Chapter 7. Polymers in the Liquid Crystalline State

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- 7.4.2. Importance of χ_1 parameter

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7.1. Definition of Liquid Crystal

- **Liquid Crystals**

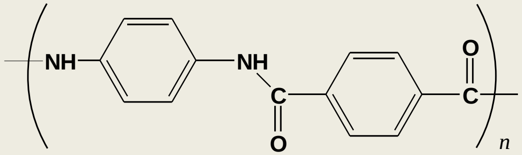
: substances that exhibit long-range order in one or two dimensions, but not all three.

: lie in-between of amorphous and crystalline in properties

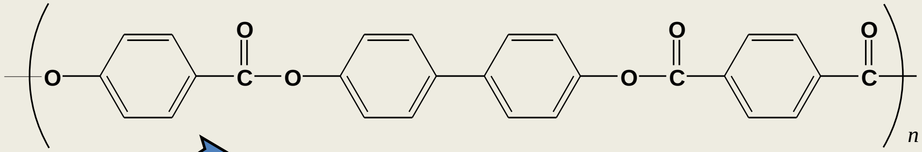
: direct consequence of molecule asymmetry. It arises because two molecules cannot occupy the same space at the same space time and is largely entropically derived.

: For new classes of high-modulus fibers, high-temperature plastics and a host of new electronic and data storage materials

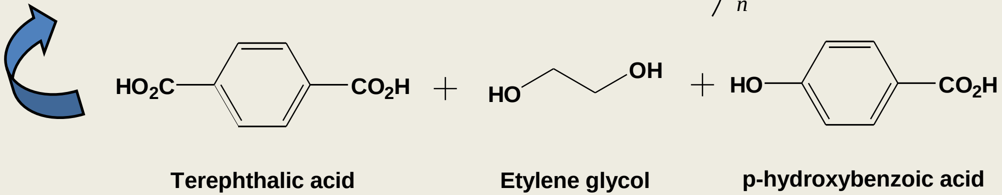
- **Rod-Shape Chemical Structures**



Poly(*p*-phenylene terephthalamide) : Kevlar® by du Pont



Copolyester



7.2. Liquid Crystalline mesophases

7.2.1. Mesophase topologies

Nematic : 1D organization of molecules

: with their chains lying parallel to each other at equilibrium

Smectic : ordered in 2D (exist a large number of smetic mesophases

Cholesteric : 2D twisted nematic mesophase

Discotic : like stacks of dishes or coins

- Some LC chemical structures
  → Fig 7.2

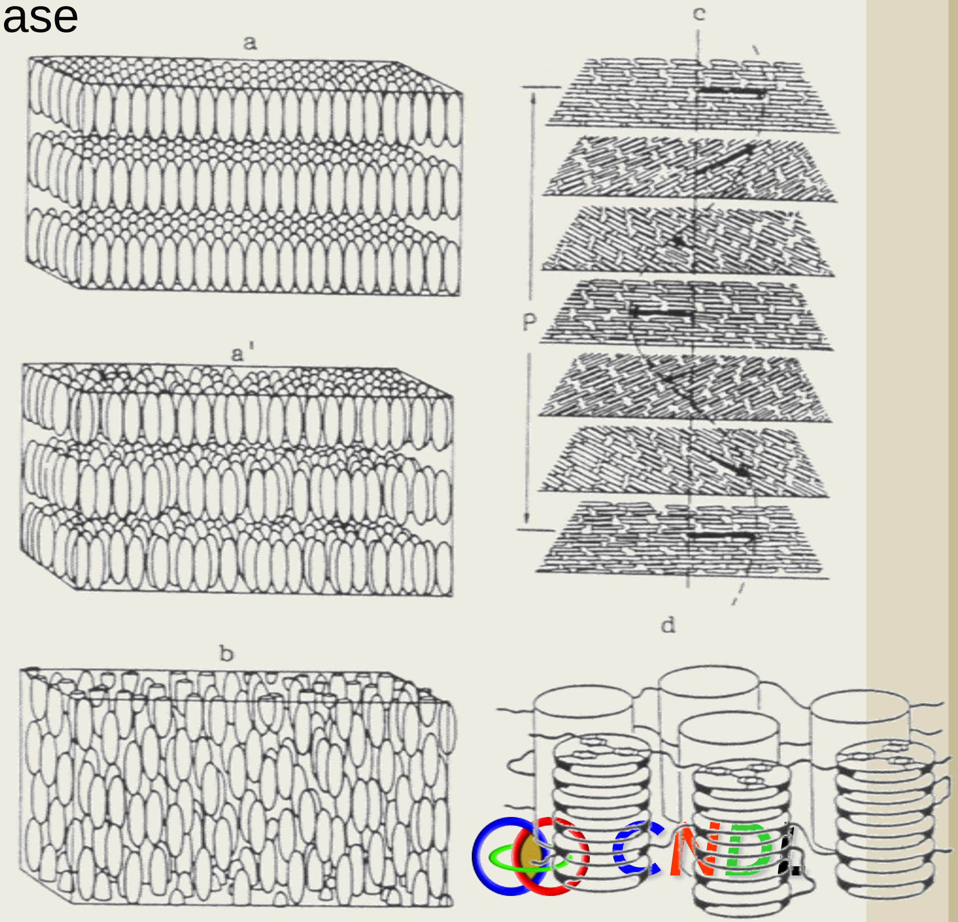
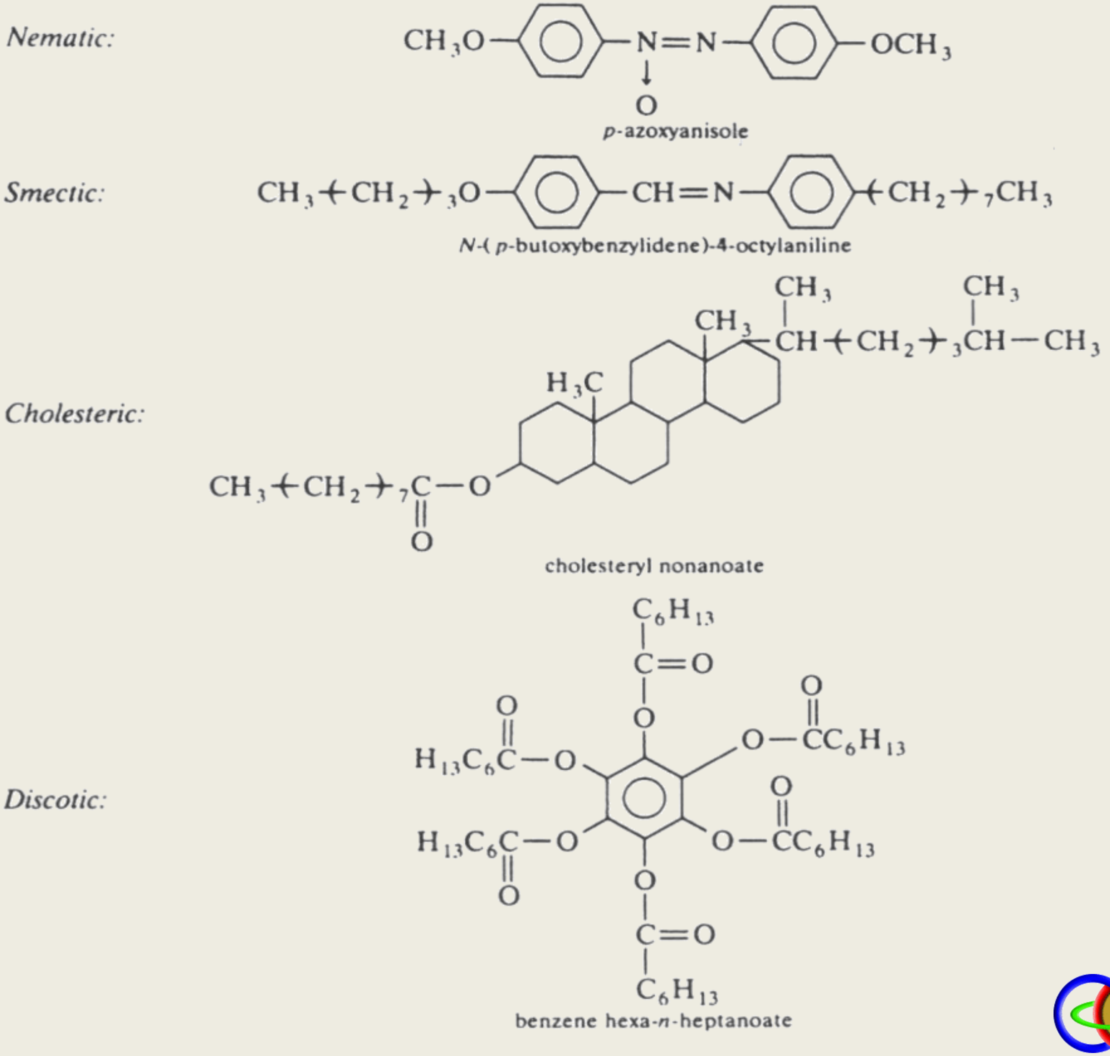


