This article was downloaded by:
On: *26 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Liquid-crystalline polysiloxanes with fluoro-substituted side chains

G. Nestor[a]; G. W. Gray[a]; D. Lacey[a]; K. J. Toyne[a]
[a] School of Chemistry, The University, Hull, England

To cite this Article Nestor, G. , Gray, G. W. , Lacey, D. and Toyne, K. J.(1990) 'Liquid-crystalline polysiloxanes with fluoro-substituted side chains', Liquid Crystals, 7: 5, 669 — 681

To link to this Article: DOI: 10.1080/02678299008036750

URL: http://dx.doi.org/10.1080/02678299008036750

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

LIQUID CRYSTALS, 1990, VOL. 7, NO. 5, 669-681

Liquid-crystalline polysiloxanes with fluoro-substituted side chains

by G. NESTOR, G. W. GRAY, D. LACEY and K. J. TOYNE
School of Chemistry, The University, Hull, HU6 7RX, England

(*Received 3 November 1989; accepted 1 December 1989*)

Sixteen new side chain liquid polysiloxanes, either homopolymers derived from poly(hydrogenmethyl)siloxane or copolymers derived from poly(hydrogenmethyl-dimethylsiloxane), are reported with side chains carrying fluoro-substituents. The known effects of fluoro-substitution in low molar mass liquid crystals are strongly echoed in the polymeric analogues and interesting comparisons are made between homo- and co-polymers carrying the same fluorinated side chains.

Downloaded At: 14:06 26 January 2011

1. Introduction

The effects and advantages of fluoro-substitution in low molar mass liquid crystal materials, in general, are well-known [1-18], and depend critically on the manner in which the fluorine is introduced into the mesogenic molecule. The relative stabilities of smectic and nematic phases may in fact be inverted by altering the site of substitution. The reason for introducing fluorine into the molecule is its high electronegativity in relation to its size; it can, therefore, exert a large influence on the permittivity, whilst causing the minimum of change in the length-to-breadth ratio of the molecule. In principle, there exist three different sites of substitution in a mesogenic molecule. These are where the fluorine is introduced as a terminal group, as a substituent in the end chain of the molecule, or as a lateral substituent in the rigid molecular core. The use of fluorine as a terminal group in mesogenic systems has not been studied as widely as its use as a lateral substituent, due mainly to the more limited applications expected for such materials [3]. However, terminal fluoro-substituted systems have been shown to be useful as additives to mixtures of more conventional cyano-terminated mesogens, since, whilst possessing a modest positive dielectric anisotropy, they also exhibit low viscosities due to the absence of antiparallel correlations [3, 4, 18]. When the liquid crystal thermal stabilities of terminal fluoro-substituted systems are compared with those for systems with terminal cyano-functions, although the number of examples is limited, it appears that terminal fluorine reduces both nematic and smectic thermal stabilities [2-4]. The effects upon the melting point are variable, but in general are not great.

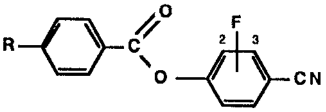
The use of fluorine as a substituent in the end chain of a molecule has been studied for low molar mass materials, both as the trifluoromethyl group [3, 5-8] and as larger perfluoroalkyl chains [3, 6]. However, in this work, only the trifluoromethyl group has been used, and discussion has been limited to this case. The influence of the trifluoromethyl group as a terminal group, relative to cyano is fairly well established [3, 5, 6]; it reduces the nematic thermal stability, increases smectic thermal stability (and often the degree of smectic order), and increases the crystalline stability i.e. the melting point. The use of a terminal trifluoromethyl group has also been shown to produce a crystal smectic B phase in some Schiff's base materials [7, 8]. Lateral

0267-8292/90 $3.00 © 1990 Taylor & Francis Ltd

fluoro-substitution in liquid crystal systems has been extensively studied [1–4, 9–18], and specifically, many examples of lateral substitution in 4-cyanophenyl benzoates can be found [1, 14–17]. Lateral substituents exert two opposing effects on the thermal stabilities of mesophases. First, the substituent increases the polarity and polarizability (less important for the small fluoro-substituent) of the molecule, and this tends to increase nematic and smectic thermal stabilities. However, the size of the lateral group decreases the length-to-breadth ratio, and this tends to decrease the thermal stabilities of both nematic and smectic states, as a result of the increased lateral separation.

