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HIGH TEMPERATURE FERROELECTRIC LIQUID CRYSTALS

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Abstract Liquid crystals at high temperature are useful for, among other purposes, broad temperature pressure sensors. In an attempt to design high-temperature smectic C phase materials, we synthesized a variety of mesogenic oligomers and polymers. We obtained, to our knowledge, 1) the first carbon-based smectic C main chain polymer, 2) the first imide-containing smectic C liquid crystal, 3) the third highest temperature smectic A phase reported (317°C), and 4) the highest temperature chiral smectic A phase reported (304°C).

INTRODUCTION

Most liquid crystal applications involve temperatures within the normal operating temperature range of -20°C to 70°C. However, certain applications require operations at well above this range. For example, liquid crystals have been used in gas flow sensors for wind tunnels, yet the surface temperatures of advanced air- and spacecraft in wind tunnels can exceed 400°C. We accordingly decided to investigate strategies for increasing the operating temperature for liquid crystals, specifically aiming at making S_C^* or electroclinic materials functional at high temperatures.

Decreasing a liquid crystal's degrees of freedom should increase the order and thus increase the phase transition points. In previous work[1], we found that attaching liquid crystal mesogens to a polymer backbone gave mesogenic materials with increased phases transition temperatures. In addition, it is well known that increasing the number of aromatic rings in a liquid crystal tends to increase its phase transition temperatures. Thus, in our quest to make high temperature liquid crystals, a natural starting point was the polymerization of three-ring liquid crystals.

We herein introduce several new types of liquid crystals specifically designed to have liquid crystals phases at over 100°C. These liquid crystals include polymers and oligomers, with the liquid crystal moiety either part of the main chain or a side pendant.

The materials fall into five major classes: polysiloxanes, polyacrylates, diimides, polyesters, and polyvinyl ethers. Many of these classes have further subdivisions. For instance, there are crosslinked and non-crosslinked polysiloxanes, chiral and achiral polyacrylates, as well as one polymethacrylate, chiral and achiral polyesters, symmetric and mixed diimides, and chiral and achiral diimides, and also crosslinked diimides.

The initial thrust of this work was to make high temperature liquid crystals, so little effort was put into making chiral compounds. Thus, of the twenty-five new materials presented, only eight are chiral.

SYNTHESIS AND TESTING OF THE NEW MATERIALS

The new materials were made by standard synthetic techniques. Specifically, the polysiloxanes were made by treating a liquid crystal moiety having a terminal alkene with a polymethylsiloxane and a palladium catalyst[2]. The polysiloxane elastomers were made by treating the polysiloxane with a mixture of the liquid crystal and 1,2-epoxy-9-decene, followed by crosslinking using an acid catalyst either in solution ($ZnCl_2$ in chloroform[3]) or neat, using a photoactivated iodinium antimonate[4].

The diimides were made by mixing a phthalic anhydride dimer and the appropriate aniline, and heating the melt to 290°C. When asymmetric diimides were desired, the appropriate amounts of the two anilines were mixed with the anhydride, and this mixture was heated, giving a statistical mixture of the various possible products. Hence, if the aniline ratio in the **Table** of diimides is 1:1, then the result would be a 1:2:1 mixture of the A/A:A/B:B/B compounds. Our preliminary studies into methods of selectively making just the "A/B" asymmetric compounds were unsuccessful. The polydiimides were made by using an compound with a terminal alkene as one of the anilines when making the diimide, then epoxidizing the alkene and crosslinking using an acid catalyst.

The polyvinyl ether was made by treating a liquid crystal containing a vinyl ether with the antimonate catalyst. The polyacrylates were made by treating the monomers with 1% AIBN in refluxing chloroform. The polyesters were made by treating decanedicarbonyl chloride with a bisphenol in the presence of triethylamine.

All polymers were tested for their liquid crystalline properties by differential scanning calorimetry, followed by optical confirmation of the phases by polarizing microscopy. Our hotstage has a temperature limit of 210°C, limiting the determination of phases above this temperature to the DSC and to a rough optical confirmation by heating the sample on a hot plate and observing the phase changes upon cooling. In addition, the stability of at least one member of each class of compounds was tested for thermal stability at temperatures up to 400°C.