Fig.7.1 Schematic representation of the different types of mesophases: Smetic with ordered (a) and unordered (a'); (b) nematic; (c) cholesteric; and (d) discotic

7.2. Liquid Crystalline mesophases

Fig. 7.2 Asymmetric organic molecules in the form of rods or plates may form liquid crystal structures

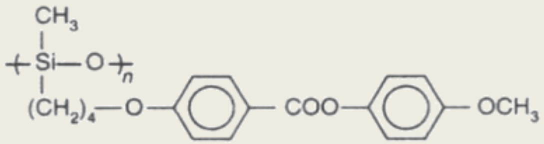


7.2. Liquid Crystalline mesophases

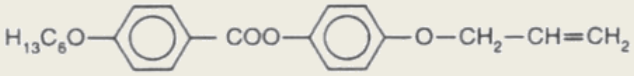
7.2.2. Phase diagrams

- Note that the monomer by itself crystallizes.
- The nematic mixure clears in the temperature range of 360 to 370 K

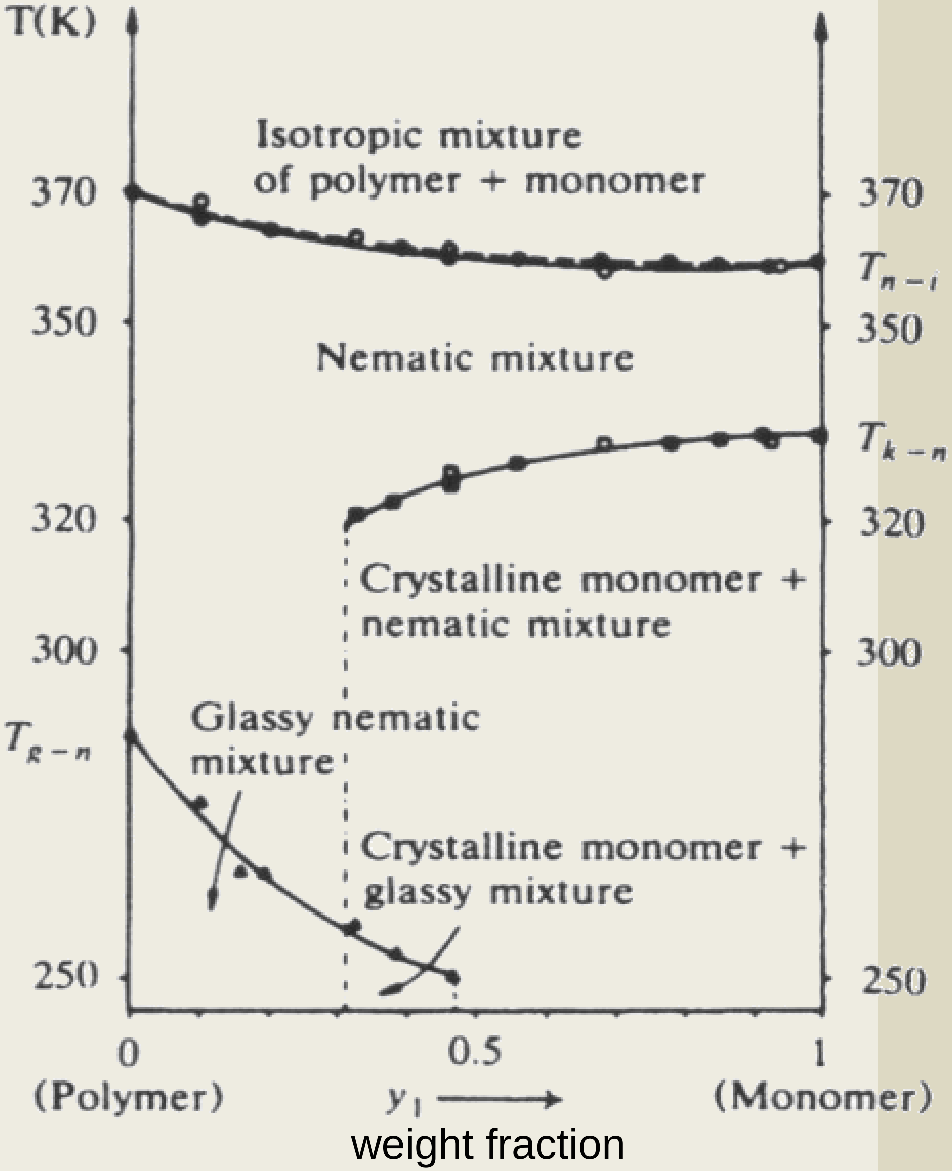
Fig. 7.3 Phase diagrams illustrate the expected behavior of a material as a function of temperature and composition. Here, a mixture of polymer



and the monomer



- filled symbols : DSC measurement
- open symbols : polarizing microscope



7.2. Liquid Crystalline mesophases

7.2.3. First-order transitions

※ LC - forming polymer may exhibit multiple mesophases at different Ts or Ps.
As T↑, the polymer goes through multiple first order transitions.