Of these two effects, the latter broadening effect dominates the situation as far as the nematic state is concerned, whilst a combination of breadth and dipolar effects is important when considering the smectic state. In the smectic layers, dipole moments acting across the molecular long axes may reinforce one another, and be of considerable importance in enhancing the lateral attractions which retain the order. The greater importance of such dipoles in counteracting breadth effects of substituents in the smectic state can be appreciated, since in the nematic state, such dipoles may as often lead to repulsion as attraction. The broadening effect of a lateral substituent generally results in decrease in smectic thermal stability, but if we are considering two substituents of similar size but different dipolarities, the effect is smaller for the more dipolar substituent.

Another property which may be influenced by fluoro-substitution, and which is of importance to the practical application of such materials in electro-optical devices, is the degree of antiparallel correlation. It has been shown that for certain 4-cyanophenyl esters, introduction of a 3-fluoro-substituent results in an exceptionally high positive dielectric anisotropy; this is a result of the virtual elimination of antiparallel correlation effects caused by the lateral fluoro-substituent *ortho* to the cyano group [17]. When the mesophase thermal stabilities of lateral fluoro-substituted 4-cyanophenyl benzoates [1, 4–17] in particular are considered, it is generally observed that the nematic thermal stability is reduced whether the fluoro-substituent is in the lateral/central (2) or lateral/terminal (3) position of the cyanophenyl ring. However, the reduction is more marked for the lateral/terminal case, since the broadening effect of the fluorine is greater, and because antiparallel correlations are minimised. Conversely, the smectic thermal stability is reduced to a greater extent for the lateral/central (2) fluoro-substituted systems, due probably to repulsive interactions between the ring-F and C = O dipoles which distort the molecule from planarity. However, for lateral/terminal (3) fluoro-substituted systems, the smectic thermal stability is variable, increasing in some cases and decreasing in others; often, however, it is not affected to a great extent. Interpretation of this behaviour is complicated by the effects on antiparallel correlation referred to above.



The general summary of the effects of fluoro-substitution in low molar mass liquid crystals has been given, with particular reference to phenyl benzoates, because of its relevance to the nature of the side chain (see figure 1) used in the polymers that are now to be described. Indeed, it was to discover how closely trends in structure/

Downloaded At: 14:06 26 January 2011

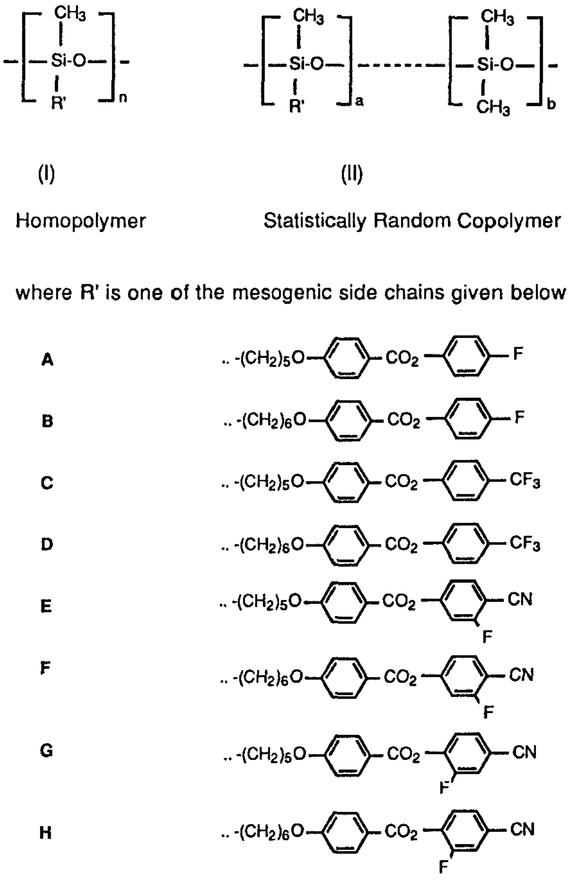


Figure 1. Structures of liquid crystal polysiloxanes ((I) and (II)).

Downloaded At: 14:06 26 January 2011

property correlations for low molar mass fluorinated, liquid crystal materials are followed by their polymeric analogues that the two series of polysiloxanes with fluoro-substituents in the mesogenic side chains were synthesised.

2. Results and discussion

The side chain liquid crystal polymers synthesised were based on two different polysiloxane backbones: poly(hydrogenmethylsiloxane) (PHMS, Wacker-Chemie, Munchen, F.R. Germany) and poly(hydrogenmethyl-dimethylsiloxane) copolymer (P(HM/DM)S, Petrarch PS122.5) as specified previously [19]. These backbones were separately combined with each of eight different alkenes which constituted the mesogenic side chains. The polymers are represented by structures (I) and (II) (see figure 1).

