

6.5 Liquid-crystalline polymers

Liquid crystal : flow properties of a liquid & anisotropy of a solid crystal
(= *mesomorphic*)

Rigid-rod polymers display an anisotropic LC phase dependent on "*aspect ratio*"
(length to width ratio)

Lyotropic - ordered states in concentrated solutions

"aromatic polyamides"

critical concentration (v_2^*) for the formation of an LC phase.

$$v_2^* = \frac{8}{x} \left(1 - \frac{2}{x} \right) \quad : \quad x \sim \text{aspect ratio of the polymer}$$
$$\approx \frac{8}{x} \quad \text{for } x \gg 1$$

Thermotropic - melt processable (stable within a certain T region)

"aromatic copolyesters"

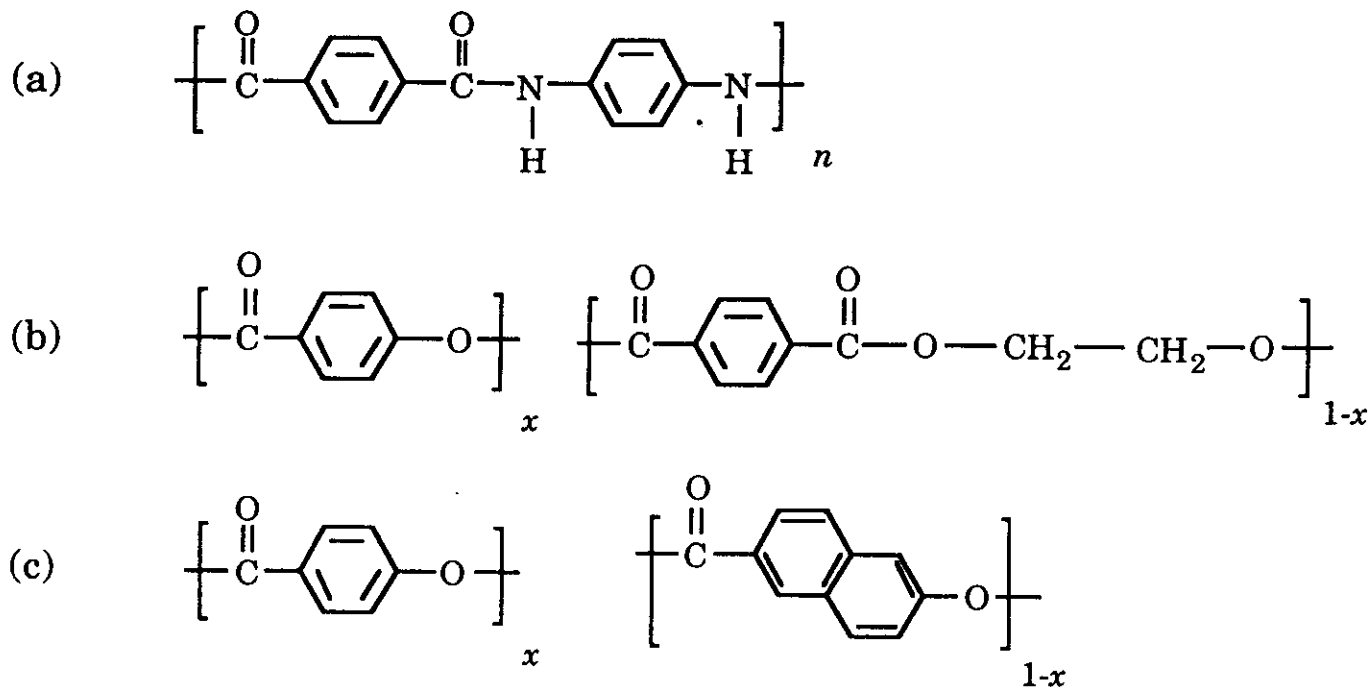
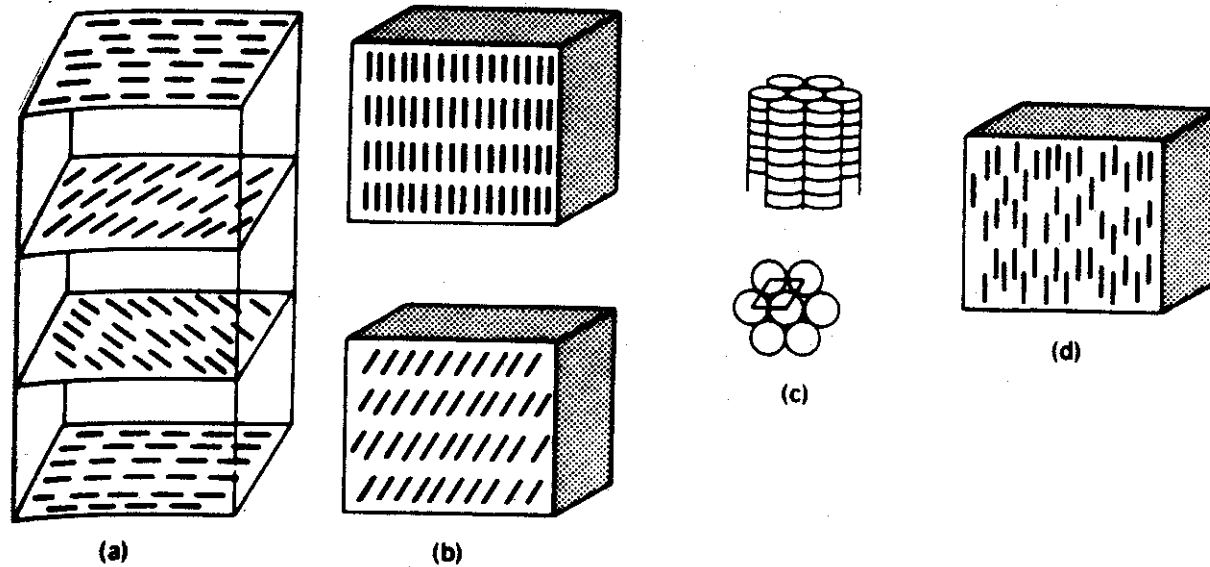