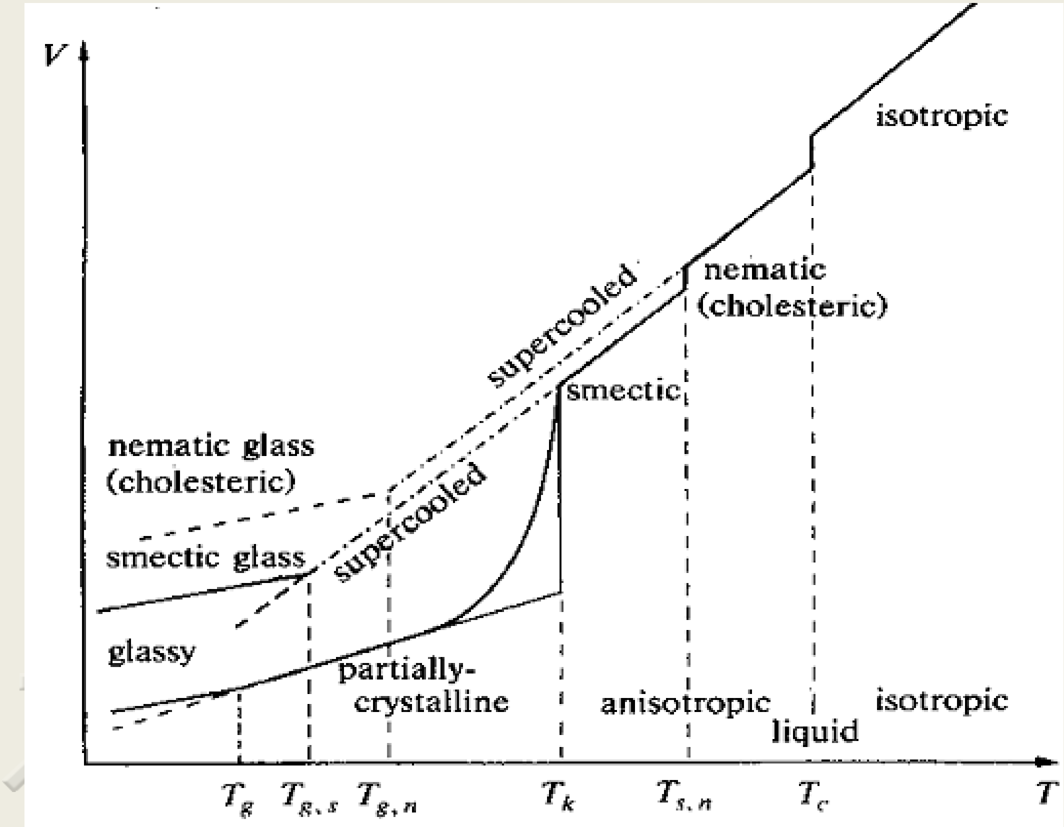
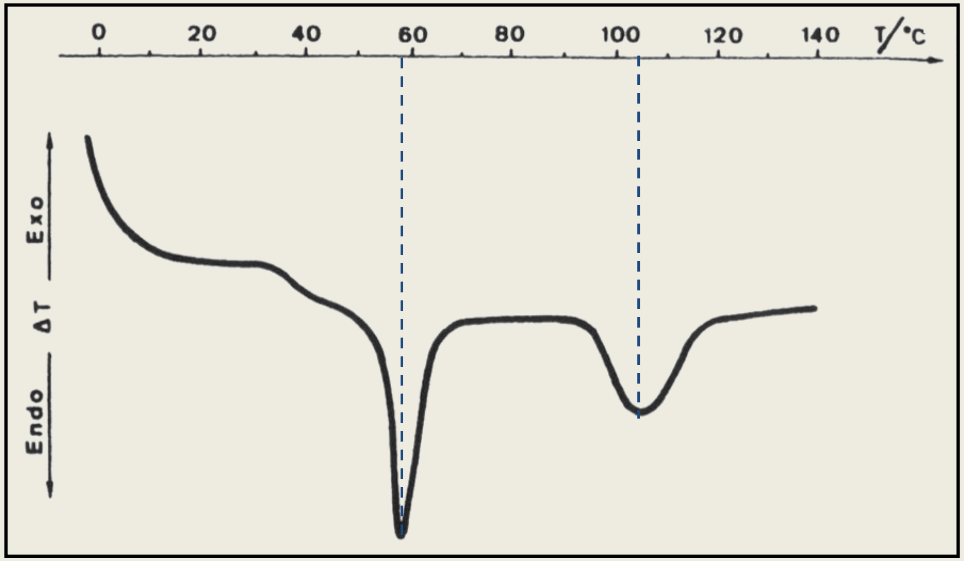


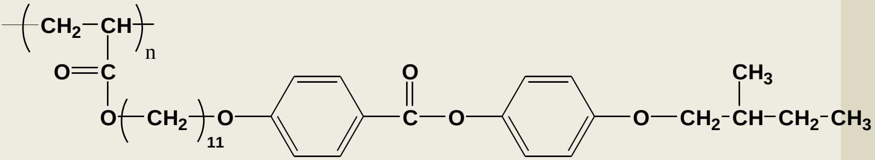
Fig. 7.4 Liquid crystal-forming polymers may undergo many first-order transitions. Here, as the temperature is raised, the polymer first melts to a smectic structure, then to a nematic structure, and then to an isotropic melt.

7.2. Liquid Crystalline mesophases

- The nature of the first-order transitions is best illustrated by observing the behavior of these materials in a differential scanning calorimeter (DSC).

Fig. 7.5 DSC heating trace of an acrylic, liquid crystal-forming polymer.
Note two first-order transitions.





- The presence of multiple endotherms provides direct evidence of the multiplicity of first-order transitions in this polymer.
- T_m=59℃→ Smetic phase (*via* microscopy)
- Near 100℃→ transform to a cholesteric phase (however, the isotropic melt phase appears at same temperature)
  → heating the polymer at a slower rate
  → separate the transitions

- Not all polymers go through LC mesophases.
- Polymers that form random coils melt directly to the isotropic liquid state.
- Some portion of the chain or side chain must be rod- or disk-shaped to form a LC mesophase.

7.3. Classification of Liquid Crystal

┌ Lyotropic - in concentrated (~ 30%) solution
│ Thermotropic - in melts
└ Mesogenic side group compositions - random coil backbone rod shaped side group
(subclass of thermotropic LCs)

7.3.1. Lyotropic Liquid Crystalline Chemical Structures

- Form nematic mesophases
- Aromatic polyamides with aromatic ring structures, as shown in Table 7.1
- Heterocyclic polymers yield materials with outstanding high-temperature performance (see Table 7.2).→have ladder or semi-ladder chemical structures
- Some natural polymers → include cellulose derivatives