The results of (i) thermal and optical analyses of the liquid crystal polysiloxanes of structures (I) and (II) are summarized in tables 1 and 3, respectively, and of (ii) the 28 day crystallinity studies in tables 2 and 4, respectively. A number of useful conclusions can be reached by comparing the properties of these fluoro-substituted liquid crystal polymers with those of the simple terminally cyano-substituted

Downloaded At: 14:06 26 January 2011

Table 1. Thermal data for the glass, melt and mesophase transitions of the polymers (I).

Polymer	T_g/°C	T_{m_c}/°C	T_m/°C	$T_{S_BS_A}$/°C	T_{S_AI}/°C	PW/°C	ΔC_p/ J g^{-1} at T_g	$\Delta H_{T_{m_c}}$/J g^{-1}, $\Delta S_{T_{m_c}}$/10^{-3} J K g^{-1}	ΔH_{T_m}/J g^{-1}, ΔS_{T_m}/10^{-3} J K g^{-1}	$\Delta H_{S_BS_A}$/J g^{-1}, $\Delta S_{S_BS_A}$/10^{-3} J K g^{-1}	ΔH_{S_AI}/J g^{-1}, ΔS_{S_AI}/10^{-3} J K g^{-1}
1*A*	–	–	–	–	154	30	–	–, –	–, –	–, –	10·2, 23·9
1*B*	–	17	56	–	132	27	–	12·9, 44·4	10·6, 32·2	–, –	7·3, 18·0
1*C*	–	–	105	113	204	34	–	–, –	10·1†, 26·7†	‡, ‡	10·6, 22·1
1*D*	–	–	95	99	185	34	–	–, –	9·2†, 25·1†	‡, ‡	11·0, 24·0
1*E*	6	–	46	–	156	22	0·2	–, –	2·5, 7·8	–, –	2·9, 6·8
1*F*	0	–	–	–	139	18	0·3	–, –	–, –	–, –	2·7, 6·5
1*G*	–	–	88	–	119	15	–	–, –	8·5, 23·6	–, –	2·6, 6·6
1*H*	19	–	46	–	118	11	0·2	–, –	5·1, 16·0	–, –	2·4, 6·1

PW = baseline peak width of clearing transition from DSC.
† = due to overlap of adjacent peaks, the value includes the S_B–S_A enthalpy/entropy.
T_{m_c} = melt transition dependent upon previous cooling rate.
‡ = value not available due to overlap of peaks.

Downloaded At: 14:06 26 January 2011

Table 2. Thermal data from 28 day crystallinity studies of the polymers (I).

Polymer	T_g/°C	T_{m_A}/°C	T_m/°C	$T_{S_BS_A}$/°C	T_{S_AI}/°C	PW/°C	ΔC_p/ J g^{-1} at T_g	$\Delta H_{T_{m_A}}$/J g^{-1}, $\Delta S_{T_{m_A}}$/10^{-3} J K g^{-1}	ΔH_{T_m}/J g^{-1}, ΔS_{T_m}/10^{-3} J K g^{-1}	$\Delta H_{S_BS_A}$/J g^{-1}, $\Delta S_{S_BS_A}$/10^{-3} J K g^{-1}	ΔH_{S_AI}/J g^{-1}, ΔS_{S_AI}/10^{-3} J K g^{-1}
1*A*	–	{50}	–	–	153	31	–	2·1, 6·5	–, –	–, –	10·4, 24·5
1*B*	–	–	57	–	133	31	–	–, –	12·9, 39·0	–, –	7·4, 15·6
1*C*	–	–	105	113	203	38	–	–, –	11·1†, 29·4†	‡, ‡	11·6, 24·3
1*D*	–	–	95	99	185	29	–	–, –	10·0†, 27·0†	‡, ‡	9·7, 21·2
1*E*	–	–	47	–	157	19	–	–, –	13·4, 41·9	–, –	2·9, 6·8
1*F*	2	–	–	–	139	18	0·3	–, –	–, –	–, –	2·7, 6·5
1*G*	–	{47}	90	–	119	14	–	0·8, 2·6	7·4, 20·5	–, –	2·1, 5·3
1*H*	20	{44}	46	–	117	13	0·2	‡, ‡	‡, ‡	–, –	2·6, 6·7

PW = baseline peak width of clearing transition from DSC.
† = due to overlap of adjacent peaks, the value includes the S_B–S_A enthalpy/entropy.
{ } = melt temperature for a crystalline phase which appears with annealing.
T_{m_A} = transition involving a crystal.
‡ = value not available due to overlap of peaks.

Downloaded At: 14:06 26 January 2011

Table 3. Thermal data for the glass, melt and mesophase transitions of the polymers (II).

