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Unusual Odd-Even Effects in Vinyl Ether and Acrylated Direactive Liquid Crystals

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Four series of direactive liquid crystals are presented and their physical properties characterised. The core groups are based on either a lateral chloro or methyl terphenyl and the reactive groups are either acrylates or vinyl ethers. It is shown that reactive liquid crystals with vinyl ether reactive groups have higher transition temperatures, birefringence, and order parameter than the corresponding acrylates.

Both the vinyl ether and acrylate series show an odd-even effect in transition temperatures, birefringence and order parameters. The odd-even effect in the vinyl ether series is particularly marked.

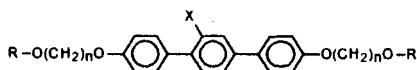
Keywords: acrylates; vinyl ethers; polymers; in-situ photopolymerisation

INTRODUCTION

The design and development of new devices based on in-situ photopolymerisation of reactive liquid crystals has stimulated much interest in developing new reactive liquid crystals.^[1,2,3] These reactive liquid crystals can be converted to an anisotropic film by photopolymerisation and, in order to obtain a thermally stable network, at least some of these liquid crystals should be direactive.^[4]

For a given $d\Delta n$ value of the anisotropic film, it is desirable for the reactive liquid crystals to have high birefringence so that only a thin film is required. Furthermore, the reactive liquid crystals should have a relatively low viscosity and modest melting point, so that good alignment of the monomer can be achieved at close to ambient temperature, prior to in-situ photopolymerisation. In this paper we will describe the properties of four series of diactive liquid crystals in which it was found that diacrylated reactive liquid crystals have significantly different physical properties to the corresponding compounds with vinyl ether reactive groups.

The terphenyl core group is known to give liquid crystals with high birefringence.^[5,6] However, such liquid crystals tend to give compounds with smectic phases and high melting points, but it has been found that the addition of a lateral substituent depresses both the melting point and smectic phase and helps to promote nematic phases.^[7] In the case of a terphenyl core substituted with two alkoxy substituents in the 4',4''-positions, two lateral fluorine substituents are usually required to give a broad nematic liquid crystal phase.^[8] Studies also show that the addition of a single, lateral methyl or chloro group gives liquid crystals with a reasonably broad nematic phase. It is the properties of these compounds (Fig. 1) we report here.



$R = CH=CH_2$, $X = Me$	2a-d
$R = CH=CH_2$, $X = Cl$	2e-f
$R = OC-CH=CH_2$, $X = Me$	1a-d
$R = OC-CH=CH_2$, $X = Cl$	1e-f
$n = 3, 4, 5 \text{ and } 6$	

FIGURE 1 Chloro and methyl terphenyl diactive liquid crystals.

The acronyms CITp and MeTp will be used to denote the chloroterphenyl and methylterphenyl core group respectively. A number will designate the number of methylene groups in the spacer and the letters Ve and Ac will differentiate between examples with vinyl ether or acrylate reactive groups. For example, CITp-3-Ve refers to compound **2e**.

EXPERIMENTAL

Synthesis

The compounds were synthesised by standard synthetic procedures involving, for example, boronic acid coupling,^[9] diazotization^[10] and standard ether and ester forming reactions.

Physical characterisation

The structure of the compounds were confirmed by ¹H NMR spectroscopy using a Jeol PMX 60 SI and G.C. mass spectrometry using a Nermag R1010S quadrupole instrument. Phase transition temperatures were measured using a Perkin Elmer DSC7. Phase types were assigned against known standard samples using polarising microscopy and a Mettler FP52 hot stage. Birefringence, Δn , and the ordinary refractive index, n_o were measured using a 7-11% w/w solution of the test compound in the nematic host mixture Merck ZLI-3086 using an Abbé refractometer and Na_D light (589.7 nm) at 20°C.

RESULTS

Transition temperature

The transition temperatures of the acrylates **1a-h** are shown in Table 1. They all possess enantiotropic smectic A and nematic phases, with the exception of the C3 homologues (compounds **1a** and **1e**) and the pentyl

homologue with a chloro substituent **1g**, which have a monotropic smectic phase. These compounds exhibit a distinct odd-even effect; the examples with an odd number of methylene units in the spacer groups having a high N-I, and lower S-N transition temperature than the examples with an even-number of methylene units. The exception being compound **1e**.

Compound Number	Number of methylene units in spacer group(n)	X	C	S _A	N	I
1a	3	Me	73	(61.1)	81	
1b	4	Me	52.5	75	76.8	
1c	5	Me	60.7	62.3	83.3	
1d	6	Me	68.8	75.3	78.6	
1e	3	Cl	83.6	(31.5)	(67.3)	
1f	4	Cl	53.4	65.3	73.4	
1g	5	Cl	63.9	(52)	84.1	
1h	6	Cl	47.9	68	78.7	

TABLE 1 Transition temperatures of acrylates **1a-h** in °C

The transition temperatures of the vinyl ether compounds (**2a-h**) are shown in Table 2. They generally have a higher melting point and N-I than their corresponding acrylates.

In common with the acrylate series, the vinyl ether series also shows a pronounced odd-even effect. However, in the vinyl ether series it is the homologues with an even number of methylene groups in the spacer that have higher N-I and S-N transitions. This is the converse of the situation with the acrylate series. Also, the magnitude of the odd-even effect is greater for the vinyl ether series. The difference in the odd-even effect of the N-I transition for the acrylate and the vinyl ether (methyl series only) is shown in Fig 2.

