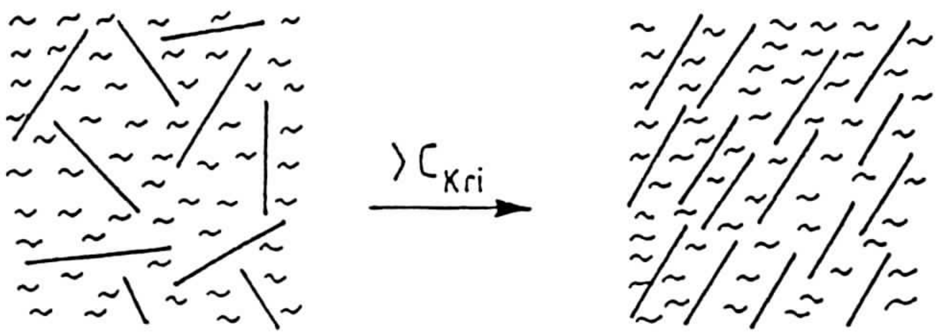
Lyotropic LC-Solutions

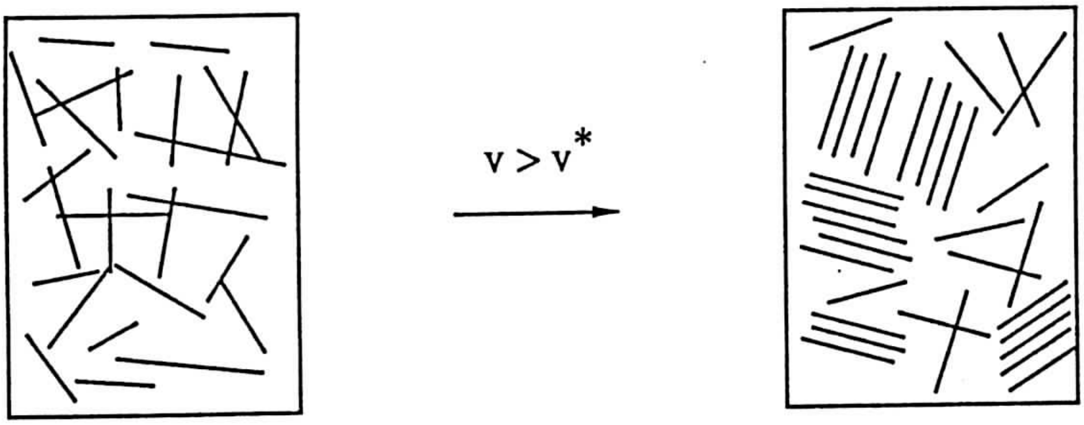


Formation depends on:

- chain stiffness (axial ratio)
- molecular weight
- concentration
- solubility
- temperature

Problems for rod-like polymers:

- viscosity
- gelation or crystallization at RT
- limited temperature stability

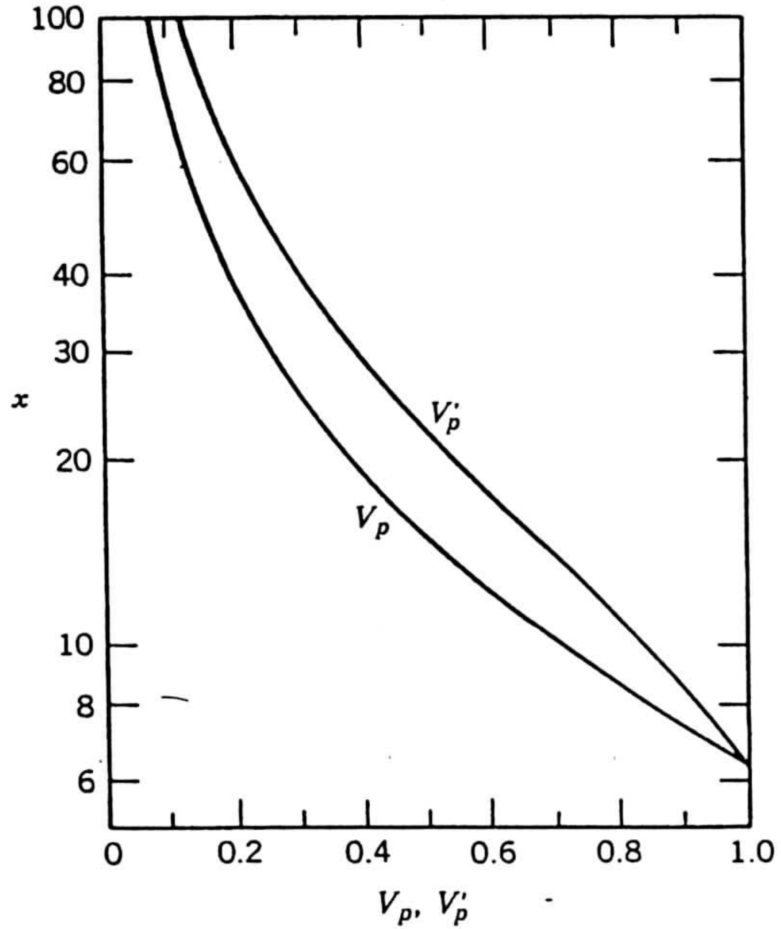


P.J. Flory, Proc. Royal Soc. (London), A 234, 73 (1956)

onset of stable anisotropy in solutions of rod-like particles:
occurs at:

$$v_2^* \sim (8/x)(1-2/x)$$

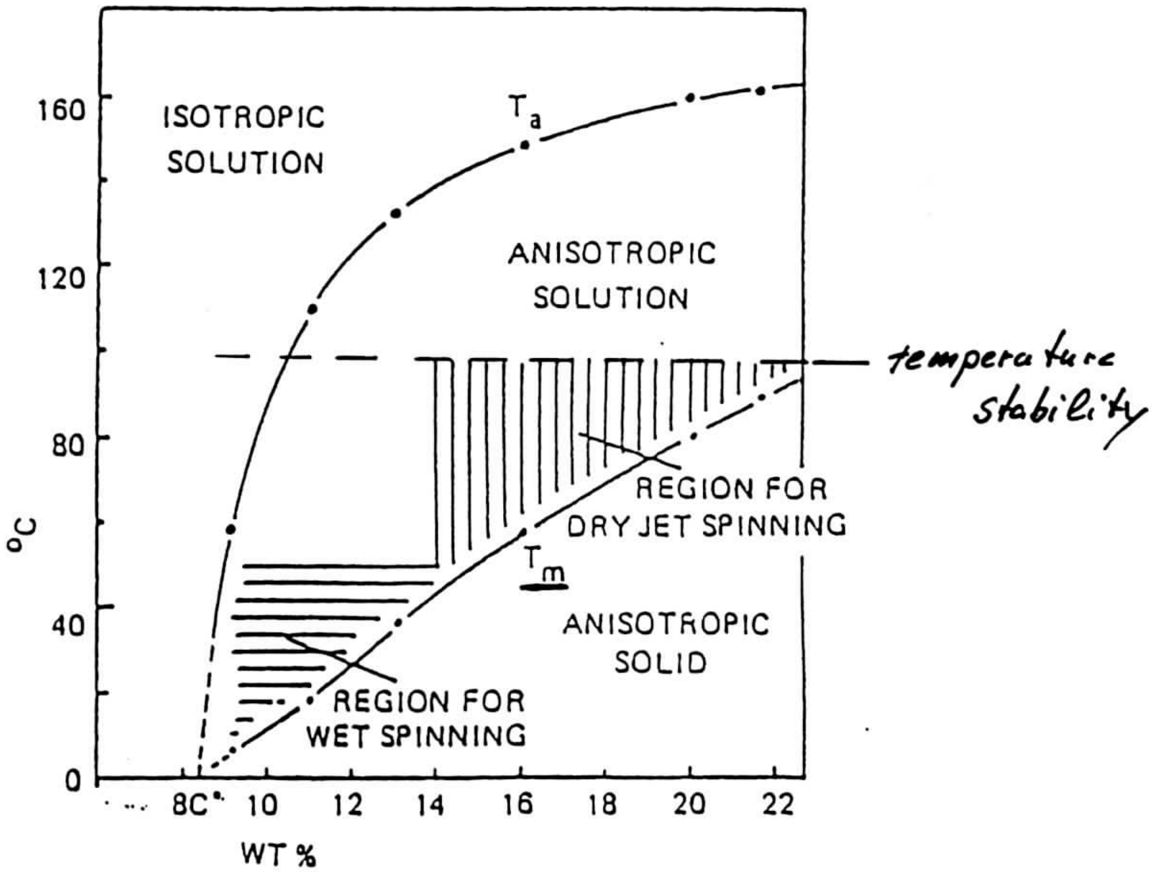
v_2 = volume fraction of rods
x = axial ratio (length/diameter)