Polymer	T_g/°C	T_{m_c}/°C	T_m/°C	$T_{S_BS_A}$/°C	T_{S_AI}/°C	PW/°C	ΔC_p/ J g^{-1} at T_g	$\Delta H_{T_{m_c}}$/J g^{-1}, $\Delta S_{T_{m_c}}$/10^{-3} J K g^{-1}	ΔH_{T_m}/J g^{-1}, ΔS_{T_m}/10^{-3} J K g^{-1}	$\Delta H_{S_BS_A}$/J g^{-1}, $\Delta S_{S_BS_A}$/10^{-3} J K g^{-1}	ΔH_{S_AI}/J g^{-1}, ΔS_{S_AI}/10^{-3} J K g^{-1}
II*A*	–	0	39	–	72	35	–	13·1, 47·8	8·5, 27·3	–, –	5·1, 14·9
II*B*	–	−7	39	–	70	34	–	3·5, 13·2	11·4, 36·4	–, –	4·6, 13·5
II*C*	–	–	76	66	112	45	–	–, –	9·7†, 27·7†	‡, ‡	8·4, 21·9
II*D*	–	–	76	62	110	50	–	–, –	9·4†, 27·0†	‡, ‡	6·8, 17·8
II*E*	−15	–	–	–	80	19	0·2	–, –	–, –	–, –	3·7, 10·6
II*F*	−19	–	–	–	78	17	0·3	–, –	–, –	–, –	3·5, 9·8
II*G*	−4	–	13	–	66	16	0·1	–, –	3·0, 10·5	–, –	3·3, 9·7
II*H*	−5	–	14	–	72	14	0·1	–, –	3·9, 13·4	–, –	3·2, 9·3

PW = baseline peak width of clearing transition from DSC.
† = due to overlap of adjacent peaks, the value includes the S_B–S_A enthalpy/entropy.
T_{m_c} = melt transition dependent upon previous cooling rate.
‡ = value not available due to overlap of peaks.

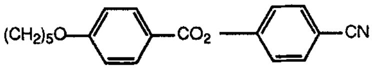
Downloaded At: 14:06 26 January 2011

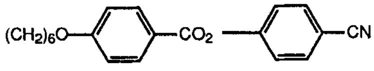
Table 4. Thermal data from 28 day crystallinity studies of the polymers (II).

Polymer	T_g/°C	T_{m_A}/°C	T_m/°C	$T_{S_BS_A}$/°C	T_{S_AI}/°C	PW/°C	ΔC_p/ J g^{-1} at T_g	$\Delta H_{T_{m_A}}$/J g^{-1}, $\Delta S_{T_{m_A}}$/10^{-3} J K g^{-1}	ΔH_{T_m}/J g^{-1}, ΔS_{T_m}/10^{-3} J K g^{-1}	$\Delta H_{S_BS_A}$/J g^{-1}, $\Delta S_{S_BS_A}$/10^{-3} J K g^{-1}	ΔH_{S_AI}/J g^{-1}, ΔS_{S_AI}/10^{-3} J K g^{-1}
II*A*	–	44	–	–	76	32	–	13·7, 43·3	–, –	–, –	5·1, 14·7
II*B*	–	41	–	–	72	34	–	15·1, 48·1	–, –	–, –	5·1, 14·7
II*C*	–	–	75	66	114	45	–	–, –	12·7†, 36·4†	§, §	6·7, 17·4
II*D*	–	–	76	62	111	45	–	–, –	12·8†, 36·8†	§, §	6·9, 17·9
II*E*	−15	–	–	–	80	20	0·2	–, –	–, –	–, –	3·8, 10·7
II*F*	−19	–	–	–	77	19	0·3	–, –	–, –	–, –	3·7, 10·6
II*G*	‡	−5	12	–	64	16	‡	0·9, 3·4	2·9, 10·3	–, –	3·0, 8·9
II*H*	‡	−6	14	–	71	15	‡	0·8, 2·9	4·7, 16·2	–, –	3·5, 10·0

PW = baseline peak width of clearing transition from DSC.
† = due to overlap of adjacent peaks, the value includes the S_B–S_A enthalpy/entropy.
‡ = obscured by new melt transition.
T_{m_A} = transition involving a crystal.
§ = values not available due to overlap of peaks.

systems [19, 20] i.e., the homopolymers (I) and copolymers (II) in which the side chains R′ are

X....


Y....


To facilitate these comparisons, the thermal properties of polymers I*X*, I*Y*, II*X*, and II*Y* are given in table 5 and the property differences between the two series (both homo- and co-polymers) are represented in tables 6 and 7, respectively. It is best to give separate consideration to the cases where (i) terminal cyano groups have been replaced and (ii) a lateral fluoro-substituent has been incorporated into the mesogenic side chains.

