



# **The Development of Side-chain Liquid Crystalline Polymres**

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## The Development Of Side-chain Liquid Crystalline Polymers

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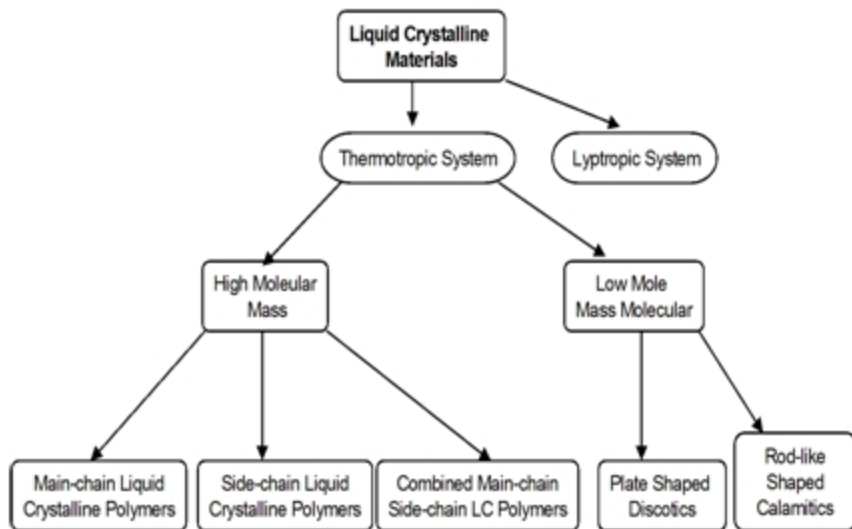
6.

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# Liquid crystal “Family Tree”





## THE NATURE OF LIQUID CRYSTALS

**Liquid** crystals are anisotropic materials whose flow properties strongly depend on their structure and molecular orientation. Molecules in the crystalline solid state are positional and orientation ordered in three dimensions, but in the isotropic liquid state this ordering is completely destroyed. Whereas LCs exhibit a degree of macroscopic orientation order that is found between the boundaries of the crystalline solid state and the isotropic, ordinary liquid, state.