7.3. Classification of Liquid Crystal

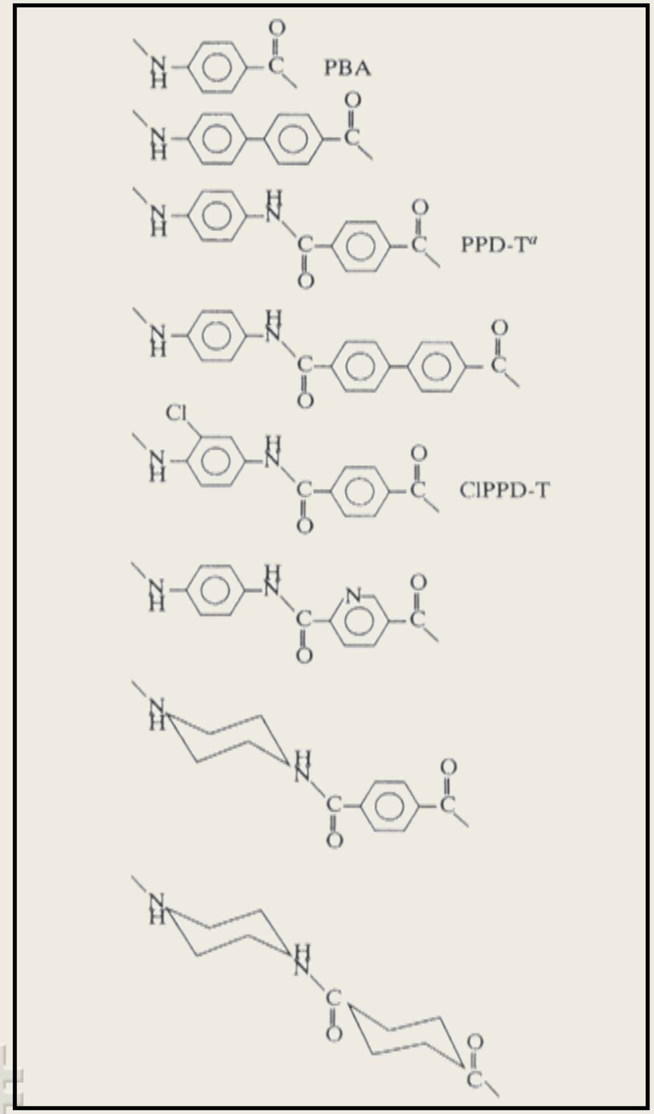
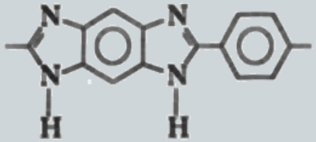
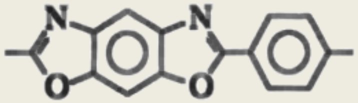
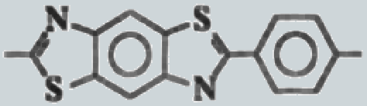
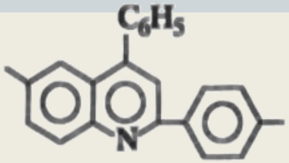
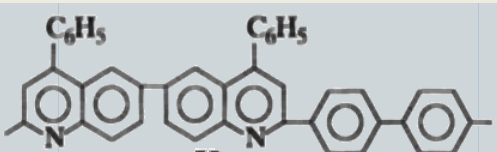
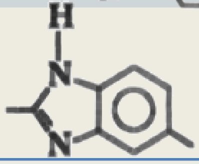


Table 7.1 Important polyamides yielding liquid crystalline mesophase

[a]The basis for the fiber "Kevlar®, widely used for bullet-proof jackets, parachutes, etc.

7.3. Classification of Liquid Crystal

Table 7.2 Lyotropic solutions of polyheterocyclic compounds

Compound	Structure	Lyotropic Solvent	Reference
Poly(1,4-phenylene-2,6-benzobisimidazole)		Methanesulfonic acid	(a)
Poly(1,4-phenylene-2,6-benzobisoxazole) (PBO)		Methanesulfonic acid Chlorosulfonic acid 100% sulfonic acid	 (b,c) (d)
Poly(1,4-phenylene-2,6-benzobisthiazole) (PBT)		5-10% in polyphosphoric acid Methanesulfonic acid	(e) (c,d,f)
Poly[2,6-(1,4-phenylene)-4-phenylquinoline]		1.0-1.5% in *m*-cresol-di-*m*-cresyl phosphate	(g)
Poly[1,1'-(4,4'-biphenylene)-6,6'-bis(4-phenylquinoline)]		>9% in *m*-cresol-di-*m*-cresyl phosphate	(g)
Poly[2,5(6)-benzimidazole] (AB-PBI)		Methanesulfonic acid	(h)

References: (a) T. E. Helminiak, F. E. Arnold, and C. L. Benner, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **16** (2), 659 (1975). (b) G. C. Berry, P. M. Cotts, and S.-G. Chu, *Br. Polym. J.*, **13**, 47 (1981); C. P. Wong, H. Ohnuma, and G. C. Berry, *J. Polym. Sci. Polym. Symp.*, **65**, 173 (1978). (c) J. F. Wolfe, B. H. Loo, and F. E. Arnold, *Macromolecules*, **14**, 915 (1981). (d) E. W. Choe and S. N. Kim, *Macromolecules*, **14**, 920 (1981). (e) J. F. Wolfe, B. H. Loo, and E. R. Sevilla, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **22** (1), 60 (1981). (f) S.-G Chu, S. Venkatraman, G. C. Berry, and Y. Einaga, *Macromolecules*, **14**, 939 (1981). (g) P. D. Sybert, W. H. Beever, and J. K. Stille, *Macromolecules*, **14**, 493 (1981). (h) A. Wereta Jr. and M. T. Gehatia, *Polym. Eng. Sci.*, **18**, 204 (1978).

7.3. Classification of Liquid Crystal

7.3.2. Thermotropic Liquid Crystalline

- Aromatic copolyesters
- Some homopolymer aromatic polyesters → too high a melting temperature to form thermotropic mesophases without decomposition
  → copolymerization reduces melting temperatures

- Several techniques to reduce the melting temperature

① Copolymerization of several mesogenic monomers, which produces random copolymers with depressed melting temperature.

② Use of monomers with bulky side group, which prevents close packing in the LC mesophase, sometimes referred to as "frustrated chain packing".

③ Use of best comonomers to interrupt the order in the system

④ Incorporation of flexible spacers, to decrease rigidity.

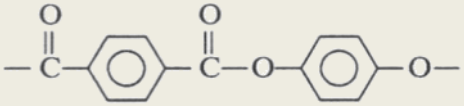
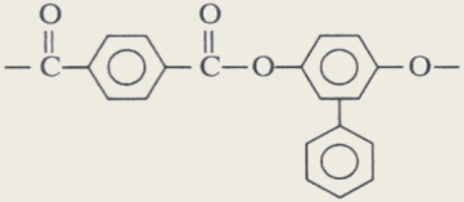
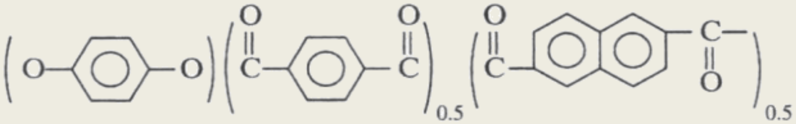
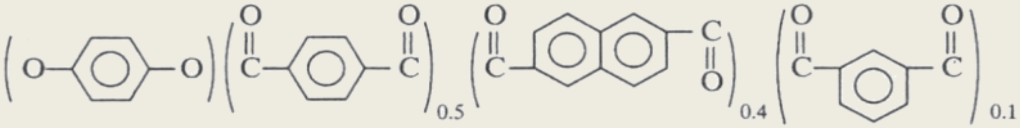
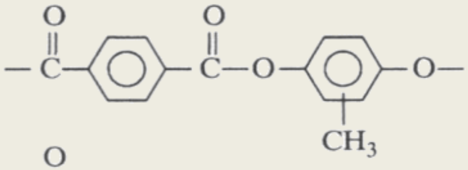
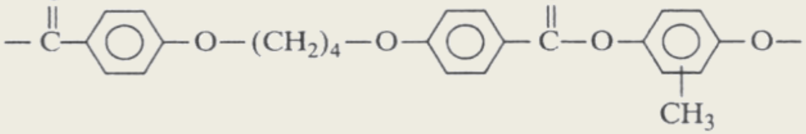
(└→Tg↓, solubility↑)

This permits the development of bends or elbows in the chain.

- Both Lyo- and Thermo- LCs are highly crystalline in actual usage, going from the LC to the crystalline state by either removing the solvent or cooling the system
  → However, the side-chain mesogenic materials usually remain in the LC state for their intended use.

