

Synthesis, structure and properties of liquid crystalline polymers

Monika Engel, Bernd Hsgen, Renate Keller, Willi Kreuder, Bernd Reck,
Helmut Ringsdorf, Hans-Werner Schmidt and Peter Tschirner

Institute of Organic Chemistry, University of Mainz, D-6500 Mainz, FRG

Abstract - A number of new liquid crystalline polymers have been synthesized and their mesophase behaviour studied. Two different approaches have been chosen to chemically vary the "classical" thermotropic side group polymers in order to obtain more insight into the structure-property-relationships of these molecules. (i) The constituents (polymer main chain, spacer and mesogenic units) have been widely varied. Thus, side group polymers with polyester main chains, spacers with oligoethylene oxide or siloxane units, non-mesogenic comonomers (dyes), and disc-like mesogenic units (as side groups as well as within the polymer main chain) have been investigated. (ii) The structural principles of liquid crystalline polymers have been varied by synthesizing side group polymers with paired mesogens (containing two mesogenic units per monomer unit) and of combined main chain and side group polymers (containing mesogenic units as side groups and within the polymer main chain).

INTRODUCTION

Thermotropic liquid crystalline polymers are, in principle, built out of three constituents: (i) polymer main chain; (ii) spacer; (iii) mesogenic unit (formanisotropic moiety, rod- or disc-like). Two routes have been chosen to combine these constituents into liquid crystalline polymers: main chain and side group polymers.

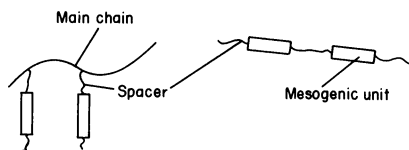
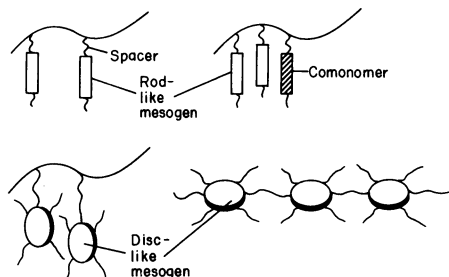


Fig. 1. Structure of thermotropic liquid crystalline polymers

With the side group polymers the spacer has been proved to be especially necessary for the systematic synthesis of liquid crystalline polymers. The spacer weakens the mutual influence of main chain and mesogens by separating them via a flexible alkyl chain. In main chain polymers spacers are used to decrease the very high melting points of the rigid polymers. Following these principles a large number of liquid crystalline polymers has been synthesized over the last decade (refs. 1,2). In this contribution chemical variations leading to new types of liquid crystalline polymers, as summarized in Fig. 2, are discussed.

VARIATION OF THE CONSTITUENTS



VARIATION OF THE STRUCTURAL PRINCIPLE

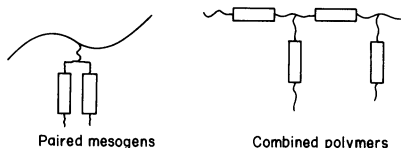


Fig. 2. Chemical variations of the structure of liquid crystalline polymers

VARIATION OF THE CONSTITUENTS

Polar and sterically hindered spacers. So far the spacers in liquid crystalline side group polymers have always been alkyl chains. The concept of the spacer has been the decoupling of the motions of main chain and mesogens, thus allowing each of them to follow their preferential tendencies of orientation.