**Crystalline**

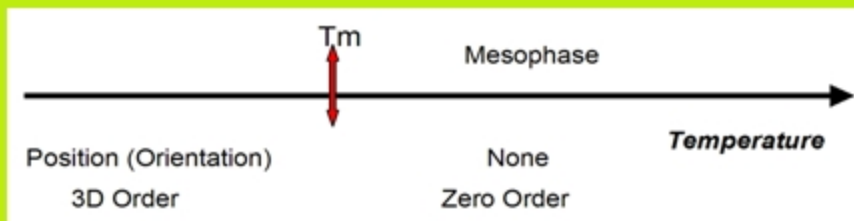


**liquid crystalline**

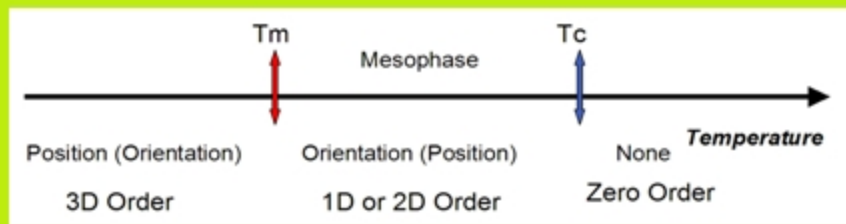


**isotropic liquid**

**Figure 1 Schematic representation of molecular order**



**Figure 2 Ordinary solid-isotropic liquid transition**



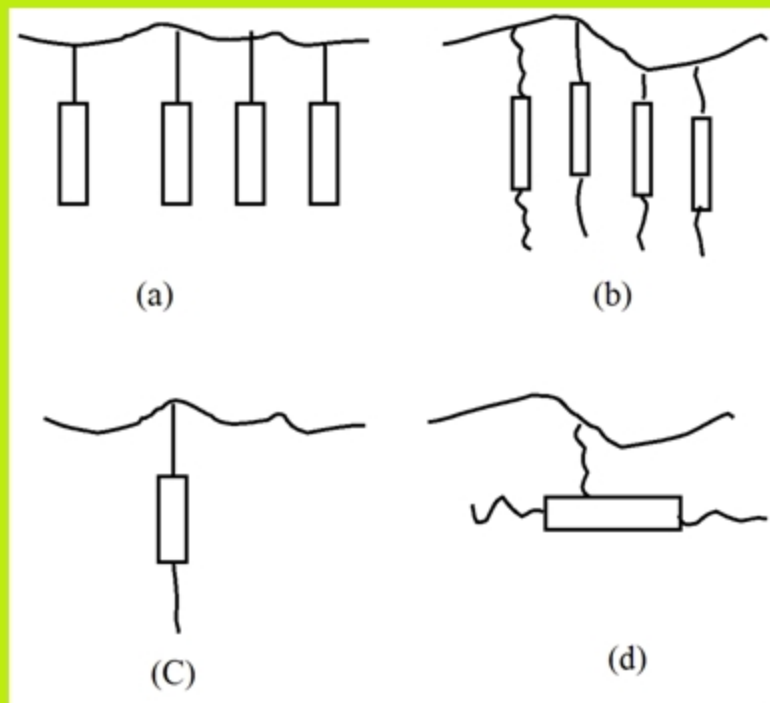
**Figure 3 Thermotropic liquid crystalline transition**





## TYPICAL MOLECULAR STRUCTURES

SCLCPs polymers have the mesogenic moieties attached as side groups or chains along the polymer backbone, like teeth on a comb. In SCLCPs the mesogenic groups are linked directly to an existing polymer backbone or via a flexible spacer. Nevertheless, when the mesogenic core ordering is sufficiently strong to overcome the normal barriers associated with the random-coil conformation of the backbone, the polymer should exhibit LC properties. Decoupling of the side groups by using a flexible spacer allows the main chain motions to occur without disturbance of the anisotropic arrangement of the side chains. The polymer then may exhibit LC phases.



**Figure 4** SCLCPs containing rod-like mesogens



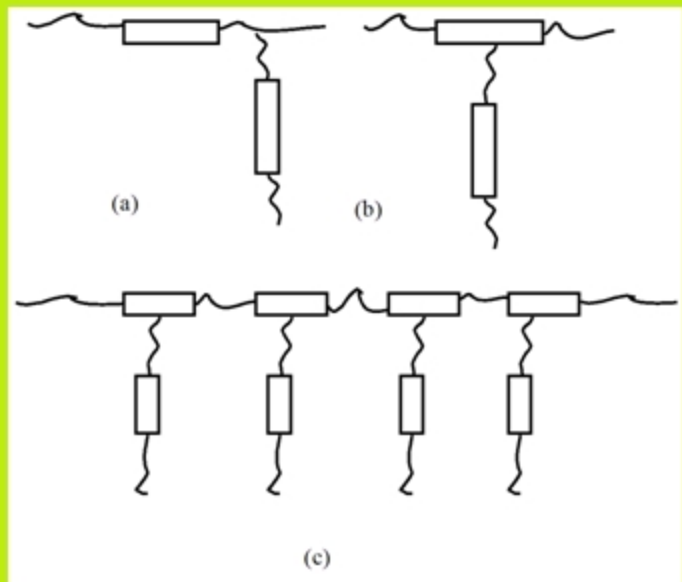


Figure 5 Combined liquid crystalline polymers containing mesogenic units in the main chain and as side groups