Figure 6.17 Repeating unit structures of (a) poly(*p*-phenylene terephthalamide) (Kevlar); (b) copolyester of *p*-hydroxybenzoic acid and ethylene terephthalate; (c) copolyester of *p*-hydroxybenzoic acid and 2,6-hydroxynaphthoic acid (Vectra).

• Physical structure of LC polymers



(a) *cholesteric* (2-dimensional or twisted nematic) (b) *smectic* (ordered in 2-dimension)
 (c) *discotic* (2-dimensional disc-shaped) (d) *nematic* (one dimensional)

- **Order parameter** (or *Hermans orientation function*)

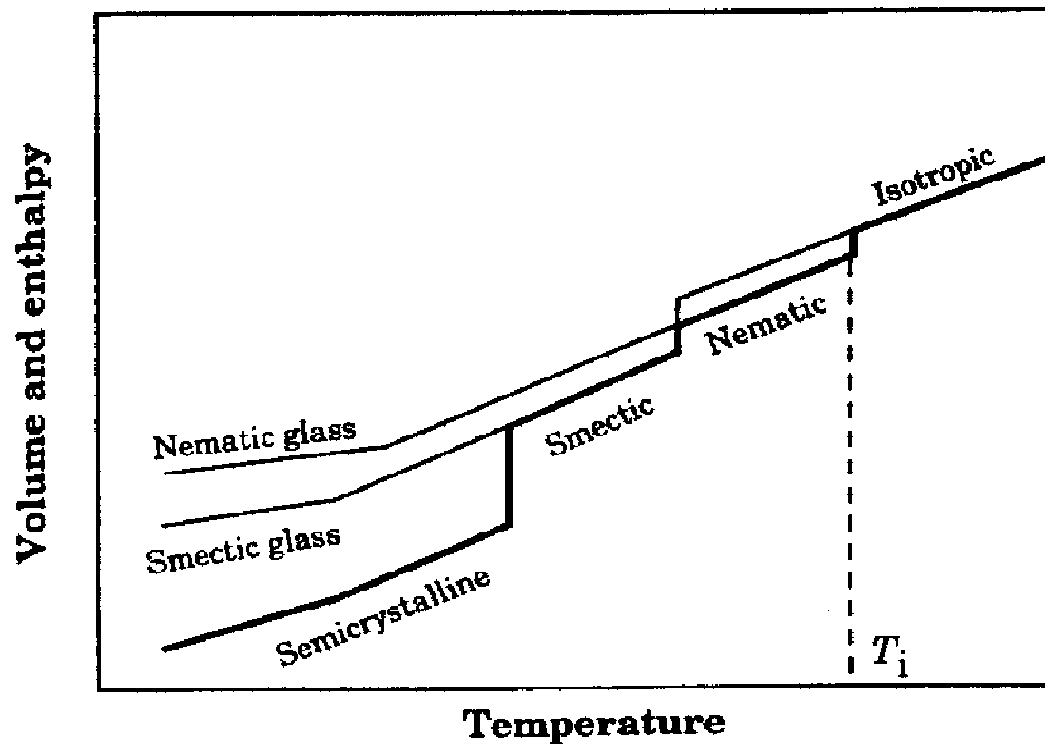
$$S = \frac{3\langle \cos^2 \theta \rangle - 1}{2}$$

