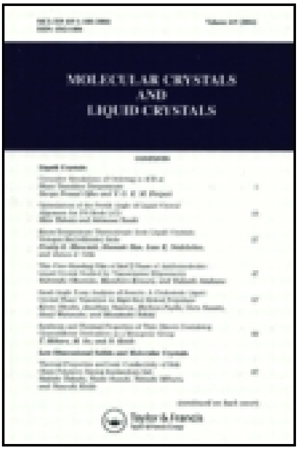

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Liquid Crystal Polymers of Improved Modulus Retention with Temperature

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Version of record first published: 13 Dec 2006.

To cite this article: William A Macdonald (1987): Liquid Crystal Polymers of Improved Modulus Retention with Temperature, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 153:1, 311-320

To link to this article: http://dx.doi.org/10.1080/00268948708074547

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 311-320
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Printed in the United States of America

LIQUID CRYSTAL POLYMERS OF IMPROVED MODULUS RETENTION WITH TEMPERATURE

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ABSTRACT

Non crystalline, liquid crystal polymers containing meta-amide and/or sulphone groups exhibiting improved modulus retention with temperature are described.

INTRODUCTION

Liquid crystal polymers, (LCP's) exhibit a unique combination of properties, offering high performance precision mouldings of outstanding dimensional stability and chemical resistance. However Dynamic Mechanical Analysis (DMA) studies of main chain aromatic liquid crystalline polyesters reveal that compared to aromatic isotropic polyester analogues, LCP's have anomalously low glass transition temperatures and poor modulus retention with temperature (Fig 1). This type of temperature performance, although offset by the high initial stiffness achievable with LCP's, is obviously undesirable in an engineering resin. Raising the Tg in crystalline polymers, however, can lead to an increasingly high Tm and intractability. The approach discussed in this paper has been therefore to design high Tg, non crystalline, liquid crystalline polymers.

Several authors have proposed correlations between chemical structure and the Tg of polymers. Their methods are usually based on the assumption that the structural groups in the repeating units provide weighed additive contributions to the Tg, and Van Krevelen and Hoflyzer[1] derived the following equation:

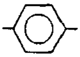
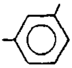
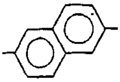
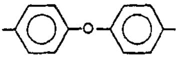
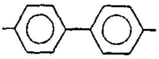
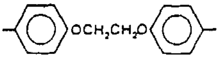
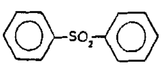
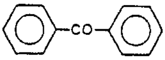
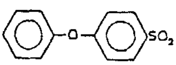
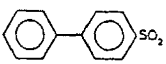
$$Tg = \frac{\sum_i Y_{gi}}{M}$$

Yg - molar glass transition function Kg/mol

M - molecular weight of repeat unit

By applying this equation to available literature on the Tg's of polymers, group contributions and structural corrections were obtained. Although the above formula does not give an accurate value for the Tg's of LCPs, dividing the Yg of a given group by its molecular weight gives a qualitative indication of how a group might influence Tg. Thus from Table 1 it can be seen that substituting a benzene ring with, for example naphthalene, would not be expected to alter Tg, but the inclusion of amide bonds or sulphone links might be expected to raise the Tg. Systematic series of LCP's containing amide groups and/or sulphone groups were therefore prepared and characterised by DMA.

TABLE 1 Correlation between chemical structure and Tg

	$\frac{Y_g}{M}$		$\frac{Y_g}{M}$
	421		368
	444		494
	572		365
	565		506
	608		671
 $\overset{O}{\overset{\|}{C}}-O$	182	 $\overset{O}{\overset{\|}{C}}NH$	512

EXPERIMENTAL

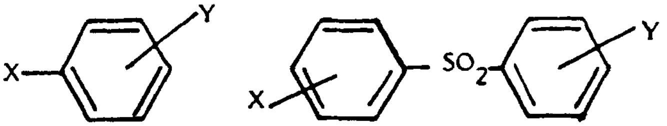
The polyesters were prepared by standard melt acidolysis techniques as exemplified in patents[2].