7.3. Classification of Liquid Crystal

Table 7.3 Melting point versus structure for selected thermotropic LC polyesters

Bulky side group	*T (melting) °C*
	>600
	≈340
Bent monomer	*T (melting) °C*
	≈400
	≈350
Flexible group	*T (melting) °C*
	>400
	≈210

7.3. Classification of Liquid Crystal

- Flexible spacers placed in the main chain achieve both improved solubility and the lowering of transition temperatures.
- The flexible spacer may be hydrocarbon based, as in Table 7.3

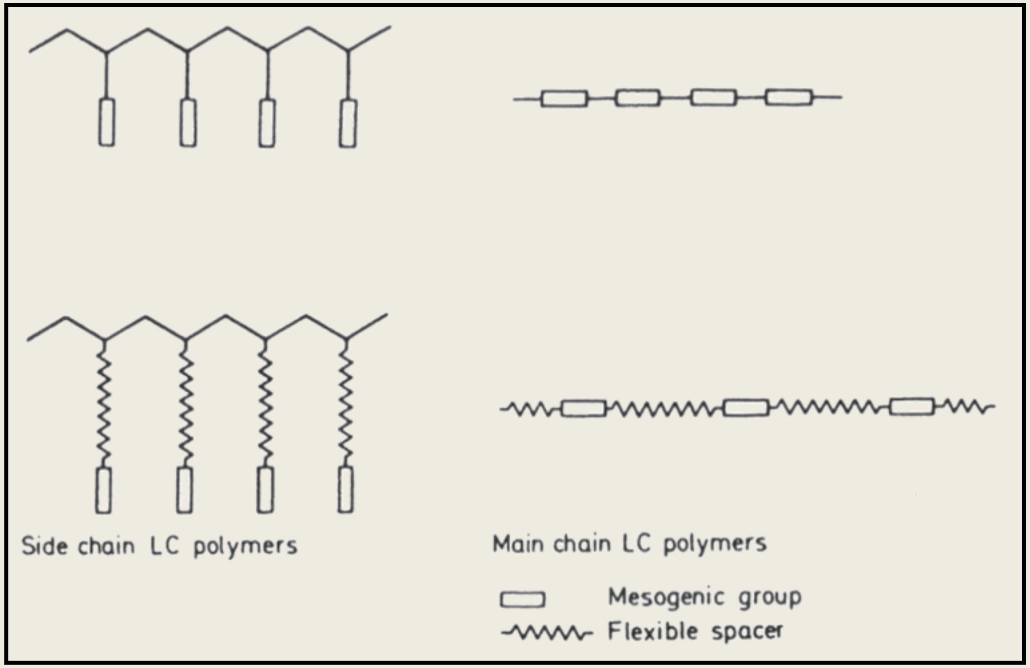


Fig. 7.6 One way of classifying thermotropic LC polymers is to examine whether the mesogenic unit is in the main chain or in the side chain

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7.3. Classification of Liquid Crystal

7.3.3. Side-chain Liquid Crystalline

- Polymers here have rod- or disk-shaped side groups placed on ordinary random coil polymers, frequently acrylics or siloxanes (see Table 7.4)
- The first attempts to form side-chain LC structures involved attachment of short rod-shaped moieties directly to the main chain (Fig 7.7) → disappointing
  → the reasons why
  ① T_g of polymers is always at much higher temperatures that for the corresponding polymers without mesogenic side chains
  ② During the polymerization process, the LC packing of the monomers was destroyed by steric requirements.

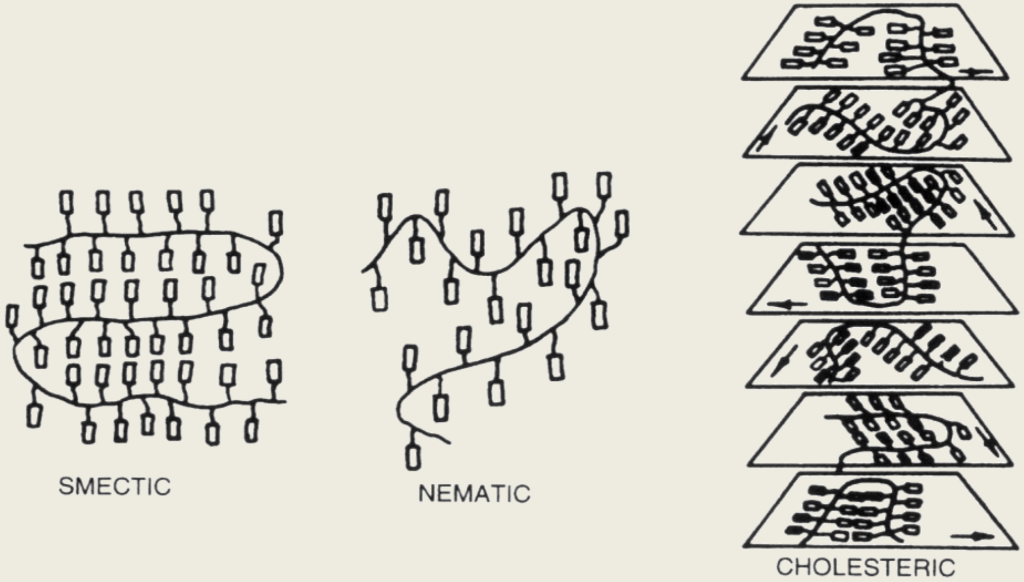
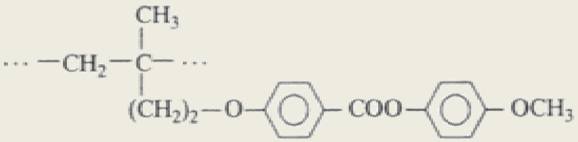
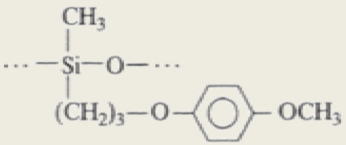
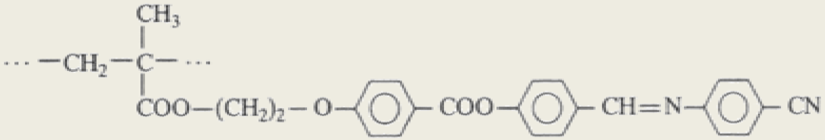
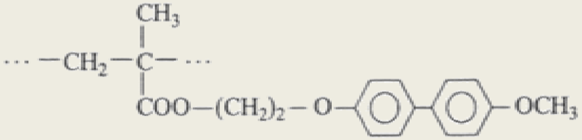


Fig. 7.7 A schematic showing how mesogenic LC side-chain polymers can be organized into different mesophases.