: $S = 1$ (aligned to the director)

0 (completely random)

-0.5 (perpendicular to the director)

- Phase transitions in thermotropic liquid-crystalline polymers



• **Chemical Structure of LC polymers**

"Mesogenic" units ~ anisotropic rod shape

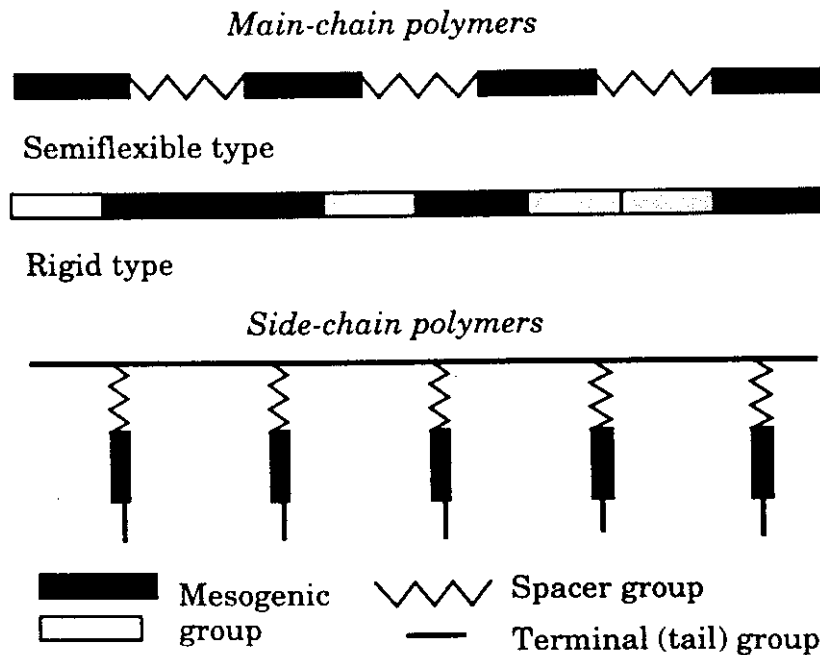


Figure 6.19 Schematic representation of mesogen

Figure 6.18 Main-chain and side-chain liquid crystalline polymers.