Polymers were compression moulded into sheets 25mm x 12mm by heating for four minutes to a temperature 30°C above the temperature at which melt flow was observed for each individual sample. These were examined with a Du Pont 981 DMA with a cryogenic attachment over the temperature range - 120°C to 350°C at 10°C min^{-1}. The DMA modulus versus temperature graphs were normalised relative to the DMA stiffness at 0°C to eliminate variable DMA stiffness arising between different polymer samples. The Tg was measured at the intersection of the DMA modulus plots above and below the Tg process.

RESULTS AND DISCUSSION

COMPOSITION

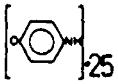
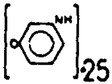
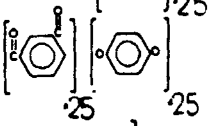
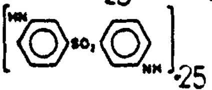
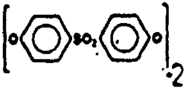
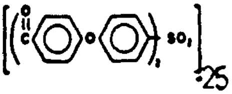
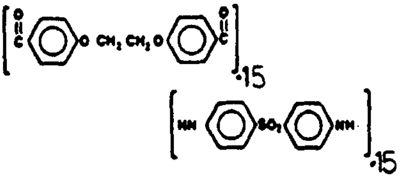
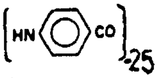
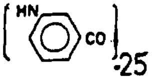
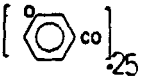
The main scheme of compositions studied involved examining the effect of systematically replacing para linked units in the control polymers (based on either (i) 2,6 - hydroxynaphthoic acid (HNA), terephthalic acid (TA) and hydroquinone (HQ) (polymerised in the ratio 50:25:25) (Control A) or (ii) 2,6 - hydroxynaphthoic acid and 4 - hydroxybenzoic acid (HBA) (polymerised in the ratio 27:73) (Control B)) with 25% of the monomer units ofthe type illustrated in Fig 2.



X,Y = OH, CO_2H, NH_2

FIGURE 2

The series of polymers based on Control A and B, A(i) - (viii), B(i) - (iv)(see next page) exhibited melt flow in the temperature range 215-350°C and showed the characteristic whitening effect associated with anisotropic melts when sheared between glass slides. The transition from liquid crystal to isotropic melt was not observed below 400°C in any of the examples studied.

CODE	POLYMER FORMULATION
CONTROL A	HNA$_{\cdot 5}$ TA$_{\cdot 25}$ HQ$_{\cdot 25}$
A(i)	HNA$_{\cdot 5}$ TA$_{\cdot 25}$ 
A(ii)	HNA$_{\cdot 5}$ TA$_{\cdot 25}$ 
A(iii)	HNA$_{\cdot 5}$ TA$_{\cdot 25}$ 
A(iv)	HNA$_{\cdot 5}$ 
A(v)	HNA$_{\cdot 5}$ TA$_{\cdot 25}$ 
A(vi)	HNA$_{\cdot 6}$ TA$_{\cdot 2}$ 
A(vii)	HNA$_{5}$  HQ$_{\cdot 25}$
A(viii)	HNA$_{\cdot 7}$ 
CONTROL B	HBA$_{\cdot 73}$ HNA$_{\cdot 27}$
B(i)	HBA$_{\cdot 337}$ HNA$_{\cdot 413}$ 
B(ii)	HBA$_{\cdot 48}$ HNA$_{\cdot 27}$ 
B(iii)	HBA$_{\cdot 48}$ HNA$_{\cdot 27}$ 

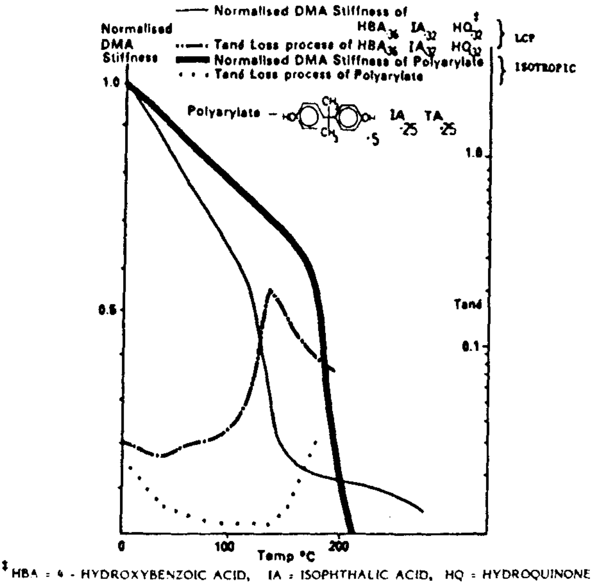


FIGURE 1 DMA of an LCP and an isotropic aromatic polyester.