7.3. Classification of Liquid Crystal

Table 7.4 Examples of smectic polymers by lengthening the segments A and B

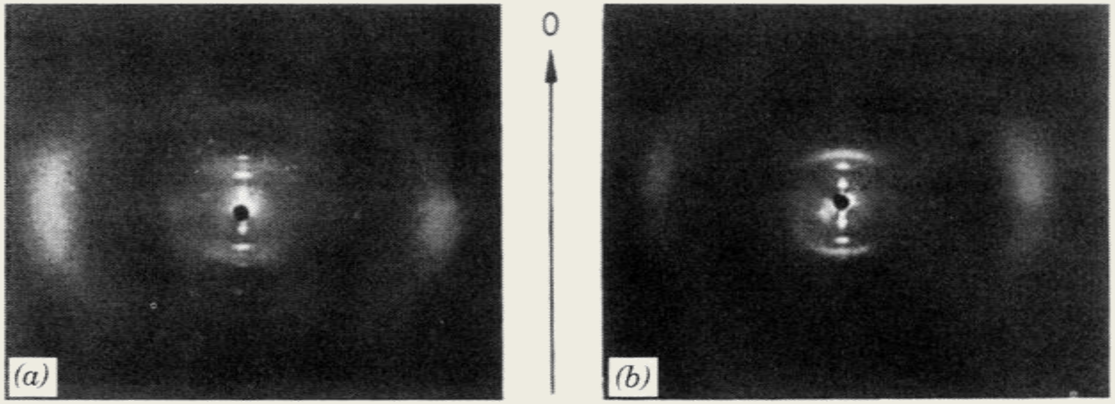
Number	Polymer	*A*	Phase Transitions (K)	$\Delta\tilde{H}_{LC\text{-}i}$ (J/g)
1			g 369, n 394, i	2.3
2		$-OC_6H_{13}$	g 410, s 451, i	11.5
3			g 288, n 334, i	2.2
4		$-OC_6H_{13}$	g 288, s 385, i	11.6

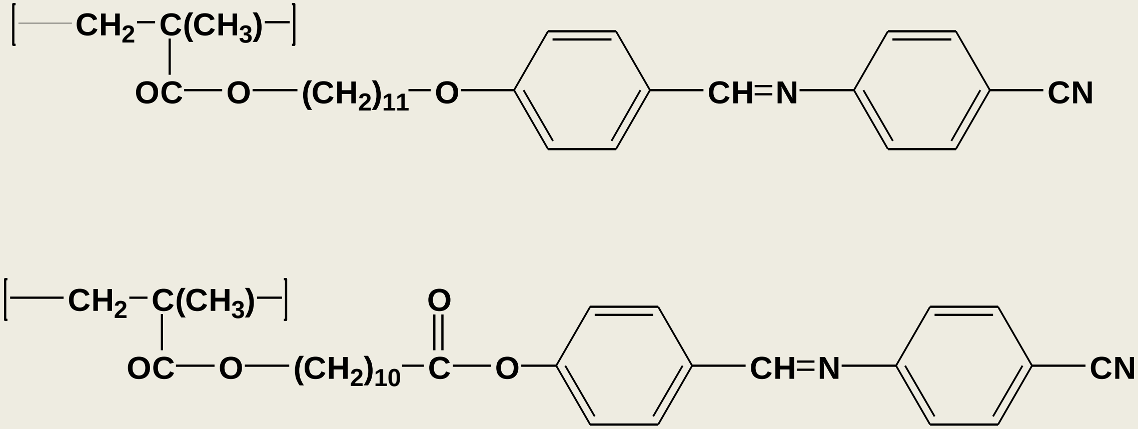
Number	Polymer	*B*	Phase Transitions (K)	$\Delta\tilde{H}_{LC\text{-}i}$ (J/g)
1			g 361, n 580, i	—
2		$-(CH_2)_6$	g 324, s 607, i	—
3			g 393, n, 425, i	2.8
4		$-(CH_2)_6$	g, 119, s 136, i	7.1

7.3. Classification of Liquid Crystal

- The structure of these LC phases was determined by X-ray analysis. (Fig 7.8)

Fig. 7.8 Oriented smectic LC polymers yield very distinctive X-ray patterns. Here, the smectic mesophase (S_A) is shown for polymers having the structures.

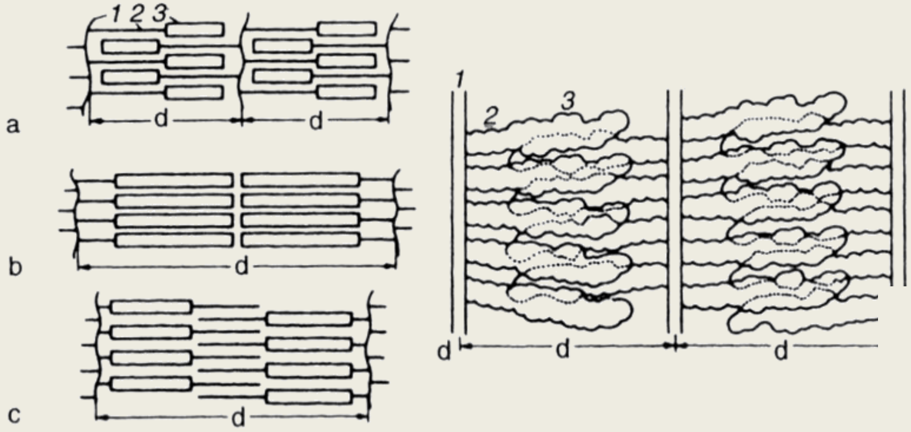




7.3. Classification of Liquid Crystal

- The packing arrangement of these materials is illustrated in Fig 7.9
- The side chains can be arranged in either single-layer or double-layer packing arrangements, Fig 7.9a and b, respectively.
  Packing with partial overlap is also possible; Fig 7.9c and d
- The selection of the probable packing mode was based on the d spacing shown in Fig 7.9, which corresponds to the thickness of the smetic layer.
- In contrast to the backbone types of LC, the side-chain types exhibit neither high modulus nor high strength. →However, provides highly interesting for structual and optical properties (especially as transformed by electric and magnetic fields)

Fig. 7.9 LC side chains can be packed in several arrangements, even considering only the smectic A mesophase: (a) single-layer packing, (b) two-layer packing, (c) packing with overlapping alkyl “tails,” and (d) packing with partial overlapping of the mesogenic side chains. 1, Main chain; 2, spacer; 3, mesogenic group; d, repeat distance, as revealed by X rays.



7.4. Thermodynamics and Phase Diagrams

7.4.1. Historical Aspects

- LCs were first noted for organic molecules about 100 years ago; a peculiar melting behavior of a number of cholesterol esters by Reinitzer. → The crystals of the substances melted sharply to form an opaque melt instead of the usual clear melt.
- Lehmann reported the turbid states between the truly crystalline and the truly isotropic fluid state → introduced the term "Flussige Kristalle", or liquid crystals
- The first polymeric LC : poly(γ-benzly L-glutamate) in 1950

Flory. critical volume concentration $v_2^* = \frac{8}{x}\left(1-\frac{2}{x}\right)$

where χ : no. of isodiametric segments

→ axial ratio of the molecule

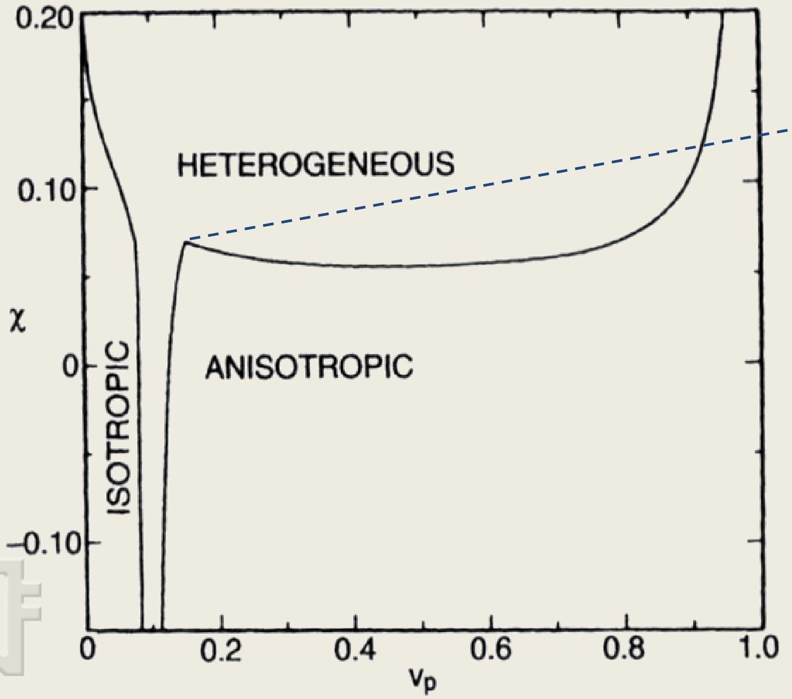
: a transition from complete disorder to partial order was predicted to occur abruptly and discontinuously.