* Chemical structure and phase transitions

• Effect of mesogenic group

- polymer with a mesogenic group with a high aspect ratio
→ high isotropization T

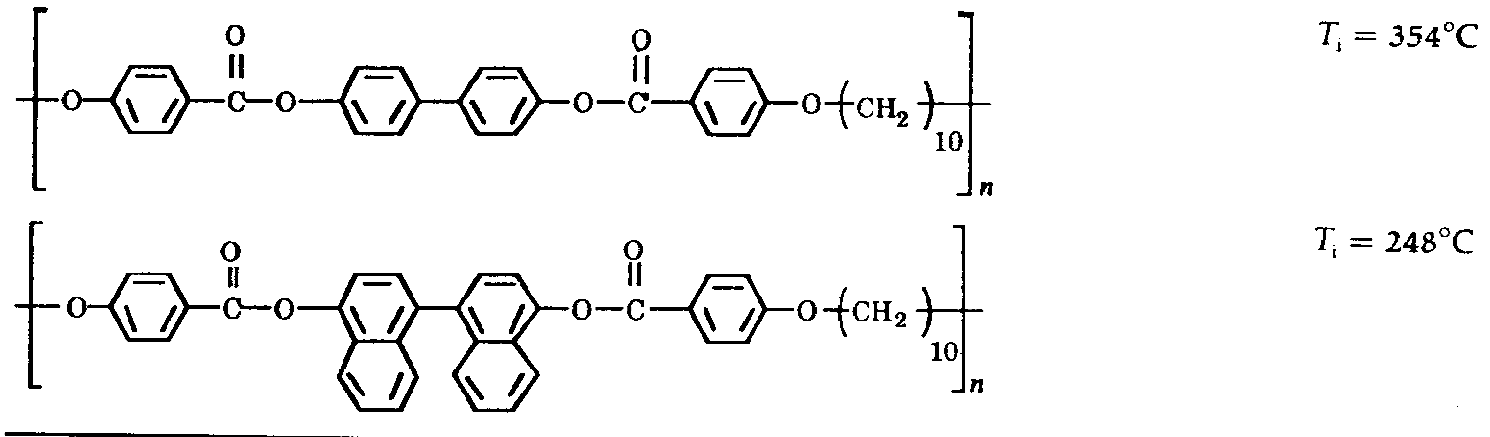
Table 6.3 Effect of length of mesogenic group on isotropization temperature

$\left[\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_{10} \right]_n$	$T_i = 160^\circ\text{C}$
$\left[\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_{10} \right]_n$	$T_i = 311^\circ\text{C}$

Source: Meurisse *et al.* (1981).

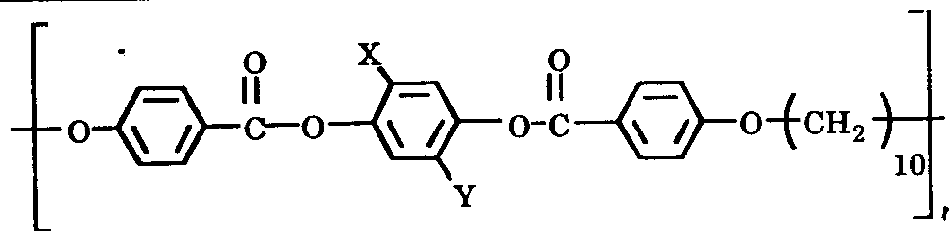
- shape of mesogen ~ important
(rather than polarity & intermolecular interaction)