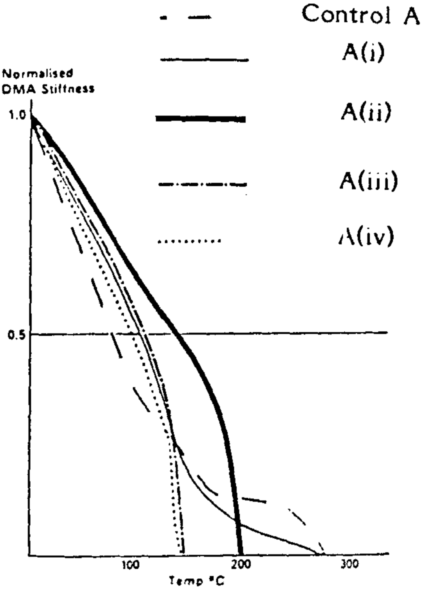


FIGURE 3 Normalised DMA stiffness plots of polymers A (i)-(iv).

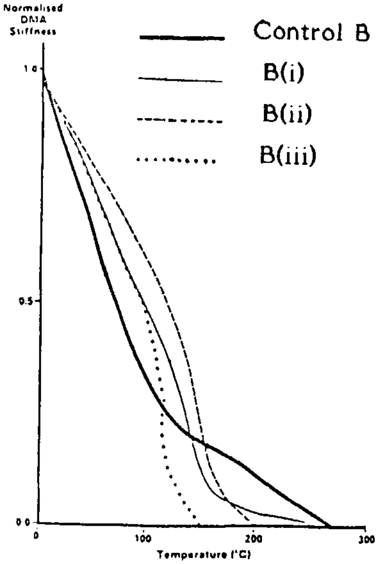


FIGURE 4 Normalised DMA stiffness plots of polymers B (i)-(iii).

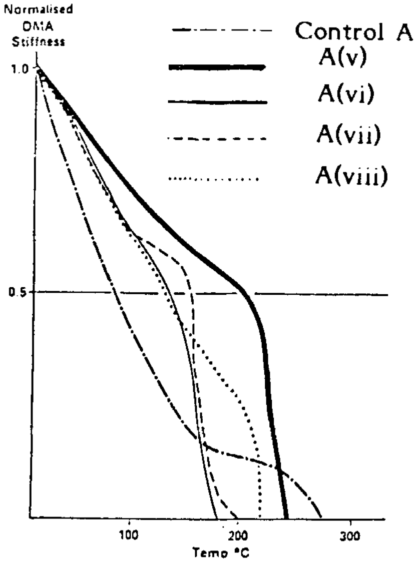


FIGURE 5 Normalised DMA stiffness plots of polymers A (v)-(viii).

DYNAMIC MECHANICAL ANALYSIS

Amide Containing LCP's

TABLE 2

Tg and modulus retention with temperature for polymers A(i)-(iv)

	Tg °C	Temp X°C where $\frac{\text{DMA stiffness at X°C}}{\text{DMA stiffness at 0°C}}$ = .50	= .25
CONTROL A	135	80	135
A (i)	122	110	140
A (ii)	178	145	180
A (iii)	130	110	135
A (iv)	127	100	135

Taking first the series of polymers based on Control A it can be seen from fig 3 that replacing the hydroquinone with para-aminophenol (A(i)) had little effect on the Tg (Table 2), although it did improve modulus retention with temperature as evidenced by the temperature at which the sample has retained 50% and 25% of the DMA stiffness at 0°C.

Replacing hydroquinone with meta-aminophenol (A(ii)), it would be expected from theoretical calculations[1] that the presence of para-amide rather than meta-amide groups might raise Tg. Surprisingly it was observed that Tg and the modulus retention of A(ii) was significantly improved relative to Control A and A(i). Furthermore A(ii), unlike Control A and A(i), was essentially non crystalline as evidenced by no retention of stiffness above the Tg.