RESULTS AND DISCUSSION

Two polysiloxanes with cyclic pentamer siloxane rings were synthesized. They showed broad C phases with the higher one, **MDW 824**, showing an I to C transition at 193°C. Although they are smectogenic, they have relatively low thermal stability, as evidenced by the changing character of the DSC spectrum when the materials are heated above 250°C. These materials are thus not optimal for high temperature applications.

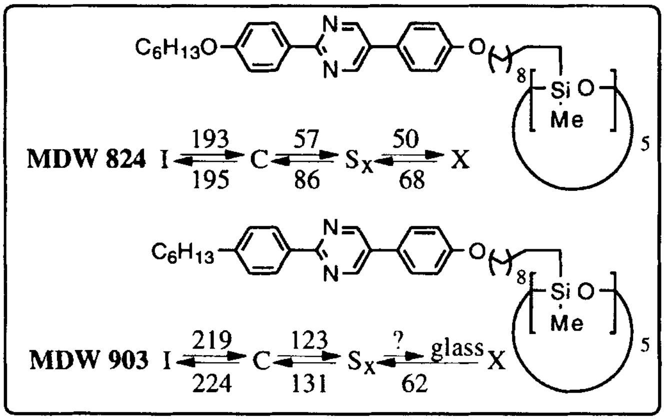


Figure 1. High-temperature polysiloxanes.

In an effort to increase thermal stability, we tried cross-linking the siloxanes. **MDW 905**, upon cross-linking at 5%, showed stabilization of the smectic C phase and suppression of the non-crosslinked precursor's (**MDW 903**) higher ordered phase. Its thermal stability was not significantly enhanced by cross-linking. The phase diagrams of a 2% cross-linked material, **MDW 902**, and its non-crosslinked precursor **MDW 898** are also compared in **Figure 2**. Since we expected crosslinking to increase the material's phase transition temperatures, the lower phase transition temperatures of the crosslinked material are somewhat surprising. Note that the numbers beside each pendant indicate the proportions of that constituent in the pre-polymerization mixture. Thus, for **MDW 905** a 20:1 mesogen:epoxyalkene mixture was coupled to the silane.

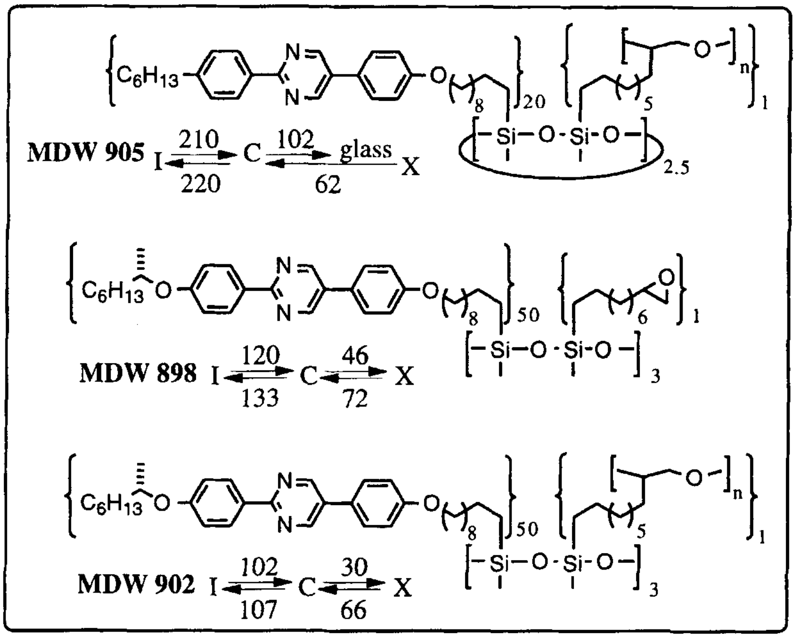


Figure 2. Polysiloxane elastomers.

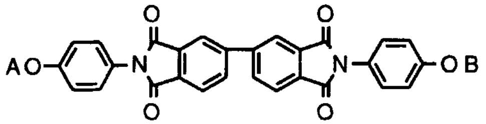
A high temperature smectic A phase for a symmetric diimide system was recently reported by Eiselt[5] et al. We synthesized similar compounds, and were pleasantly surprised to find that one symmetric homologue, the C-12 compound, possessed a broad, high temperature S_C phase, while the other two possessed unidentified smectic phases. Three of the mixed homologues also showed S_C phases. Due to the nature of the synthesis, the asymmetric diimide analogs are actually composed of a 1:2:1 mixture of the asymmetric and the two symmetric diimides. The results of these experiments are listed in **Table 1**. The essential structure is shown at the top, and the two tails, their ratio, and the phase diagram of each resultant product, is listed in the **Table**.