for high χ, $\upsilon_2^* = \frac{8}{\chi}$

7.4. Thermodynamics and Phase Diagrams

7.4.2. Importance of χ_1 parameter

- The statistical thermodynamic theory described above pertains to rods devoid of interactions other than the short-range repulsions, which preclude intrusion of one rod on the space occupied by another.
  → theoretical deductions stem solely from the geometrical aspects of the molecules
- Introduction of the polymer-solvent interaction parameter χ_1, for lyotropic systems
  → Fig 7.10



(-) χ_1 value does not affect the biphasic gap.

(+) χ_1 value, critical volume exists at =0.055

χ_1 =0.070 : triple point

- dilute isotropic
- dilute anisotropic
- concentrated anisotropic

Fig. 7.10 Phase diagram for rods of axial ratio x=100. The positions of the coexisting phases are determined by the value of the parameter χ. The minimum of the shallow concave portion of the diagram is a critical point marking the emergence of two anisotropic phases, in addition to the isotropic phase appearing on the left of the figure.

※ Mesophase Identification in Thermotropic polymers

- A major question in the LC field → the identification of the various mesophases

- Several methods may be used

① Optical pattern or texture observations with a polarizing microscope.

┌ Isotropic liquid - no texture
└ liquid crystals - have the texture

② Nematic and smectic phases can be distinguished by DSC on the basis of the magnitude of the enthalpy changes accompanying the transition to the isotropic phase. → measure $\triangle H_{trans}$

③ Miscibility with known liquid crystals to form isomorphous mesophases.

→ See Fig 7.3

④ Possibilities of inducing significant molecular orientation by either supporting surface treatment or external electrical or magnetic fields.

⑤ Small-angle X-ray to study molecular long-range order

⑥ Small-angle light scattering between crossed nicols

→ different patterns for different mesophases.

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※ Mesophase Identification in Thermotropic polymers

- The most widely used method : optical microscopy (between crossed polarizers) → Identify the appearance of mesophases and transitions between the various mesophases and isotropic materials
- Many LC polymers exhibit *Schlieren* textures : display dark brushes → See Fig 7.11 → correspond to extinction positions of the mesophase
- At certain points, two or more dark brushes meet : disclinations (like dislocations in crystalline solid, where domains of differing orientation melt)
- The disclination strength is calculated from the number of dark brushes meeting at one point:

$$|S| = \frac{\text{number of brushes meeting}}{4}$$

S : positive when the brushes turn in the same direction as the rotated polarizers
: negative when they turn in the opposite direction

$S = \pm \frac{1}{2}$ or ± 1 Nematic (indicated by a mixture of two and four point disclinations)
$S = \pm 1$ Smectic (exhibits only four point diaclinations)

Mesophase Identification in Thermotropic polymers

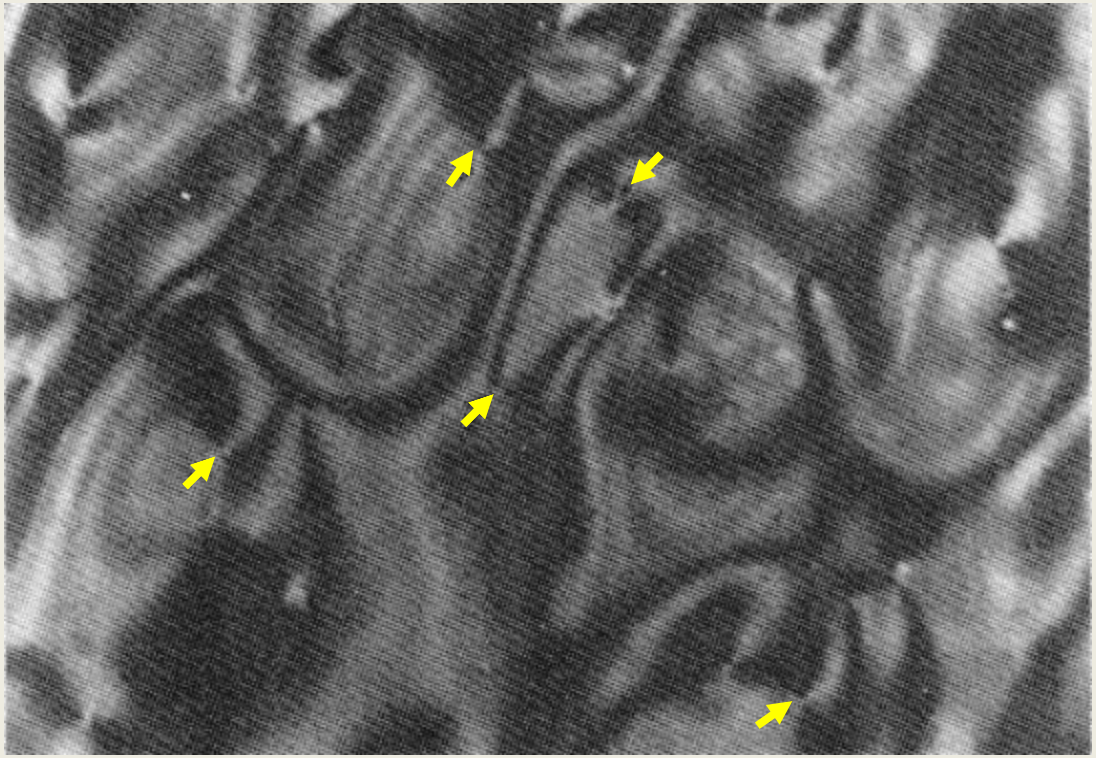
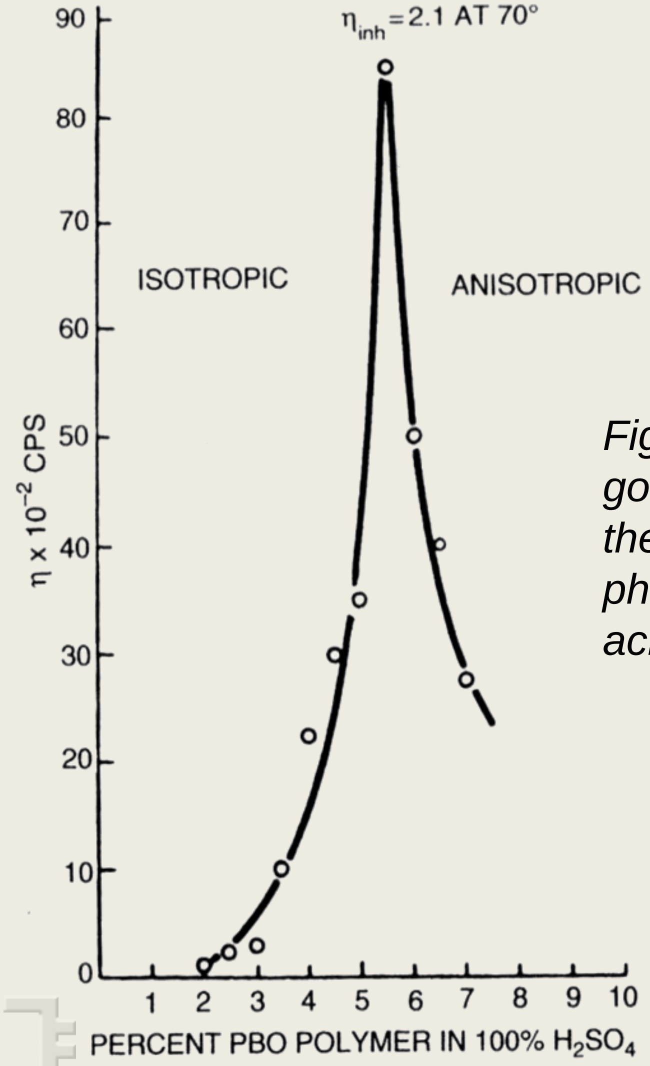