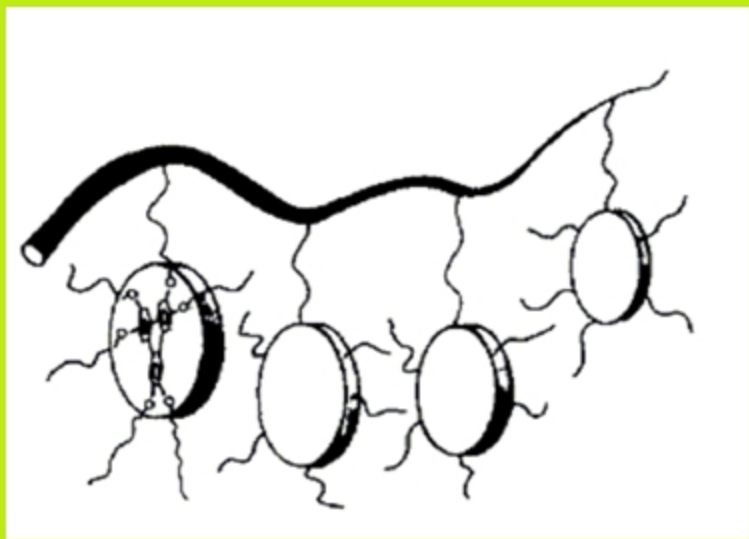


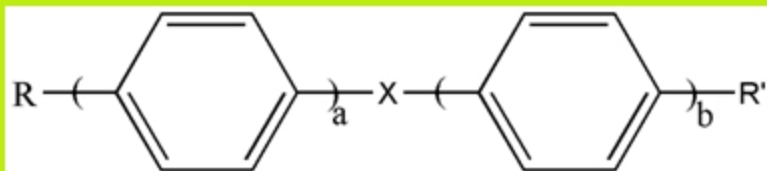
Figure 7 SCLCPs containing disc-like mesogens





# Mesogens

The vast majority of mesogens that give LCs on heating are based on 'rod-like' molecules. The mesophases formed by these molecules were initially studied largely by organic chemists particularly interested in the relationships between the chemical constitutions of the mesogens and the types and temperature of the pure mesophases. p-Azoxyanisole (Figure. 9) is a typical LC compound with a nearly linear structure. From a steric point of view, the rigid rod of length is about 20 Å and width is about 5 Å.



- (1) Where R and R' represent a range of terminal substituents such as alkyl, alkoxy and cyano;
- (2) a, b have small integral values ;
- (3) X represents a linking unit in the core structure  
 (— CH=N — ; — N=N — ; — COO — ; — CH=CH —  
 — C≡C —)

Figure 9 Typical LC compound with a nearly linear structure

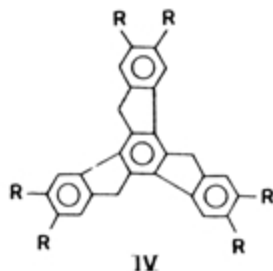
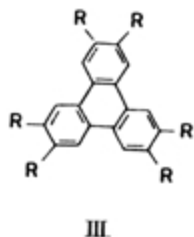
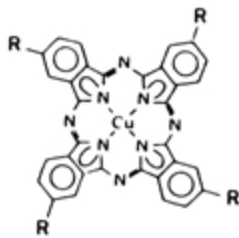
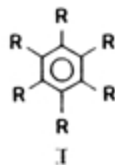


Figure 10 Disc-like mesogens (Perronet et al. 2004; Lee et al. 2004b; Monobe et al. 2003)



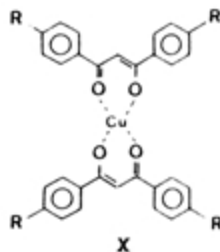
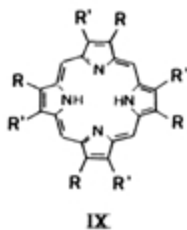
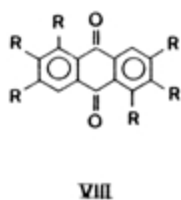
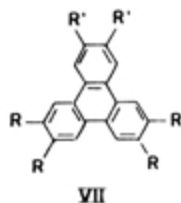
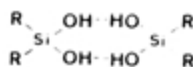
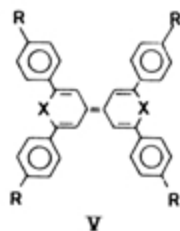


Figure 11 Disc-like with binary thermally averaged (Dubois et al. 1984)