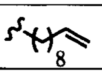
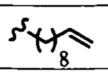
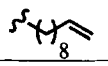
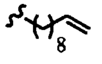
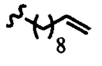
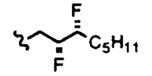
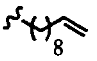
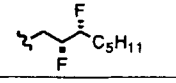
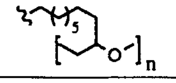
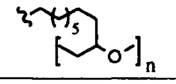
Two chiral diimides containing a high polarization difluoroalkoxy tail were made, and one, **MDW 871**, showed a broad smectic A phase from 304°C to 211°C. This is the highest A phase reported in a chiral material; the 317°C A phase exhibited by **MDW 869** was the third highest smectic A phase ever reported.

Two diimides (**MDWs 879** and **883**) were epoxidized and polymerized, giving polydiimides. By varying the percentage of alkene aniline precursor in the diimide formation, the level of cross-linking was controlled. One polydiimide, the lightly cross-linked **MDW 901**, showed a broad C phase from 232°C with supercooling down to 84°C, while the more heavily cross-linked **MDW 900** showed a slightly lower transition and froze into a glass at 75°C. The phase sequence and range of these polymers are quite similar to their monomeric precursors, but the polymerized material changes to a rubbery consistency indicating polymerization with some cross-linking.

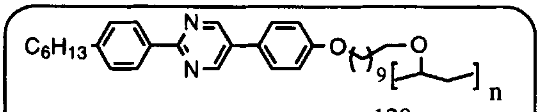
Overall, these new diimide materials represent a very promising lead in developing high temperature FLC materials. Their thermal stability is outstanding, they give very high temperature S_A phases, and they tend to give S_C phases, particularly when made as mixed diimides.

Table 1: Diimides with the structure:



MDW#	A	B	A:B	Phase Diagram
869	C_6H_{13}	C_6H_{13}	1:1	$\mathrm{I} \xrightarrow{317} \mathrm{A} \xrightarrow{251} \mathrm{S_X} \xrightarrow{241} \mathrm{X}$
877	$C_{12}H_{25}$	$C_{12}H_{25}$	1:1	$\mathrm{I} \xrightarrow{280} \mathrm{A} \xrightarrow{236} \mathrm{C} \underset{\xleftarrow[170]{}}{\xrightarrow{123} \mathrm{S_x} \xrightarrow{113}} \mathrm{X}$
874			1:1	$\mathrm{I} \xrightarrow{285} \mathrm{A} \xrightarrow{240} \mathrm{S_X} \xrightarrow{159} \mathrm{X}$
870	C_6H_{13}		1:1	$\mathrm{I} \xrightarrow{301} \mathrm{A} \xrightarrow{239} \mathrm{C} \xrightarrow{?} \mathrm{S_X} \xrightarrow{231} \mathrm{X}$
879	$C_{12}H_{25}$		1:1	$\mathrm{I} \xrightarrow{283} \mathrm{A} \xrightarrow{233} \mathrm{C} \underset{\xleftarrow[154]{}}{\xrightarrow{69} \mathrm{glass}} \mathrm{X}$
883	$C_{12}H_{25}$		4:1	$\mathrm{I} \xrightarrow{277} \mathrm{A} \xrightarrow{226} \mathrm{C} \underset{\xleftarrow[156]{}}{\xrightarrow{81} \mathrm{S_x} \xrightarrow{70}} \mathrm{X}$
878	C_6H_{13}	$(CH_2)_9SiEt_3$	1:1	does not melt
871	C_6H_{13}		1:1	$\mathrm{I} \xrightarrow{304} \mathrm{A} \xrightarrow{211} \mathrm{X}$
875			1:1	decomposes
900	$C_{12}H_{25}$		1:1	$\mathrm{I} \underset{263}{\overset{266}{\rightleftarrows}} \mathrm{A} \underset{233}{\overset{226}{\rightleftarrows}} \mathrm{C} \underset{\xleftarrow[155]{}}{\xrightarrow{75} \mathrm{glass}} \mathrm{X}$
901	$C_{12}H_{25}$		4:1	$\mathrm{I} \xrightarrow{271} \mathrm{A} \xrightarrow{232} \mathrm{C} \underset{\xleftarrow[167]{}}{\xrightarrow{84} \mathrm{S_x} \xrightarrow{75}} \mathrm{X}$