For low molar mass liquid crystals, a terminal fluorine results in reduced mesophase stabilities and increased crystal stability. This is also observed for the side chain liquid crystal polysiloxanes when a terminal fluoro-substituent is used (positive values in tables 6 and 7 indicate destabilisation relative to the analogous terminal cyano-polymer). The increased crystal stability is more marked for the copolymers (II*A* and II*B*) than for the homopolymers (I*A* and I*B*). Replacement of the terminal cyano-function with the trifluoromethyl group has resulted in a stabilisation of both the smectic and crystal phases, reflected in both temperature and enthalpy/entropy, and has also produced additional, higher order crystal smectic B phases. This is all in keeping with low molar mass liquid crystal systems. It is worth noting that the increased smectic thermal stability is more marked for the homopolymners (I*C* and I*D*), whilst the increased crystal stability is significantly larger for the copolymers (II*C* and II*D*). All of the terminal fluoro and trifluoromethyl liquid crystal polymers are crystalline in nature, and do not exhibit glass transitions. The significance of these results will be discussed shortly.

Lateral fluoro-substitution of the mesogenic side chains of the side chain liquid crystal polysiloxanes also produces similar effects to those for lateral fluoro-substitution of low molar mass liquid crystal systems. Lateral/terminal (3) fluoro-substitution has resulted in a moderate destabilisation of the smectic phase on the grounds of both temperature and enthalpy/entropy of the clearing transitions. However, this substitution causes a marked decrease in crystal stability and tendency to crystallise; this effect is particularly noticeable for the copolymers (II*E* and II*F*), which do not possess any melt transitions. This is especially important when we consider that these are the materials expected to have an exceptionally high positive dielectric anisotropy, and therefore to be of special interest for application in electro-optic devices.

Lateral/central (2) fluoro-substitution results in a greater destabilisation of the smectic phase, as expected due to loss of planarity, particularly for the homopolymers (I*G* and I*H*). Substitution in this position also results in a moderate destabilisation of the crystal phase, more marked now for the copolymers (II*G* and II*H*). These laterally fluoro- and terminally cyano-substituted side chain liquid crystal polysiloxanes do possess glass transitions, but these have not been greatly affected by the fluoro-substitution. Lateral/terminal (3) fluoro-substitution gives a moderate

Downloaded At: 14:06 26 January 2011

Downloaded At: 14:06 26 January 2011

Table 5. Thermal data for the polymers (I) and (II) with $R' = X$ or Y ([19]).

Polymer	T_g/°C	T_m/°C	T_{S_AI}/°C	PW/°C	ΔC_p/Jg^{-1} at T_g	ΔH_{T_m}/J g^{-1}, ΔS_{T_m}/10^{-3} J K g^{-1}	ΔH_{S_AI}/J g^{-1}, ΔS_{S_AI}/10^{-3} J K g^{-1}
IX	–	84	170	24	–	12·9, 36·2	3·3, 7·5
IY	18	[40]	167	15	0·1	7·4, 23·6	3·6, 8·1
IIX	−9	6	98	19	0·1	0·8, 2·9	4·6, 12·5
IIY	−10	[1]	100	22	0·1	0·5, 1·7	4·5, 12·1

PW = baseline peak width of clearing transition from DSC.
[ ] = metastable phase.

Table 6. Differences in thermal data for analogous homopolymers of structures (I) (Δ' = data from table 5 minus table 1).

Polymer	$\Delta' T_g$/°C	$\Delta' T_{m_A}$/°C	$\Delta' T_m$/°C	$\Delta' T_{S_AI}$/°C	$\Delta'(\Delta H_{T_{m_A}})$/J g^{-1}, $\Delta'(\Delta S_{T_{m_A}})$/10^{-3} J K g^{-1}	$\Delta'(\Delta H_{T_m})$/J g^{-1}, $\Delta'(\Delta S_{T_m})$/10^{-3} J K g^{-1}	$\Delta'(\Delta H_{S_AI})$/J g^{-1}, $\Delta'(\Delta S_{S_AI})$/10^{-3} J K g^{-1}
I(X–A)	–	−1	–	16	0·2, 0·6	–, –	−6·9, −16·4
I(Y–B)	–		−16	35	–, –	−3·2, −8·6	−3·7, −9·9
I(X–C)	–	–	−21	−34	–, –	2·8†, 9·5†	−7·3, −14·6
I(Y–D)	–	–	−55	−18	–, –	−1·8, −1·5†	−7·4, −15·9
I(X–E)	–	–	38	14	–, –	10·4, 28·4	0·4, 0·7
I(Y–F)	18	–	–	28	–, –	–, –	0·9, 1·6
I(X–G)	–	2	−4	51	1·5, 4·5	4·4, 12·6	0·7, 0·9
I(Y–H)	−1	−6	−1	49	‡, ‡	2·3, 7·6	1·2, 2·0

‡ = values not available due to coincidence of peaks.
† = due to overlap of adjacent peaks, the difference includes an S_B–S_A enthalpy/entropy.
$\Delta' T_{m_A}$ data obtained using 28 day crystallinity results in [19].

