2H), 7.86 (broad, 4H), 8.18 (broad, 2H).

Synthesis of siloxane polymers (VI a, b)

A mixture of **IV**(a or b) and poly (hydromethyl siloxane[17] with a 10% molar excess of vinyl groups was stirred in dry toluene at 90°C under nitrogen. The hydrosilylation catalyst (chloroplatinic acid in isopropan-1-ol) was added and the reaction monitored by observing the disappearance of the Si-H band at 2165 cm^{-1}. The polymer was recovered by removal of solvent and reprecipitation of the residue from dichloromethane solution into methanol.

^{1}H nmr: δ_H ($CDCl_3$ standard TMS; 270 MHz) for **(VI b)**. 1.4–1.8 (broad, 6H), 2.52 (t, J 6 Hz, 2H), 4.02 (s, 2H), 4.65 (broad, 4H), 7.01 (broad, 2H), 7.92 (broad, 4H), 8.21(broad, 2H). IR (KBr): υ_{max}1690cm^{-1} (C=O). 1256 cm^{-1} (Si-CH_2).

Physical Measurements

Identification of phases was carried out using a Linkam hotstage apparatus with a Nikon microscope. Differential scanning calorimetry was carried out using a DuPont thermosystem with a heating/cooling scan rate of (usually) 5°C per minute.

RESULTS AND DISCUSSION

Effect of hydrocarbon chain length on 4'-[(carboxy-1,1,2,2-Tetrahydroperfluorooctyl)]-4-(ω-bromo-alkoxy) azobenzene compounds (III a-I)

The effect of the terminal bromoalkyl chain length of the azobenzene precursors (used subsequently to synthesise the side chain polymers) on the phase behaviour was investigated. The compounds investigated were those in which the bromoalkyl group was varied from two to seven methylene units and the perfluoroalkyl chain was fixed at eight fluorinated carbon atoms (III). All of the compounds that we investigated showed Smectic A focal conic fan texture. The clearing temperatures decreased with the length of the hydrocarbon chain as did the thermotropic temperature range which also showed an odd-even effect with the odd number of methylene groups giving the higher values as shown in table I. This is also reflected in the clearing entropies. Effects of this sort have usually been observed when studying the role of the terminal alkyl group on the thermotropic behaviour of low molar mass mesogens[10] and can be normally accounted for in terms of the molecular geometry of the hydrocarbon chain in relation to the mesogenic core[11].

Effect of perfluoroalkyl chain length on 4'-[(carboxy-1,1,2,2-Tetrahydroperfluoroalkyl)]-4-(ω-bromo-alkoxy) azobenzene compounds (III a-l)

The effect of increasing the perfluoroalkyl part of the azobenzene precursor compounds was investigated for the ω-bromopropyloxy and ω-bromopentyloxy homologues. The thermal data is shown in table II. Increasing the length of the perfluoroalkyl chain generally increases the clearing temperature from the smectic A phase. Also, the compounds with shorter perfluoroalkyl chains exhibit monotropic phases but those with longer ones do not. The clearing entropies (expressed as a dimensionless quantity ΔS/R) show a steady increase and this is observed for both ω-bromoalkyl compounds. A lack of commercially available perfluoroalcohols prevented us from studying a wider range of compounds and establishing whether or not there is an odd-even effect in the perfluorinated chain length as seen for the ω-bromoalkyl compounds. In these studies the perfluoroalkyl chain appears to behave as if it were part of the mesogenic core of the molecule. Studies of the thermotropic behaviour of perfluoroalkyl 4-(4-alkoxybenzyloyloxy) benzoates[9] have been made where the only differences in comparison to our molecules are an ester rather than an azo linkage and the absence of a terminal bromo group. Much the same observations as ours were recorded both in terms of the effect of perfluorocarbon chain length and hydrocarbon chain length. The apparent mesogenic behaviour of the perfluorocarbon chain might be rationalised by considering the relative stiffness of the perflurocarbon chain compared to that of the hydrocarbon part[12]. Possibly a more important contribution may be the very strong repulsion between the hydrocarbon and fluorocarbon units, a "fluorophobic" interaction.