A polyvinyl backbone, since it is essentially just a polyalkane, was expected to provide good thermal stability and reasonable mesogenicity. We made one polyvinyl ether, which showed a broad S_C phase, with its S_C to I transition at 173°C, and which cooled to a glass phase at 129°C. This material showed remarkable thermal stability, and its reasonably high temperature S_A and S_C phases indicate that it is a very promising class of high temperature materials.



MDW 868 $\mathrm{I} \xrightarrow{186} \mathrm{A} \xrightarrow{173} \mathrm{C} \underset{\xleftarrow[122]{}}{\xrightarrow{129} \mathrm{glass}} \mathrm{X}$

Figure 6. Polyvinyl ether.

Four polyacrylates and one polymethacrylate were also investigated. Three showed smectic C phases with the highest S_C to S_A transition being 178°C for **MDW 858**. **MDW 866**, one of the chiral polyacrylates, showed a broad S_C^* phase from 161°C with supercooling to 71°C. The polymethacrylate also showed the desirable property of freezing into a glass phase retaining the smectic C texture. In general, the polyacrylates and polymethacrylates exhibited their smectic phases at lower temperatures than did the diimides, and appeared to be less stable at very high temperatures.

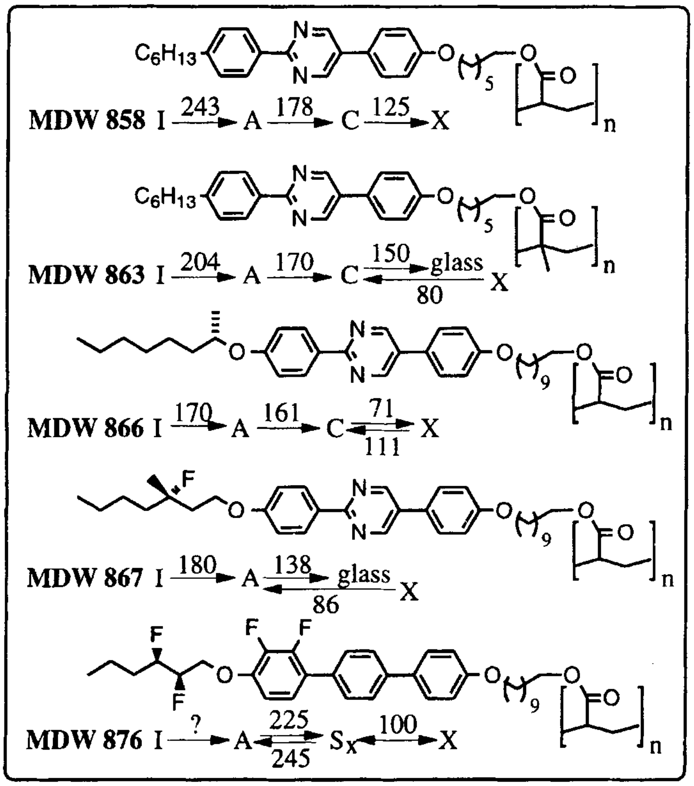


Figure 7. Polyacrylates and polymethacrylates.

Main chain polyesters were also investigated for their ability to give high temperature smectic liquid crystals. Two materials made from the diphenylpyrimidine core showed smectic phases, one which was made with an achiral diacid and one which was made with 3R-methyladipic acid, a chiral diacid. The straight chain analog, **MDW 839**, showed an unidentified smectic phase at 262°C. The chiral version showed a smectic C phase from 228°C up to 352°C. A planar sample of this material selectively reflects light indicating a relatively tight S_C^* helical pitch. At 352°C, the polymer undergoes an irreversible change to another material which shows a liquid crystalline transition at 259°C and a glass transition at 104°C.This new material is distinctly different in character from the virgin material. We postulate that the material cross-links to a new LC matrix. The finding that a main chain polymer can possess a smectic C phase is a very encouraging result and, to our knowledge, represents the first carbon-based smectic C main chain polymer[6]. Due to hotstage constraints, we cannot ascertain that the material does not enter the S_A phase at some point between 228°C and 352°C. However, if our assessment of the compound is correct, we believe it is the highest temperature S_C phase ever reported.