Fig.7.11 Optical microscopy reveals a Schlieren texture for a copolyester formed by the transesterification of poly(ethylene-1,2-diphenoxyethane-p,p'-dicarboxylate) with p-acetoxybenzoic acid. Recognizable singularities S=±1/2 are marked with arrows. Crossed polarizers, 260 ℃, ×200

7.5. Fiber Formation

❑ Viscosity of Lyotropic Solutions



The viscosity of lyotropic solutions in shear flow is lower than that of random coil solutions of the same molecular weight and concentration.

⇒ due to the lack of molecular entanglements in the nematic phase.

Fig. 7.12 The viscosity of rod-shaped polymers usually goes through a maximum as the chains organize from the isotropic state to a mesostate. Data for poly(p-phenylene benzobisoxazole) in concentrated sulfuric acid.

❑ Molecular Orientation

through spinning, shear induced orientation achieved on removing the solvent, polymer crystallizes→ because of the lack of chain foldings and other perfections, the fibers have higher moduli and higher strength.

7.6. Comparison of Major Polymer Types

❑ Molecular conformation

Table 7.5 Comparison of major polymer types

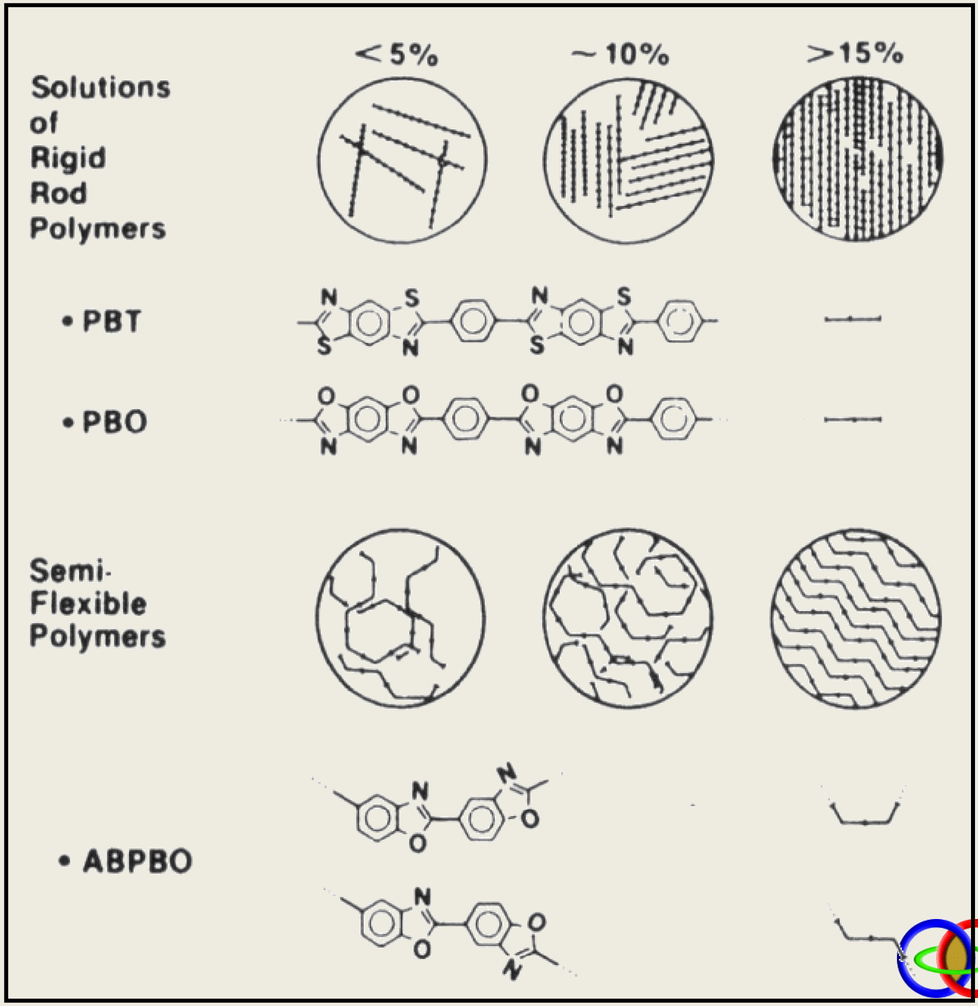
Property	**Rigid Rod**	**Extended Chain**	**Random Coils**
LC v_2* critical concentration, %	4-5	14-15	None
Dilute solution			
conformation	Rod	Worm	Coil
T_g	No[a]	No[a]	Yes
T_f	No[b]	No[b]	Yes
Persistence length, Å	>500	90-130	10
Mark-Houwink *a* value	1.8	1.0	0.5-0.8
Catenation angle, degrees	180	150-162	109-120
Max [η], dl/g	48-60	15-25	0.1-3

[a] May be difficult to observe if highly crystalline.

[b] May decompose before melting.

7.6. Comparison of Major Polymer Types

Fig. 7.13 Rigid-chain and semiflexible-chain ordered assemblies as the concentration of the polymer is increased.



※ Basic Requirements for Liquid Crystal Formation

- Regardless of molecular size or shape, a liquid crystal must satisfy three basic requirements.

1. There must be a first-order transition between the true crystalline state at the lower T found leading to the liquid crystalline state, and another first-order transition leading to the isotropic liquid state (or another liquid crystal state) at the upper T found of the liquid crystalline state.
2. A liquid crystal must exhibit one-or-two dimensional order only : true crystals have 3D order, and the isotropic liquid is completely disordered.
3. A liquid crystalline material must display some degree of fluidity

   : although for polymers the viscosity may be high.

Experiment	Amorphous	Crystalline	Liquid Crystalline
X-ray	Amorphous halo	3-D order	1- or 2-D order
Polarizing microscope	No texture	Spherulites	Schlieren texture
DSC, dilatometric	Only T_g	T_g and T_f	Tg and two or more first-order transitions

Keywords in Chapter 8

- Hydrophilic-lipophilic balance (HLB)

- Critical packing parameter

- χN vs f phase diagram for block copolymers

- Phase diagram for ternary amphiphilic block copolymer – water – oil system

- Applications of copolymers

CNDL