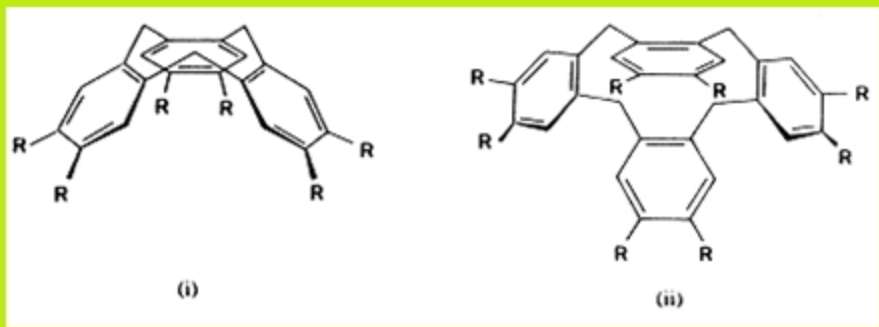


Figure 12 Pyramid-like mesogens (Zimmermann et al. 1985, 1986).

# The Synthesis of SCLCPs

1

**Chain  
polymerisation  
reactions**

2

**Step  
polymerisation  
reactions**

3

**Polymer  
homologous  
reactions**

4

**Noncovalent  
interaction**



## 一、 Chain polymerisation reactions

Therefore, the most convenient method to polymerise mesogenic monomers is by radical initiation.

1、 Monomers containing mesogenic groups are most frequently synthesized as methacrylates, acrylates, acrylamides, chloroacrylates and styrene derivatives

2、 Therefore, the most convenient method to polymerise mesogenic monomers is by radical initiation. However, in order to obtain different tacticity and molecular masses, and narrow molecular mass distributions, methacrylate, acrylates and styrene derivatives could be suitably polymerised anionically

3、 The cationic polymerization of nucleophilic olefins and heterocyclic monomers offers additional synthetic avenues to vary the nature of the polymer backbone and to eventually achieve living polymerizations.

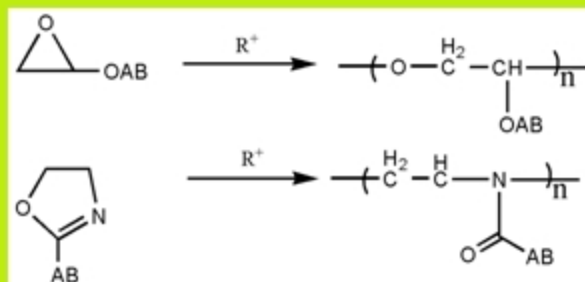
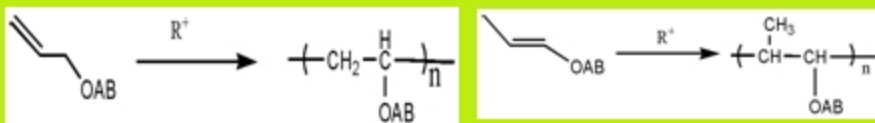
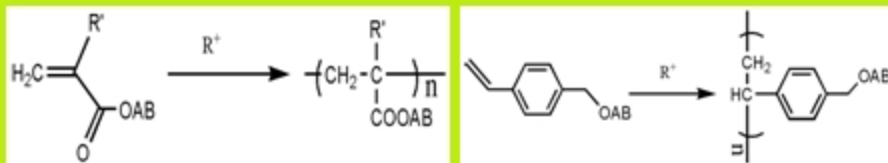


Figure 13 Polymerisation of some representative classes of monomers containing mesogenic groups.

A decorative border on the left and right sides of the slide features a field of pink flowers with dark brown centers, likely Echinacea, growing on green stems. The background of the slide is a solid light blue color.

## 二、 Step polymerisation reactions

A large variety of side chain liquid crystalline polyesters containing mesogenic side groups were successfully synthesized in the recent decades after the first polyester was synthesized by Ringsdorf and co-worker

One synthetic route is to attach the mesogenic side group to a monomer such as a substituted malonate derivative that gives raise to the flexible spacer, and then polyesterifying it with a diol or with a diol containing a mesogenic unit. Alternatively, the mesogenic side groups can be attached to hydroquinone, and then condensed with either a flexible or a rigid dicarboxylic acid. These two routes allow insertion of the pendant mesogenic side groups into either a flexible or a rigid structural unit (Figure 14).