STRUCTURAL PROBLEMS IN DESIGNING LIQUID CRYSTALLINE POLYMERS

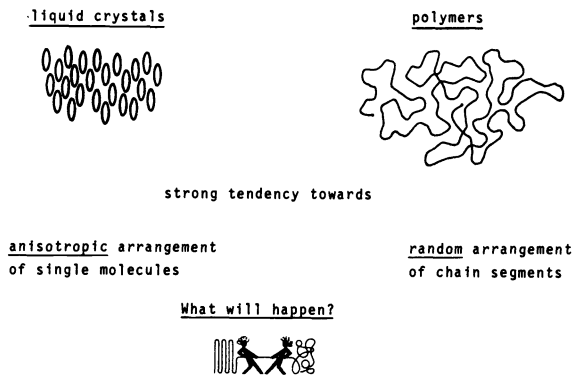


Fig. 3. Conflict of interests between mesophase- and random-coil-formation

Experimental facts, however, have shown that no complete decoupling exists: ESR spin-probe studies indicate dynamic coupling of main- and side-chain motions via the spacer (ref. 3). $^2\text{H-NMR}$ measurements of selectively deuterated polymers have revealed that parts of the spacer take part in the anisotropic orientation of the mesogens (ref. 4). It thus was interesting to incorporate more flexible units such as oligoethylene or siloxane units into the spacer and see whether a more complete decoupling can be achieved (ref. 5). Table 1 shows polymers with oligoethylene oxide units in the spacer and compares them to analogous polymers with only alkyl units in the spacer. The table also features the corresponding monomers.

TABLE 1. Comparison of monomers and side group polymers with oligoethylene oxide units and alkyl units in the spacer

$\text{H}_2\text{C}=\text{CH}-\text{COO}-(\text{CH}_2)_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_4-\text{COO}-\text{HC}(\text{H}_2\text{C})_n-\text{COO}-(\text{CH}_2)_2-\text{C}_6\text{H}_4-\text{CH}_2-\text{CH}_2-\text{C}_6\text{H}_4-\text{COO}-$

Monomers Polymers

		Phase transitions (°C)	
		Monomers	Polymers
-CH ₂ -	-O-C ₆ H ₄ -COO-C ₆ H ₄ -CN	k 87 i	g 24 n 67 i
-CH ₂ -	-O-C ₆ H ₄ -COO-C ₆ H ₄ -C ₆ H ₄ -OCH ₃	k 102 n 202 i	g 67 k 87 s 127 n 290 i

-O-	-O-C ₆ H ₄ -COO-C ₆ H ₄ -CN	k 87 i	g 46 i
-O-	-O-C ₆ H ₄ -COO-C ₆ H ₄ -C ₆ H ₄ -OCH ₃	k 108 n 174 i	k 137 n 277 i

-OCH ₂ CH ₂ O-	-O-C ₆ H ₄ -COO-C ₆ H ₄ -CN	k 3 i	g -5 i
-OCH ₂ CH ₂ O-	-O-C ₆ H ₄ -COO-C ₆ H ₄ -C ₆ H ₄ -OCH ₃	k 76 n 134 i	k 115 n 237 i

The polymers with alkyl spacers exhibit different phase behaviour from their corresponding monomers. The mesophases are enormously stabilized on polymerization and additional phases are encountered for the polymeric liquid crystals. In the case of oligoethylene oxide spacers the polymers only form mesophases if the monomers do. Nevertheless, where nematic phases exist in the monomers, they are stabilized on polymerization. Thus, with spacers containing oligoethylene oxide units the decoupling of polymer main chain and mesogens is already much more effective than with alkyl spacers.

With the sterically hindered siloxane units in the spacer (see Table 2) the situation is more complex. First of all, the very bulky siloxane groups disturb the liquid crystalline order. Consequently mesophases are only found with long alkyl chains or triple-core mesogens. The behaviour of the monomers and the polymers is in principle comparable.

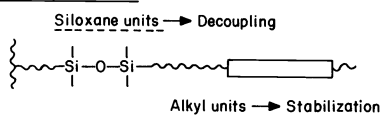
TABLE 2. Monomers and side group polymers with siloxane units in the spacer

	x	Phase transitions (°C)	
		Monomers	Polymers
-O--COO--CN	3	k 6 i	g 4 i
	5	k l i	g 0 i
	11	k-4 n 54 i	g-20 n 37 i
-O--COO---C3H7	3	k 27 n 73 i	g 27 s 102 i
	5	k 16 s 38 n 54 i	g 0 s 131 i
	11	k 30 s 42 n 102 i	g 11 k 54 s 177 i

Thus, the decoupling is again rather effective.

Furthermore, in these siloxane-containing spacers the two functions of a spacer - decoupling of polymer main chain and mesogens and stabilization of the mesophases - can be separately attributed to different parts of the spacer:

Subdivision of spacer :



Dye-containing copolymers

Dye-containing liquid crystalline systems are very important because of their application in displays. In low molecular weight guest-host-mixtures a dye molecule is simply dissolved in a liquid crystalline phase. The problems usually encountered are very low and temperature-dependant solubilities of the dyes.