Downloaded At: 14:06 26 January 2011

Table 7. Differences in thermal data for analogous copolymers of structures (II) (Δ' = data from table 5 minus table 3).

Polymer	$\Delta' T_g$/°C	$\Delta' T_{m_A}$/°C	$\Delta' T_m$/°C	$\Delta' T_{S_A I}$/°C	$\Delta'(\Delta H_{T_{m_A}})$/J g^{-1}, $\Delta'(\Delta S_{T_{m_A}})$/10^{-3} J K g^{-1}	$\Delta'(\Delta H_{T_m})$/J g^{-1}, $\Delta'(\Delta S_{T_m})$/10^{-3} J K g^{-1}	$\Delta'(\Delta H_{S_A I})$/J g^{-1}, $\Delta'(\Delta S_{S_A I})$/10^{-3} J K g^{-1}
II(*X*-*A*)	–	–	−33	26	–, –	−7·7, −24·4	−0·5, −214
II(*Y*-*B*)	–	6	−38	30	−1·8, −6·7	−10·9, −34·7	−0·1, −1·4
II(*X*-*C*)	–	–	−70	−14	–, –	−8·9†, −24·8†	−3·8, −9·4
II(*Y*-*D*)	–	–	−75	−10	–, –	−8·9†, −25·3†	−2·3, −5·7
II(*X*-*E*)	6	–	–	18	–, –	–, –	0·9, 1·9
II(*Y*-*F*)	9	–	–	22	–, –	–, –	1·0, 2·3
II(*X*-*G*)	−5	–	−7	32	–, –	−2·2, −7·6	1·3, 2·8
II(*Y*-*H*)	−5	53	−13	28	12·5, 38·5	−3·4, −11·7	1·3, 2·8

† = due to overlap of adjacent peaks, the difference includes an S_B–S_A enthalpy/entropy.
$\Delta' T_{m_A}$ data obtained using 28 day crystallinity results in [19].

Table 8. Differences in thermal data for polymers of structures (I) and (II) (Δ' = data from table 1 minus table 3).

Polymer	$\Delta' T_g$/°C	$\Delta' T_m$/°C	$\Delta' T_{S_B S_A}$/°C	$\Delta' T_{S_A I}$/°C	$\Delta'(\Delta H_{T_m})$/J g^{-1}, $\Delta'(\Delta S_{T_m})$/10^{-3} J K g^{-1}	$\Delta'(\Delta H_{S_B S_A})$/J g^{-1}, $\Delta'(\Delta S_{S_{S_B S_A}})$/10^{-3} J K g^{-1}	$\Delta'(\Delta H_{S_A I})$/J g^{-1}, $\Delta'(\Delta S_{S_A I})$/10^{-3} J K g^{-1}
A	–	–	–	82	–, –	–, –	5·1, 9·0
B	–	17	–	62	−0·8, −4·2	–, –	2·7, 4·5
C	–	29	47	92	0·4†, −1·0†	‡, ‡	2·2, 0·2
D	–	19	37	75	−0·2†, −1·9†	‡, ‡	4·2, 6·2
E	21	–	–	76	–, –	–, –	−0·8, −3·8
F	19	–	–	61	–, –	–, –	−0·8, −3·3
G	–	75	–	53	5·5, 13·1	–, –	−0·7, −3·1
H	–	32	–	46	1·2, 2·2·6	–, –	−0·8, −3·2

‡ = values not available due to overlap of peaks.
† = due to overlap of adjacent peaks, the difference includes an S_B–S_A enthalpy/entropy.