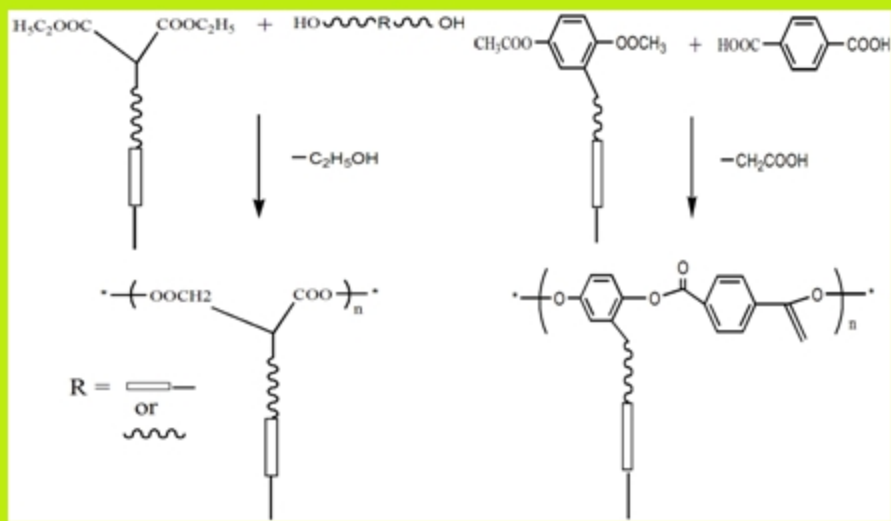


Fig 14 Synthesis of combined side chain liquid crystalline polyesters.



### 三、 Polymer homologous reactions

1、 The two organic reactions frequently used to synthesize side chain crystalline polymers by polymer homologous reactions: Nucleophilic displacement and Hydrosilation.

2、 Nucleophilic displacement reactions can be further divided into two categories. The first consists of reactions performed on a polymer backbone containing electrophilic side groups, which are displaced by mesogenic units containing a nucleophilic at the opposite end of the spacer.

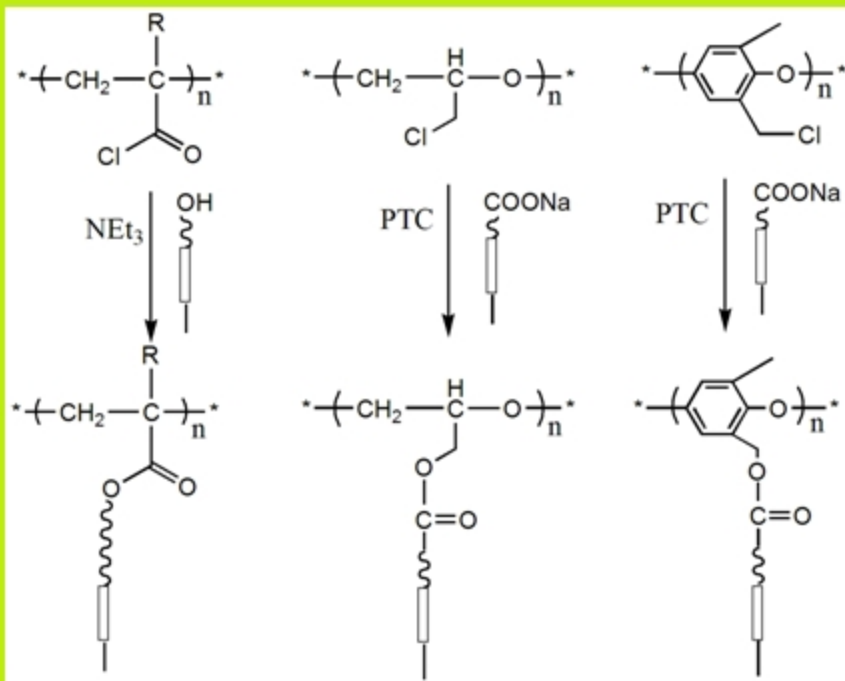


Figure 15 Synthesis of some liquid crystalline polymers by polymer homologous reactions (R = H or CH<sub>3</sub>, PTC = phase transfer catalyst).