It could be shown that via copolymers from dye-containing and mesogenic monomers both problems can be avoided: The dye-content can be as high as desired and is no longer temperature-dependant (ref. 6). Another interesting feature of the dye-containing copolymers is that the liquid crystalline order can be frozen in below the glass transition temperature (T_g), whereas in the low molecular weight mixtures it is destroyed by crystallization.

Figure 4 shows two examples for the realization of dye-containing liquid crystalline copolymers. As expected the phase behaviour of the copolymers depends strongly on the geometry of the dye. The bulky anthraquinone dye disturbs the liquid crystalline order. Above a dye content of 30% per weight the mesophase disappears. It has to be pointed out that in comparable low molar mass guest-host-mixtures the maximum content of this dye is below 1%. On the other hand, the tris-azo-dye is a mesogen and stabilizes the liquid crystalline phase.

An important criterion for the quality of a dye-containing liquid crystalline system is the order parameter of the dye in the system (S_D) (ref. 7). S_D is measured in a macroscopically oriented sample, where the director of the mesophase is uniform throughout the sample. Liquid crystalline polymers can be macroscopically oriented by surface effects or magnetic fields in the same way as low molar mass liquid crystals. For a dichroic dye the absorption of an oriented sample is maximal when the polarization plane is parallel to the director ($A_{||}$) and minimal when it is perpendicular to the director (A_{\perp}), leading to S_D (ref. 8):

$$S_D = \frac{A_{||} - A_{\perp}}{A_{||} + 2A_{\perp}}$$

Table 3 lists the order parameters for the two dichroic dyes (shown in Fig. 4) in glassy liquid crystalline copolymers. Depending on the mesogen (substituent R) the copolymers exhibit nematic or smectic phases. A relatively low dye content of 2% was chosen because otherwise the absorption of the coloured copolymers is too high to be measured accurately. The orientation of the dyes is better in the more ordered smectic phases and it depends on the geometry of the dye: the mesogenic tris-azo-dye aligns better than the bulky anthraquinone dye. The order parameters for the tris-azo-dye are even slightly higher than in comparable low molar mass systems.

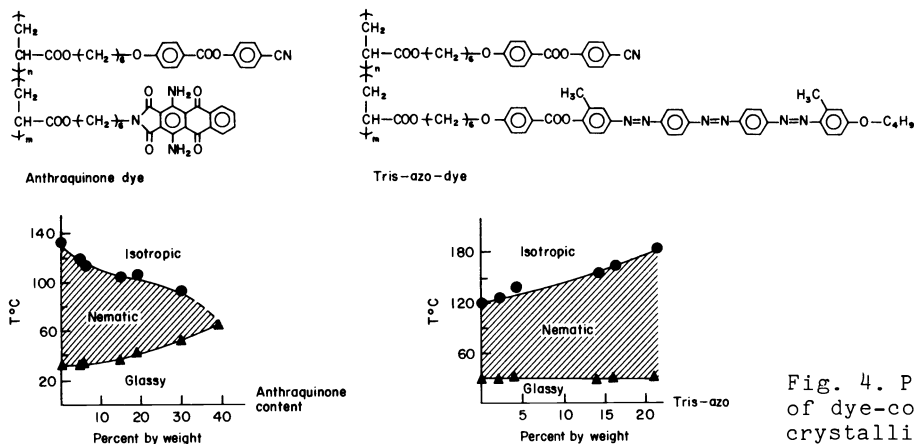


Fig. 4. Phase behaviour of dye-containing liquid crystalline copolymers

TABLE 3. Order parameters of dichroic dyes in the glassy state
Dye-content: 2% by weight

The table includes chemical structures for the copolymers and two data tables. The left table is for the Anthraquinone dye copolymer, and the right table is for the Tris-azo-dye copolymer. Both tables list the substituent -R, the glass transition temperature T_g, the order parameter S₀, and the order parameter S₀ for the glassy state. The formula for T_{res} is also provided.

-R	Glass	T _{res}	S ₀
-CN	n	0.77	0.67
-OCH ₃	s	0.78	0.78

-R	Glass	T _{res}	S ₀
-CN	n	0.76	0.72
-OCH ₃	s	0.76	0.83

$T_{res} = \frac{T_g(K)}{T_i(K)}$

Disc-like mesogenic units

Low molar mass discotic liquid crystals - based on disc-like mesogens - have only been discovered in the last ten years (ref. 9). Their mesophases are different from the mesophases formed by rod-like mesogens (calamitic phases). The nematic discotic phase resembles the nematic calamitic phase: the only order is the differentially parallel orientation of the molecules. Instead of the layered smectic phases, the discogens form columnar phases: the molecules are stacked in columns which are packed into 2-dimensional lattices (ref. 10).