Downloaded At: 14:06 26 January 2011

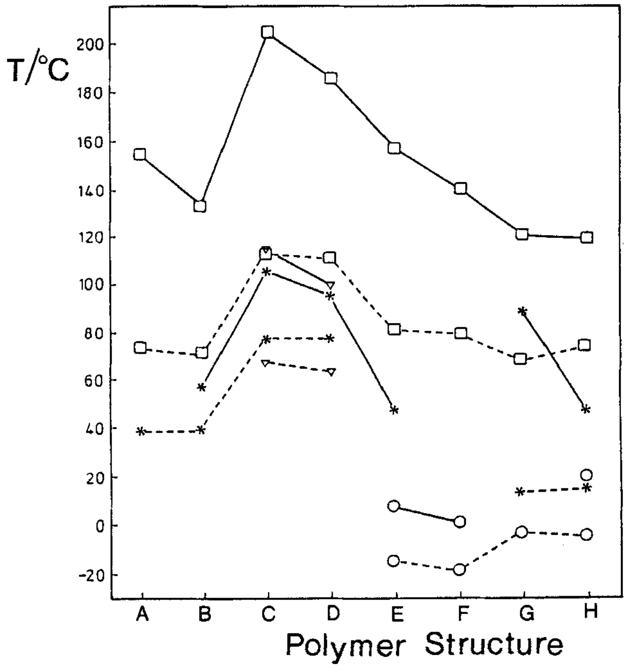


Figure 2. Representation of thermal data for polymers of structures (I) (——) and (II) (- - -); □, S_A–I; ▽, S_B–S_A; *, T_m; ○, T_g.

decrease in the glass transition temperatures (again useful for electro-optic applications), whilst lateral/central (2) fluoro-substitution causes a slight increase.

The quantitative differences between the initial analyses for the fluoro-substituted liquid crystal polymers of types (I) (table 1) and (II) (table 3) are recorded in table 8, and represented graphically for the transition temperatures in figure 2. For polymers with a terminal fluoro- or trifluoromethyl group, a general reduction is observed in the transition temperatures and the melt temperatures on passing from the homopolymers to the copolymers. However, the lowering of the melt temperatures is not as marked as that for the smectic to isotropic temperatures. When the enthalpies and entropies are considered, it is found that the values for the smectic A phases of the homopolymers are higher, implying that the smectic phases are more ordered than those of the copolymers (the converse of the situation discussed previously [19]), whilst the copolymers exhibit the slightly larger enthalpy values for their melt transitions. The importance of these results with regard to fluoro-substitution, polymer backbone flexibility, and degree of polymerization will be discussed shortly. For the terminal cyano-substituted side chain liquid crystal polysiloxanes incorporating lateral fluoro-substituents, the hypotheses presented previously [19] concerning flexibility of the polymer backbone and degree of polymerization seem still to be valid. The glass transition temperatures are lower for the copolymers, as are the melt transition temperatures and crystalline tendencies (absence of melt transitions for copolymers II*E* and II*F*). The smectic to isotropic transitions, whilst lower in temperature for the copolymers due to $\overline{DP}$ effects, are larger in terms of enthalpy and entropy, indicating that the smectic phases are more ordered for the copolymers due to the increased flexibility of the polymer backbone.

3. Conclusions

When all of the results and trends relating to these fluoro-substituted side chain liquid crystalline polysiloxanes are considerd, it is possible to make some general observations.

First, for the terminally fluoro- and trifluoromethyl-substituted liquid crystal polymers, unlike the results reported earlier [19] for homopolymers and copolymers, we find that the smectic phases are more ordered for the homopolymers than the copolymers, whilst the crystalline order of the copolymers is greater than that of the homopolymers. The higher enthalpies/entropies for the smectic-isotropic transition of the homopolymers suggest that the structural changes to the mesogenic side chains are, in these cases, as important as or more important than changes in backbone flexibility. Although the homopolymers exhibit the more thermally stable *and* more ordered smectic phases, and provided that the arguments relating to the replacement of the terminal cyano-function by a fluoro- or trifluoromethyl group in low molar mass liquid crystals are relevant to side chain liquid crystal polysiloxanes (which they seem to be), the alteration of the terminal group will try to increase the crystallinity of the system. The driving force for this appears to succeed in the copolymers but to be inhibited in the homopolymers. Consequently, for reasons that cannot yet be assessed, the emphasis placed upon polymer backbone flexibility appears to vary from system to system. For polymers involving lateral fluoro-substitution in the mesogenic side chains, it seems that the backbone flexibility and degree of polymerization are now more important than the substituent effects. The copolymer smectic phases are again (see [19]) more ordered as a consequence of backbone flexibility, and the crystalline tendencies are reduced both by the greater flexibility of the copolymer backbone and the incorporation of the lateral fluoro-substituents. In summary, it is clear that the effects of fluoro-substitution in low molar mass liquid-crystalline systems are strongly echoed in their side chain polymeric analogues, but we must always remember that the change to a macromolecular system and differences in flexibility of the polymer backbone must be taken into account.