Table 6.4 Effect of width of mesogenic group on isotropization temperature



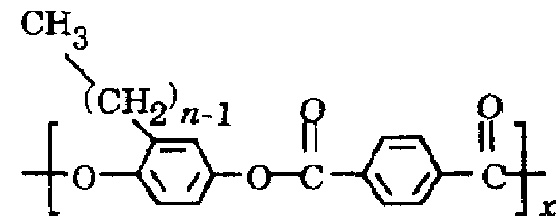
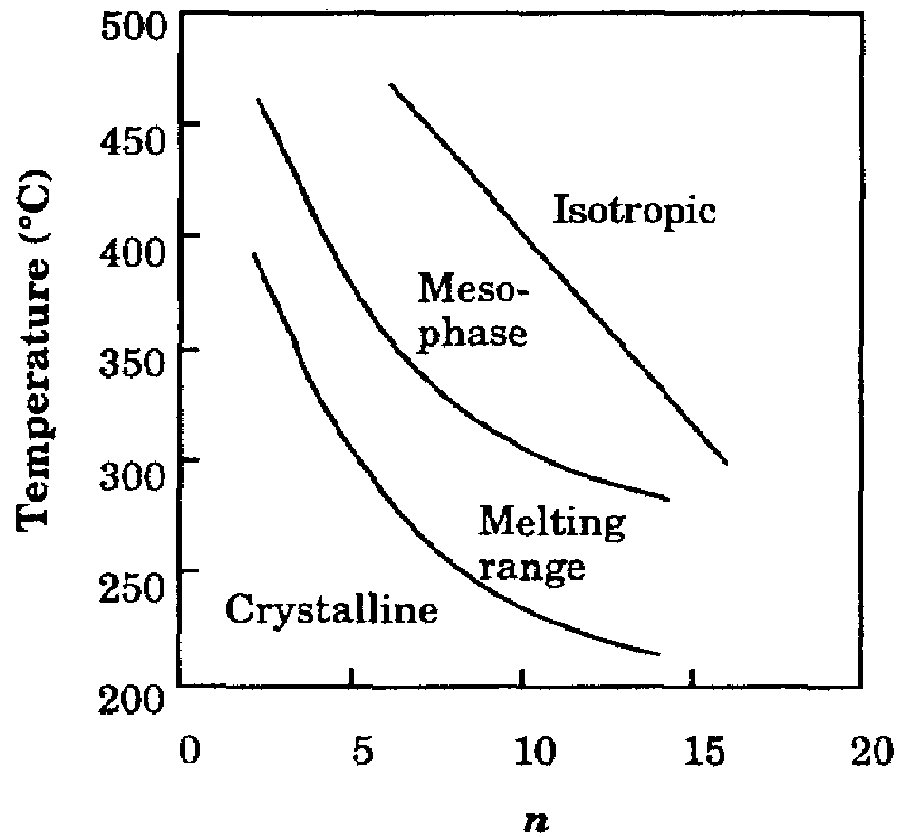
- lateral substituent

Table 6.5 Effect of lateral substituents



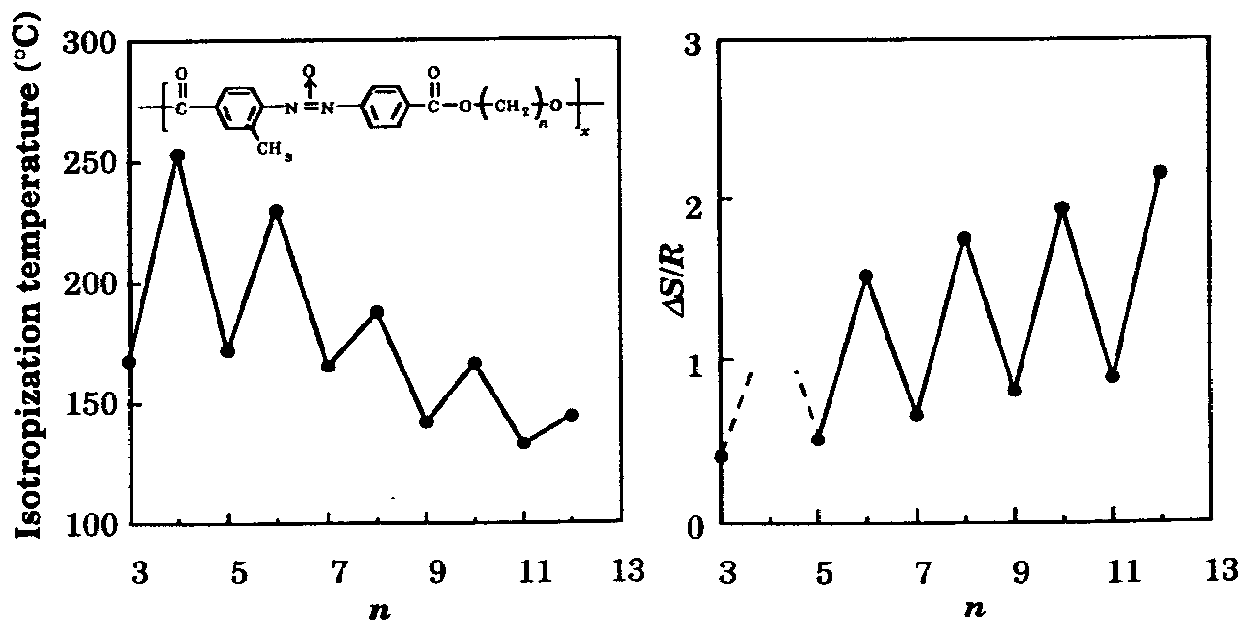
X	Y	T_i (°C)
H	H	294
H	CH ₃	274
H	Cl	279
H	Br	270
Cl	Cl	255