In principle, side group and main chain discotic polymers illustrated in Fig. 1 for rod-like mesogens can be envisaged for disc-like mesogens and both have indeed been synthesized (refs. 11, 12).

Fig. 5 shows two examples for discotic side group polymers with triphenylene derivatives as mesogens.

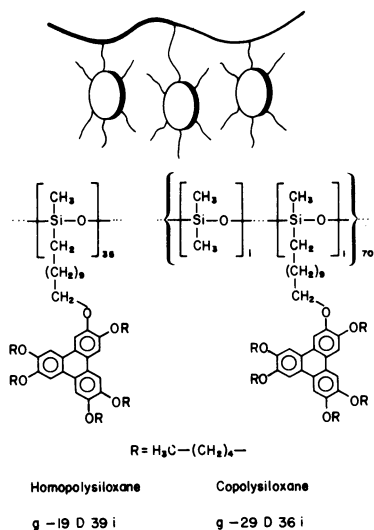


Fig. 5. Liquid crystalline side group polymers with disc-like mesogenic units

TABLE 4. Liquid crystalline main chain polymers with disc-like mesogenic units

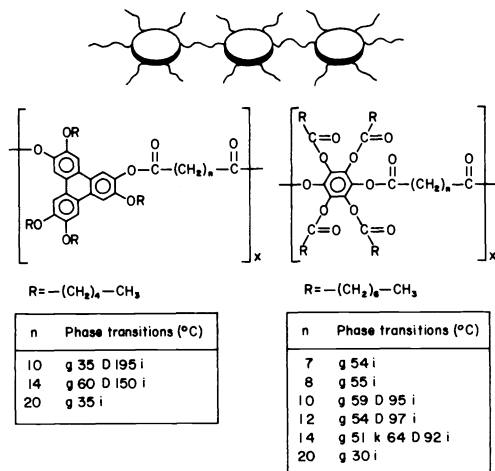
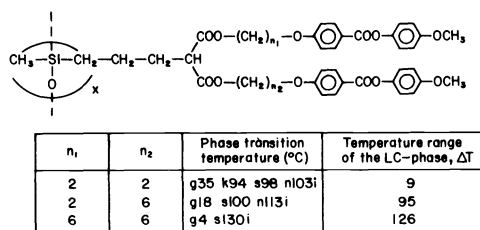


TABLE 5. Liquid crystalline side group polymers with paired mesogens



The copolysiloxane is an additional example for the concept of reducing the glass transition temperature of side group polysiloxanes via "dilution": this means introduction of non-mesogenic monomer units (ref. 13). In Table 4 two series of discotic main chain polymers are given. In both cases the discotic phases of the polymers are much wider than in comparable low molar mass discotic liquid crystals. An optimal spacer length exists for the polymers with benzene as discogen around 12 CH_2 -groups above and below which the phase width decreases.

VARIATION OF THE STRUCTURAL PRINCIPLE

Polymers with paired mesogens

In liquid crystalline side group polymers each monomer unit usually carries one mesogenic side group. In comparison to the corresponding monomers the width of the mesophases usually is increased in the polymers. The formation of mesophases may even be more favored when one monomer unit carries more than one mesogenic side group (ref. 14).

Table 5 shows an example for the realization of liquid crystalline side group polymers with paired mesogens. The phase width depends critically on the relative and absolute lengths of the two spacers (n_1 and n_2), broad mesophases can be realized.

The enhancement of mesophase formation by pairing the mesogens is illustrated by "diluted" systems. In Fig. 6 monomesogenic and paired-mesogenic copolysiloxanes are compared. The dilution lowers the glass transition temperatures. In the case of the monomesogenic copolymer the clearing temperature is also strongly depressed by dilution: at a dilution of 1:10 the mesophase disappears. By pairing the mesogens, however, the mesophase can be retained virtually unchanged up to very high dilution (1:30).