TABLE I Thermal properties of 4'-[(carboxy-1,1,2,2-Tetrahydroperfluorooctyl)]-4-(ω-bromo-alkoxy) azobenzene compounds IIIa-f (1–7) and IV a, b (8,9). Number of methylene units in bromoalkoxyl unit indicated by n. Number of carbons in 1-alkenloxy chain indicated by *. All data was obtained on the second d.s.c.heating cycle

n	$T_{K \to Sa}/°C$	$T_{Sa \to I}/°C$	$\Delta H_{K \to Sa}/kJmol^{-1}$	$\Delta H_{Sa \to I}/kJmol^{-1}$	$\Delta S_{Sa \to I}/R$
2	144	166	53	8.8	2.1
3	142	157	52.7	6.2	1.7
4	143	160	42.6	6.7	1.9
5	122	135	24.3	4.7	1.4
6	126	144	30.9	5.4	1.5
7	120	124	28.3	3.7	1.1
3*	97	152	21.1	2.3	0.6
5*	108	140	18.5	2.1	0.6

Thermal behaviour of the polymers (V and VI a-b)

Three polymers were synthesised by grafting a mesogenic unit on to a reactive polymer backbone. The extent of grafting is assumed to be complete in all cases. Evidence for grafting of **IIId** on to sodium polyacrylate is given by ^1H n.m.r. where we see the dissapearance of the triplet $C\underline{H}_2Br$ at 3.5 ppm on forming the product. For the hydrosilylation of **IVa,b** we observe the disappearance of the Si-H band at 2165 cm^{-1} in the infra-red spectrum and the alkene multiplet at 5.1 ppm in the ^1H n.m.r. spectrum. Both of the precursor polymers were obtained commercially[13,14] and the weight average molar masses are similar (1800 g mol^{-1} for the polyhydrosiloxane and 1200 g mol^{-1} for the polyacrylate). This allows some comparison to be made between the two polymer types.

The thermal data is shown in *table III*. For the acrylic polymer we see that there is an increase in the clearing and crystallisation temperature compared to the ω-bromoalkene precursor. The polymer clearly shows a focal conic fan texture indicative of the S_A phase, despite the rather low clearing entropy, which is closer to the value expected for isotropisation from a nematic phase. Another feature is that the polymer crystallises, a possible consequence of the low molar mass. For the two siloxane polymers there is a significant increase in the clearing temperature upon forming the polymer. The optical texture of the mesophase consisted of batonnets but was less well defined compared to the acrylic polymer. We therefore assign an unidentified smectic phase (S). As for the acrylic polymer, the siloxane materials do seem to crystallise and this is probably due to the low molar mass of the materials.

TABLE II Thermal properties of 4'-[(carboxy-1,1,2,2-Tetrahydroperfluoro-alkyl)]-4-(ω-bromoalkoxy) azobenzene compounds. n = number of methylene units in bromoalkyoxy unit, m = number of perfluoroalkylted carbons. All data was obtained on the second d.s.c. heating cycle. Parentheses indicate a monotropic transition

m	*n*	$T_{K\to Sa}/°C$	$T_{Sa\to I}/°C$	$\Delta H_{K\to Sa}/kJmol^{-1}$	$\Delta H_{Sa\to I}/kJmol^{-1}$	$\Delta S_{Sa\to I}/R$
4	3	116	(110)	39.7	2.4	0.8
6	3	120	125	43.7	3.4	1.0
8	3	142	157	52.7	6.2	1.7
10	3	160	173	60.1	10.2	2.8
4	5	90	(87)	21.7	1.1	0.4
6	5	102	(97)	23.8	2.7	0.9
8	5	122	135	24.3	4.7	1.4
10	5	128	160	36.7	5.7	1.6

TABLE III Thermal properties of acrylic polymer V and siloxane polymers VI a-b. The number of carbon atoms in the hydrocarbon spacer is indicated by n. For V the "S" represents a smectic A phase. For VI, the "S" represents an unidentified smectic phase

Sample	*n*	$T_{K\to S}/°C$	$T_{S\to I}/°C$	$\Delta H_{k\to S}/kJmol^{-1}$	$\Delta H_{S\to I}/kJmol^{-1}$	$\Delta S_{S\to I}/R$
V	5	130	152	13.6	2.2	0.6
VIa	3	142	196	8.1	0.8	0.2
VIb	5	121	190	9.8	0.7	0.2

CONCLUSIONS

A number of thermotropic compounds and polymers have been synthesised containing both the azobenzene group and the n-perfluoroalkyl ester chain. The thermotropic behaviour of these materials follows the pattern that an increase in the length of the perfluoroalkyl chain gives an increase in clearing temperature, whereas increasing the hydrocarbon chain length has the opposite effect. This is consistent with a system where the hydrocarbon and fluorocarbon parts of the molecule repel strongly and where the fluorocarbon chains adopt a relatively rigid conformation and behave as part of the mesogenic unit even though there are two methylene groups separating the fluorocarbon chain from the aromatic units.

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