Downloaded At: 14:06 26 January 2011

4. Experimental

The alkenes used in this study were prepared by standard methods [20–22]. IR and ^{1}H NMR spectra were run on a Perkin Elmer 580B infrared spectrophotometer and a Jeol JNM-G × 270 NMR spectrometer, respectively. The liquid crystal polysiloxanes of structure (I) were prepared by a poly(hydrosilylation) reaction between a PHMS backbone and an appropriate alkene as reported previously [22]. When a P(HM/DM)S backbone (0·6 g, 4·5 mmol (Si–H) was used to produce liquid crystal polymers of type (II), the same procedure was followed working on the basis of the molar content of Si–H present in the copolymer backbone, and employing 60 ml of toluene as the reaction solvent. Each liquid crystal polymer was synthesized twice to ensure that the results were reproducible.

The polymers were characterized by differential scanning calorimetry, polarizing optical microscopy, and thermo-optical analysis, again as detailed previously [22]. Any crystallization effects were studied by repeating the thermo-optical and DSC analyses after the original samples of the liquid crystal polymers (used either for optical microscopy or DSC) had been stored at ambient temperature (approximately 20°C) for 28 days. No preheating of these samples was, of course, carried out. The degree of polymerization ($\overline{DP}$) and ratio of weight-to-number-average molecular weight $\bar{M}_w/\bar{M}_n$ of the liquid crystal polysiloxanes were the same as for the PHMS and P(HM/DM)S prepolymers used previously [19].

The authors thank the Science and Engineering Research Council for research grants for the purchase of the DSC equipment, and for a CASE studentship to (G.N.) with G.E.C., Hirst Research Centre, Wembley and Laser-Scan Laboratories, Cambridge. Acknowledgement is due to Dr M. S. White (previously of these laboratories) for valued discussions.

References

[1] Kelly, S. M., 1984, *Helv. chim. Acta.*, **67**, 1572.
[2] Gray, G. W., 1966, *Molec. Crystals*, **1**, 333.
[3] Balkwill, P., Bishop, D., Pearson, A., and Sage, I., 1985, *Molec. Crystals liq. Crystals*, **1231**.
[4] Carr, N., Gray, G. W., and Kelly, S. M., 1985, *Molec. Crystals liq. Crystals Lett.*, **1** **(1-2)**, 53.
[5] Coates, D., and Gray, G. W., 1976, *J. chem. Soc. Perkin II*, p. 300.
[6] Misaki, S., Takamatsu, S., Suefuji, M., Mitote, T., and Matsumura, M., 1981, *Molec. Crystals liq. Crystals*, **66**, 123.
[7] Baz, N. A., Arora, S. L., Doane, J. W., and De Vries, A., 1985, *Molec. Crystals liq. Crystals*, **128**, 23.
[8] Cox, R. J., Johnson, J. F., Griffin, A. C., and Buckley, N. W., 1981, *Molec. Crystals liq. Crystals*, **69**, 293.
[9] Gray, G. W., Hogg, C., and Lacey, D., 1981, *Molec. Crystals liq. Crystals*, **67**, 1.
[10] Gray, G. W., and Kelly, S. M., 1981, *Molec Crystals liq. Crystals*, **75**, 109.
[11] Chan, L. K. M., Gray, G. W., and Lacey, D., 1985, *Molec. Crystals liq. Crystals*, **123**, 185.
[12] Fearon, J. E., Gray, G. W., Ifill, A. D., and Toyne, K. J., 1985, *Molec. Crystals liq. Crystals*, **124**, 89.
[13] Gray, G. W., Lacey, D., Stanton, J. E., and Toyne, K. J., 1986, *Liq. Crystals*, **1**, 407.
[14] Kelly, S. M., 1983, *J. chem. Soc. Chem. Commun.*, p. 366.
[15] Sasaki, M., Takeuchi, K., Sato, H., and Takatsu, H., 1984, *Molec. Crystals liq. Crystals*, **109**, 169.
[16] Kelly, S. M., and Schad, Hp., 1984, *Helv. chim, Acta*, **67**, 1580.
[17] Schad, Hp., and Kelly, S. M., 1984, *J. chim. Phys.*, **81**, 1514.
[18] Chan, L. K. M., 1987, Ph.D. Thesis, University of Hull.
[19] Nestor, G., Gray, G. W., Lacey, D., and Toyne, K. J., 1989, *Liq. Crystals*, **6**, 137.
[20] Nestor, G., 1988, Ph.D. Thesis University of Hull.
[21] Ringsdorf, H., and Schneller, A., 1982, *Makromolek. Chem., rap. Commun*, **3** 557.
[22] Nestor, G., White, M. S., Gray, G. W., Lacey, D., and Toyne, K. J., 1987, *Makromolek. Chem.*, **188**, 2759.

Downloaded At: 14:06 26 January 2011