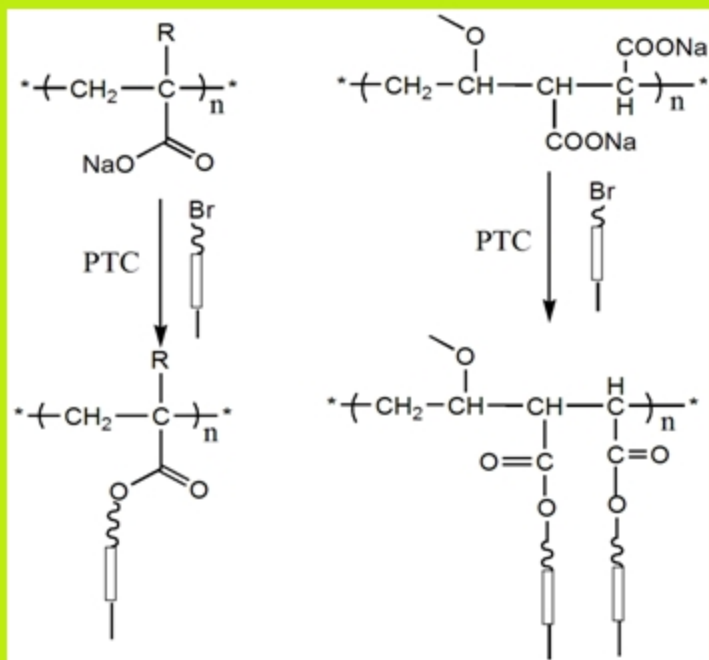


Figure 2.16 Synthesis of polyacrylates (R = H), polymethacrylates (R = CH<sub>3</sub>), poly(methylvinylether-co-maleate)s and polyitaconates by phase transfer catalysed (PTC) esterification.

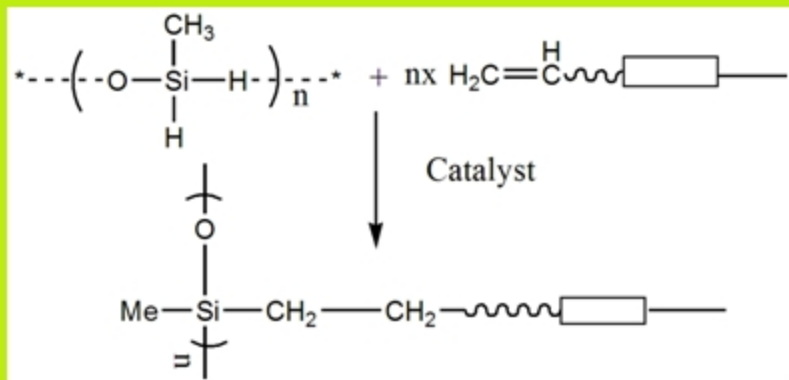


Figure 17 Synthesis SCLCPs by hydrosilylation reaction



## 四、 Noncovalent interaction

- 1、 Noncovalent interaction (as shown in Figure 1.1), such as hydrogen bonding, is a powerful tool to create novel structures of molecular self-assemblies
- 2、 H-bonding interaction is one of the most important and widely used non-covalent interaction in the design and construction of supramolecular architectures.
- 3、 Carboxylic and benzoic acid groups are widely used as hydrogen bonding donors while pyridine moieties are commonly used as hydrogen bonding acceptors.





## **MESOPHASES of LIQUID CRYSTALS**

- 1. Mesophases formed on heating such compounds are classified into three types: nematic, smectic, and cholesteric.**
- 2. There are more than ten recognized smectic modifications and these denoted are SA, SB, SC — SL.**
- 3. A description of the structural features of these phases may be found in standard books and reviews**