Core fluorination has been shown to promote S_C phases and we believed that an all-carbon aromatic core might have higher thermal stability. To test these theories, a compound containing a fluorinated terphenyl core (**MDW 844**) was made. It showed an unidentified smectic phase at 201 °C. The polyesters showed intermediate thermal stability, but quite high temperature smectic phases.

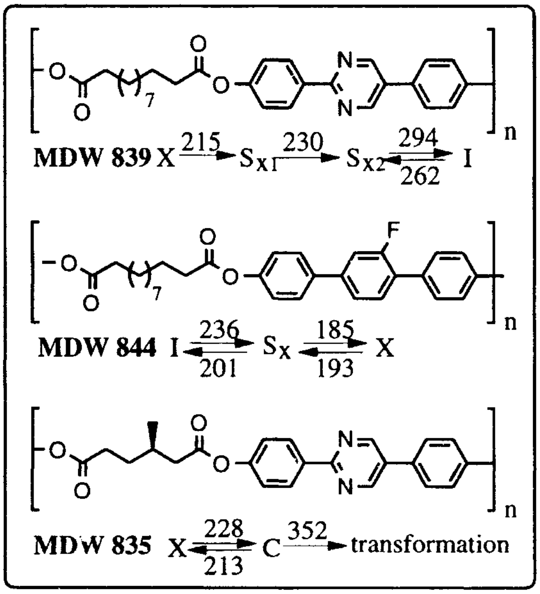


Figure 8. Polyesters.

Thermal stability of the new FLC polymers was a critical consideration. We tested each new class of materials by heating a sample in our differential scanning calorimeter (Mettler DSC 12E) at 10°/min. from 150°C to 250°C, under a nitrogen atmosphere, followed by cooling at the same rate and observing any differences in the heating and cooling cycles. If the DSC scans indicated that the material was stable, then the experiment was repeated with a 50°C higher temperature range (e.g. 200°C to 300°C, then 250°C to 350°C), until the heating and cooling cycles were no longer repeatable, indicating decomposition. These experimental conditions were designed to assess the short-term temperature stability of the materials, and to give a crude estimate of the relative stability of the various polymer types used.

Table 2 shows that siloxanes are the least stable and polyesters were of intermediate stability. Although polyacrylates and methacrylates were reported to show only intermediate thermal stability[7], we were pleasantly surprised to find that our new polyacrylates were stable up to 350°C, and the polymethacrylate showed even a further improvement in stability up to 400°C. The polyvinyl ether and diimides showed remarkable stability up to 400°C (the upper temperature limit of our DSC), although the polymers made from diimides showed some transition temperature lowering, indicating further cross-linking or possibly the start of decomposition.

Table 2. Thermal stability of several classes of materials.

Compound class	Temperature limit
siloxane	250°C
cross-linked siloxane	250°C
main chain polyester	350°C
polyacrylate	350°C
polymethacrylate	>400°C
polyvinyl ether	>400°C
diimide	>400°C
diimide/polyether	350°C

SUMMARY

Twenty-five new materials in five general classes, designed to be mesogenic at high temperature, are presented. Of these, sixteen had smectic C phases and fifteen had smectic A phases. Also, fourteen had smectic phases at temperatures over 200°C; of these, twelve had smectic A phases over 200°C (two with S_A^* phases) and eight had smectic C phases over 200°C (one with a S_C^* phase). Several of these classes of materials showed thermal stability up to 400°C.

The following notable results of this study, completed in 1994, are to our knowledge accurate:

1. The first demonstration of a carbon-based smectic C main chain polymer (**MDW 835**).
2. The first demonstration of an imide-containing liquid crystal with a smectic C phase (**MDW 877**).
3. Third highest temperature smectic A phase reported (317°C for **MDW 869**).
4. Highest temperature chiral smectic A phase reported (304°C for **MDW 871**).
5. Extremely high thermal stability (>400°C) for a smectic C-containing liquid crystal (diimides).

Acknowledgment
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