. Effect of lateral substituent on isotropization T and melting temperature range



• *Effect of flexible group & molar mass*

- polymer with longer spacer groups \rightarrow rigidity $\downarrow \rightarrow T_i \downarrow$
- even number of methylene groups \rightarrow *trans* form \rightarrow high orientation $\therefore T_{i, \text{even}} > T_{i, \text{odd}}$



- MW $\uparrow \rightarrow T_i \uparrow$
- spacer length of side chain \uparrow
 \rightarrow 꼭 $T_i \downarrow$ 인 것은 아님.

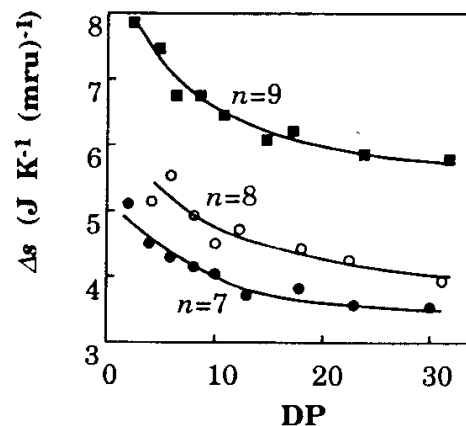
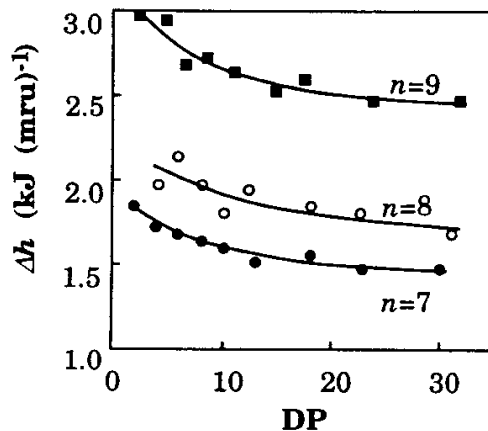
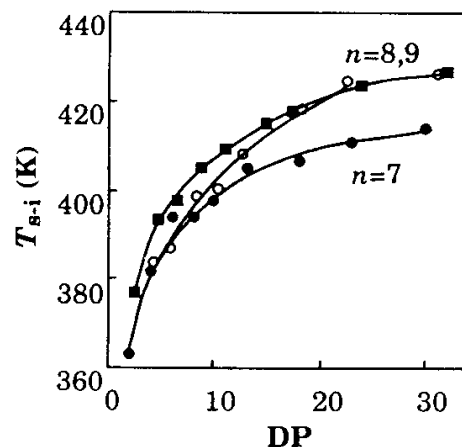
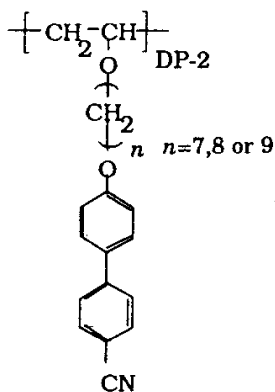


Figure 6.34 Spacer-length and molar-mass dependence of temperature, enthalpy and entropy of isotropization for a series of side-chain poly(vinyl ether)s. The abbreviation 'mru' stands for 'mole repeating units'. Data from Gedde *et al.* (1992). With permission from Butterworth-Heinemann Ltd, UK.