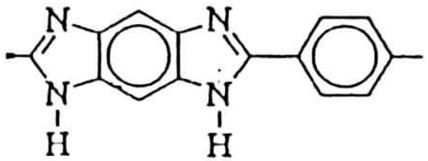
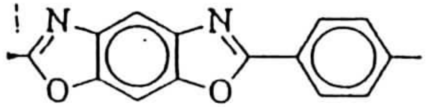
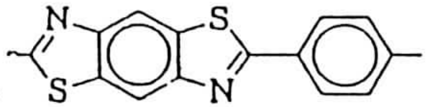
Compositions of coexisting isotropic and anisotropic phases expressed in volume fractions V_p and V'_p, respectively, as functions of the axial ratio x of hard rods in athermal solutions. Courtesy of Springer-Verlag.

(Flory, Advances in Polymer Science Series, Vol. 59 (1984)

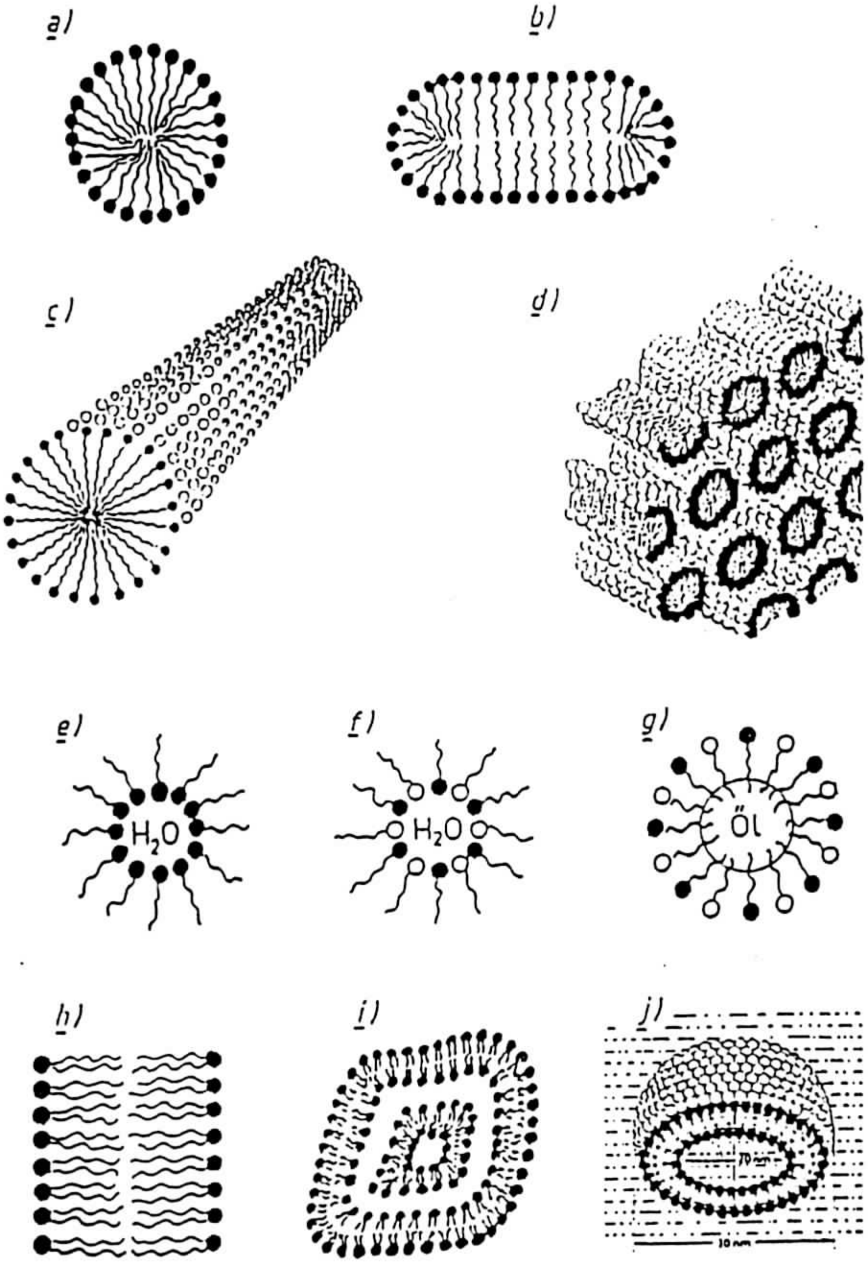
Phase diagram of PPTA in
100 % H_2SO_4



after: B. Jingsheng et al.,J. Appl. Polym. Sci., 26, 1211 (1981) rod like molecules → lyotropic LC's