It is difficult to rationalise the observed fluctuation in N-I transition temperatures for these compounds. In the case where a molecule possesses a rigid core and a terminal alkyl chain as in e.g. the 4-alkyl-4'-cyanobiphenyl

series, the odd-even effect is attributed to the geometry of the terminal alkyl chain.

Compound Number	Number of methylene units in spacer group (n)	X	C	S _A	N	I
2a	3	Me	74.4	(37.8)	(52.6)	
2b	4	Me	99.7		128	
2c	5	Me	69.7	(52.7)	(64.4)	
2d	6	Me	79.4	89.6	111.4	
2e	3	Cl	60.5	(6.2)	(35.4)	
2f	4	Cl	85.8		121.4	
2g	5	Cl	60.7	(44.2)	72.6	
2h	6	Cl	69.9	76.2	106.8	

TABLE 2 Transition temperatures of vinyl ethers 2a-h in °C.

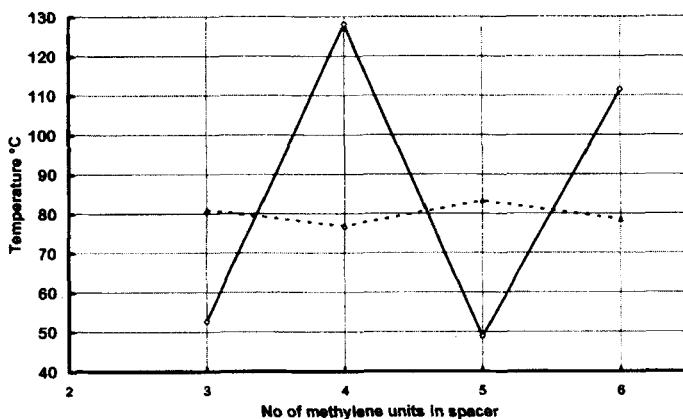


FIGURE 2 Plot of N-I transition temperatures for both the Metp-n-Ac, (1a-1d) and ——— MeTp-n-Ve (2a-2d)

Compounds with an odd number of methylene units in the terminal chain have higher N-I transitions because there are more C-C bonds along the long molecular axis, thus extending the molecular length of the molecule without

significantly increasing its width,^[11] while even members trend to “broaden” the molecule more.

Dimeric liquid crystals, with two rigid cores connected by a carbon chain, also demonstrate an odd-even effect and this is again attributed to the geometry of the spacer group.^[12,13] When the spacer is in its preferred extended all-*trans* conformation the rigid end groups can be in a *syn* or *anti* configuration depending on the odd or even number of flexible units in the spacer. The higher N-I transition is demonstrated by compounds having the more condensed ordered phase, the *anti*-configuration, in which the mesogenic groups are oriented more or less parallel to one another. The alternation in the odd-even effect of dimers and ω -phenyl alkyls^[14] is larger than that observed for materials with one rigid core.

By considering the length of the terminal chain in terms of the total number of carbon and / or oxygen atoms, both the vinyl ether and acrylates compounds with an even number of units in the chain have the highest N-I transitions. This is contrary to that demonstrated by low molar mass liquid crystals.

Odd-even effect in birefringence and order parameter

In order to measure the order parameter of these compounds against temperature, the values of birefringence at various temperatures were measured. The order parameter *S* was obtained from birefringence data using the extrapolation method originally devised by Haller^[15] and later used by Horn,^[16] Finkelmann,^[17,18] and Broer.^[4]

The results of these studies are shown below in Fig. 3 and show that for the vinyl ether series, the highest order parameter is exhibited by compounds **2b** and **2d**, which have an even number of methylene units in the spacer groups. The vinyl ethers have higher values of *S* than the acrylates. The

order parameter of the two vinyl ether series increases in the order $n = 3, 5, 4, 6$, and for the two acrylate series, increases in the order $n = 4, 6, 3, 5$.

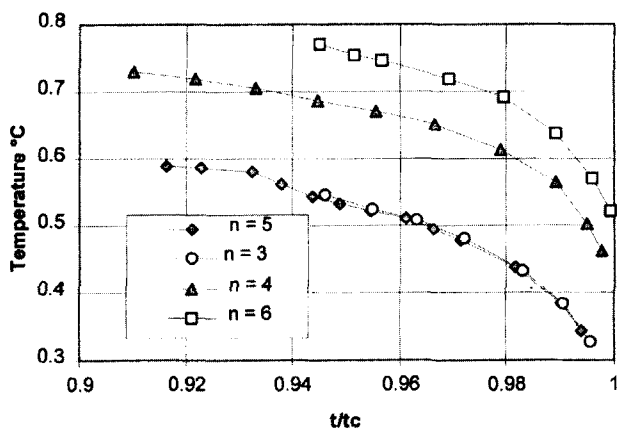


FIGURE 3 Plot of S against reduced temperature for MeTp- n -Ve (2a-2d)

Conclusions

We have shown that directive terphenyl based liquid crystals with vinyl ether reactive groups have significantly different physical properties to those shown by the corresponding compounds with an acrylate reactive group. Both the vinyl ether and acrylate series show an odd-even effect in thermal properties, birefringence and order parameter. This strong structure property relationship can be used as a predictive tool to design a reactive liquid crystal with a high N-I transition and a low S-N transitions.

Acknowledgments

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