- *Effect of copolymerization*

- copolymerization \rightarrow crystallinity $\downarrow \rightarrow T_m \downarrow$

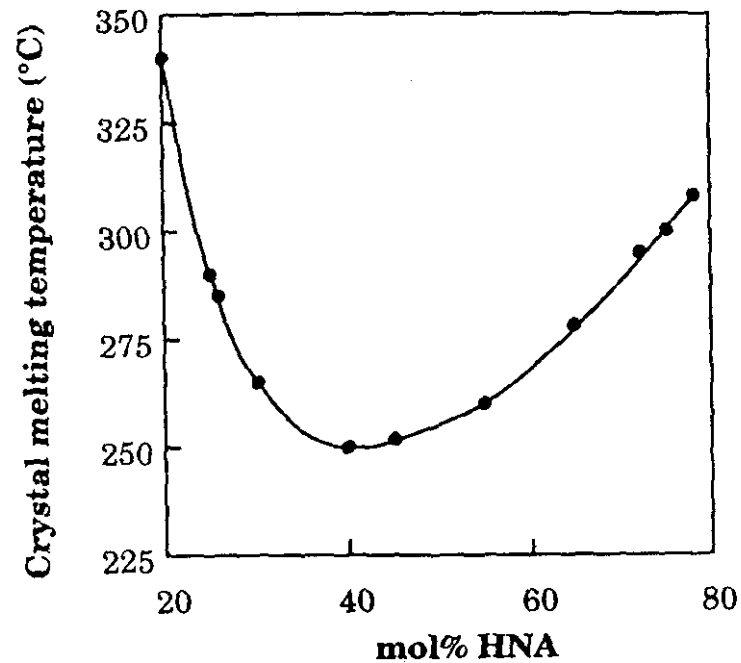


Figure 6.35 Crystal melting temperature as a function of hydroxynaphthoic acid-content of poly(hydroxynaphthoic acid-co-hydroxy-benzoic acid) (Vectra). Drawn after data from Calundann and Jaffe (1982).

※ **Viscosity** of LC polymer solutions

$$v_2 < v_2^* : \eta \uparrow \text{ with } v_2 \uparrow$$

$$v_2 > v_2^* : \eta \downarrow \text{ with } v_2 \uparrow$$

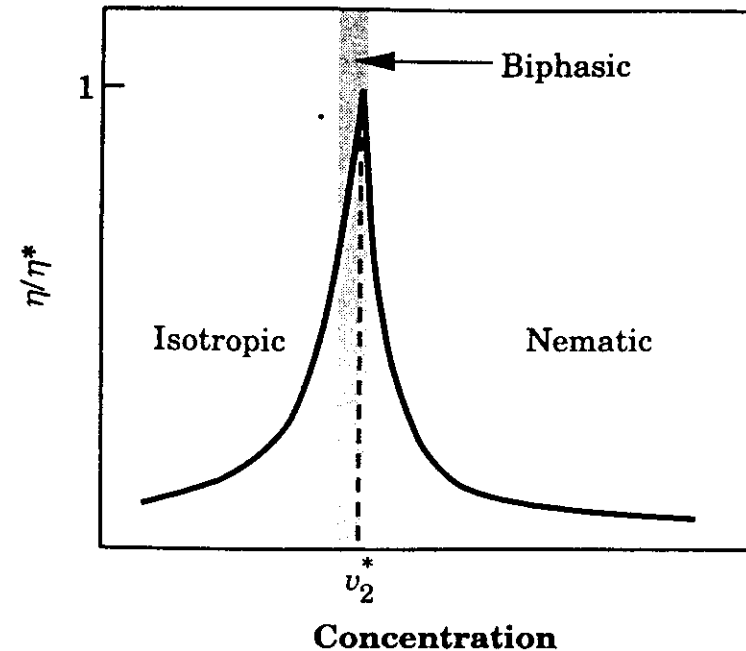


Figure 6.39 Normalized solution viscosity for a solution of a rigid-rod polymer (e.g. poly(γ -benzyl-L-glutamate)). Schematic curve. The critical concentration associated with the formation of the nematic phase is denoted v_2^* and the corresponding viscosity η^* .