The incorporation of meta-ester units to Control A, by replacing hydroquinone or terephthalic acid with resorcinol A(iii) or isophthalic acid A(iv) respectively, rendered the polymers non crystalline, but unlike with meta-amide links there was no increase in Tg, although the modulus retention with temperature was improved relative to Control A.

The series of polymers based on Control B exhibited a similar trend (fig 4 Table 3).

TABLE 3

Tg and modulus retention with temperature for polymers B(i)-(iii)

	Tg °C	Temp X°C where $\frac{\text{DMA stiffness at X°C}}{\text{DMA stiffness at 0°C}}$	
		= .50	= .25
CONTROL B	117	78	120
* B (i)	127	95	135
B (ii)	135	124	150
B (iii)	102	100	120

* The formulation of B(i) has been altered relative to Control B to render the polymer more tractable.

Thus replacing 25% of 4-hydroxybenzoic acid with meta-aminobenzoic acid B (ii) raised the Tg and improved the modulus retention with temperature, whereas incorporating meta-hydroxybenzoic acid B (iii) depressed the Tg, although the modulus retention with temperature was improved relative to Control B. In both cases the incorporation of meta links rendered the polymers non crystalline. The presence of para-aminobenzoic acid B(i) raised the Tg and improved the modulus retention relative to Control B but less so than with B(ii).

SULPHONE CONTAINING LCP's

TABLE 4

Tg and modulus retention with temperature for polymers A(v)-(viii)

	Tg °C	Temp X°C where $\frac{\text{DMA stiffness at X°C}}{\text{DMA stiffness at 0°C}}$	
		= .50	= .25
CONTROL A	135	80	135
A (v)	219	205	230
A (vi)	135	130	156
A (vii)	164	148	162
* A (viii)	182	120	180

* TA replaced by 1,2 bis (p-carboxyphenoxy)ethane.

The incorporation of sulphone containing monomers (v)-(viii) into Control A raised the Tg and improved the modulus retention with temperature in all cases. Furthermore the incorporation of 20-25% of the units gave rise to non crystalline LCP's. (The polymer in which the hydroquinone of Control A was replaced with 25% 4,4'-diaminodiphenyl sulphone was intractable below 350°. To overcome this, the polymer based on A(viii), in which flexibility has been introduced to the backbone and containing only 15% of 4,4'-diaminodiphenyl sulphone, was prepared. This makes quantitative comparison between A(viii) and other samples difficult.) The most significant effect on Tg was observed when the effect of meta-amide and sulphone groups was combined ie the HQ was replaced with 3,3'-diaminodiphenyl sulphone A(v) - the Tg was raised to 219°C and there was a significant improvement in modulus retention with temperature relative to Control A and the other polymers A(i)-(vii).

CONCLUSIONS

Relative to Control A and B.

1 The incorporation of meta links, or bent units (ie SO_2) improves the modulus retention with temperature below the Tg and renders the polymer amorphous.

2 Sulphone and/or meta-amide groups raise the Tg and improve the modulus retention with temperature significantly.

3 Para-amide groups have a modest beneficial effect on the Tg and modulus retention with temperature.

The tan δ loss spectrum of LCPs containing napthalene exhibit a β process in the region of 50°C which is attributed to the napthyl groups undergoing a coordinated rotation motion about the main polymer axis[3]. Discussion of the tan δ loss spectrum of the series of polymers A(i)-(viii) and B(i)-(iv) will not be discussed in this paper. However it is believed that the improvement in modulus retention with temperature below the Tg relative to the controls A and B (for example arising with meta-ester groups or para-amide groups) is related to suppression of this β loss process[3].

The 'stiff' sulphone group would be expected to raise Tg[1], but it is difficult to rationalise why the incorporation of meta-amide groups rather than para-amide groups raises Tg. As mentioned in the Introduction, LCPs generally have anomalously poor Tg's and modulus retention with temperature compared to isotropic aromatic polymers. This work highlights the question - what are the co-operative motions that take place at the Tg like transition of a rigid chain polymer? A more detailed understanding of the relationship between chemical formulation and molecular morphology is required to help address this problem.

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