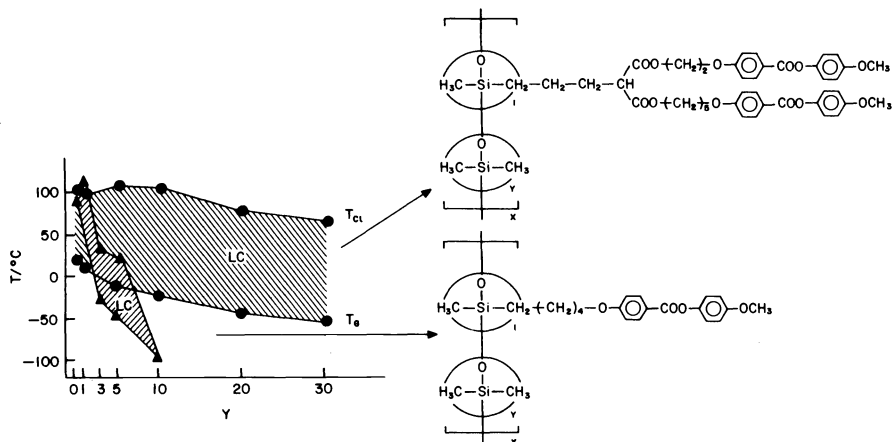


Fig. 6. Comparison of monomesogenic and paired-mesogenic side group polymers

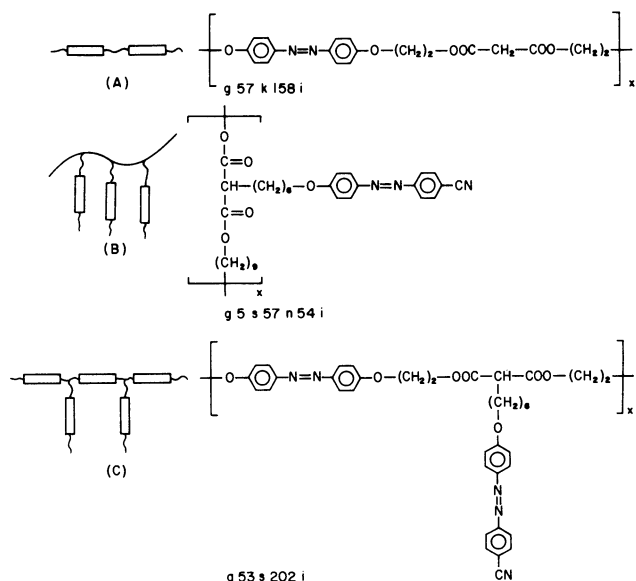
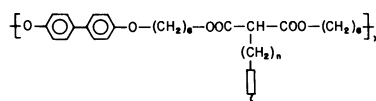


Fig. 7. From main chain and side group systems to combined liquid crystalline polymers

TABLE 6. Combined main chain and side group liquid crystalline polyesters



Structure	n	Phase transitions (°C)
—	—	g 97 s ₁ 26 s ₂ 35 s ₃ 47 i
—	10	g 72 s ₁ 20 s ₂ 36 s ₃ 54 i
—O-C ₆ H ₄ -N=N-C ₆ H ₄ -OCH ₃	6	k ₁ 108 k ₂ 112 s ₁ 131 s ₂ 136 n 155
—O-C ₆ H ₄ -N=N-C ₆ H ₄ -CN	2	k ₁ 109 k ₂ 120 n 153 i
—O-C ₆ H ₄ -N=N-C ₆ H ₄ -CN	6	g 61 s ₁ 112 s ₂ 184 i

Combined main chain and side group polymers

What will happen if the two structural principles of main chain and side group liquid crystalline polymers (see Fig. 1.) are combined within one molecule (ref. 15)?

The main chain polymer in this series (A) exhibits no mesophase. Polymer (B) is an example for a new class of liquid crystalline side group polymers with polyester main chain. The combined polymer (C) forms a very broad liquid crystalline phase. In Table 6 a series of combined polymers is shown. In general they resemble the main chain polymers in that they show a tendency towards the formation of several smectic phases, but nematic phases are encountered, too. Again the phase behaviour depends on the spacer length and broad liquid crystalline phases can be realized pointing towards a cooperative arrangement of the mesogenic units in the main chain and in the side groups.

In stretched polymers, however, the two types of mesogens are ordered perpendicular to each other leading to biaxially oriented fibres.

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