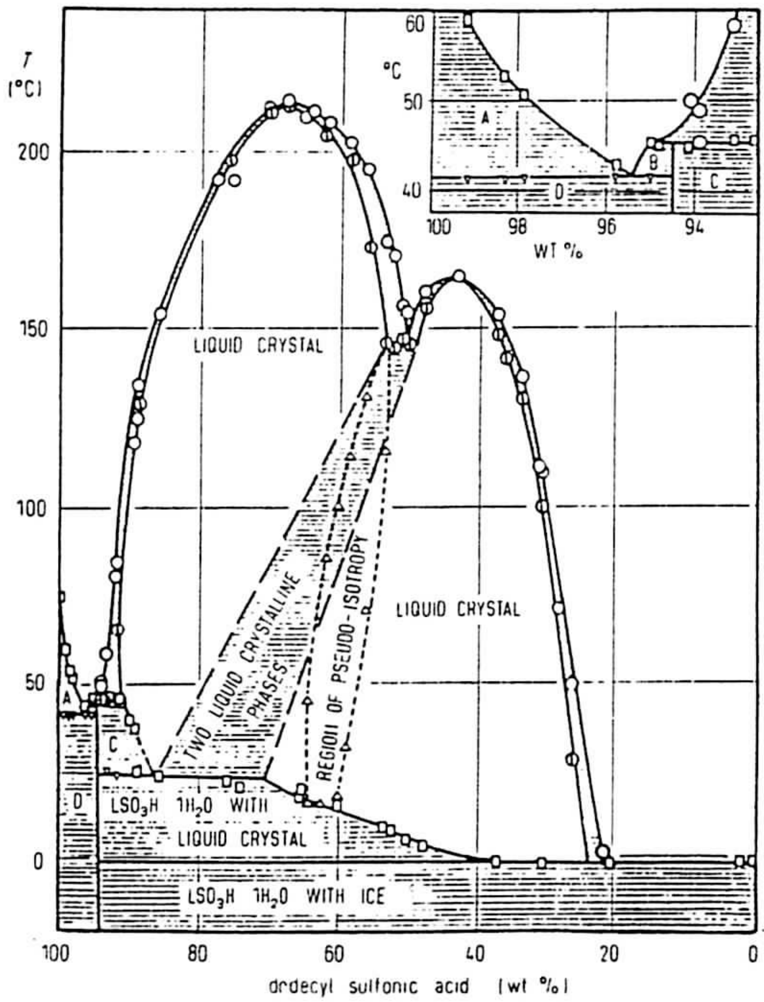
Compound	Structure	Lyotropic solution
poly(1,4-phenylene-2,6-benzobisimidazole)		methanesulfonic acid
poly(1,4-phenylene-2,6-benzobisoxazole) (PBO)		methanesulfonic acid chlorosulfonic acid 100% sulfuric acid
poly(1,4-phenylene-2,6-benzobisthiazole) (PBT)		5–10% in polyphosphoric aci methanesulfonic acid

(from Kwolek et al. Encyclopedia of Polymer Science, Vol.9)



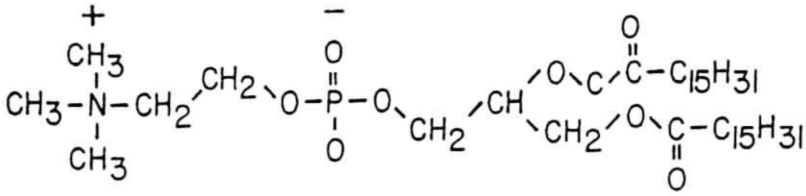
a)
b)
c)
d)
e)
H2O
f)
H2O
g)
Öl
h)
i)
j)

Phase diagram of the system dodecylsulfonic acid/ water

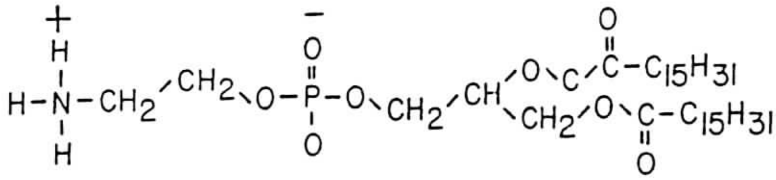


Kelker, Hans and Hatz, Rolf, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, Deerfield Beach, Florida, Basel, 1980.

Schematic diagram of a cell membrane



(a)

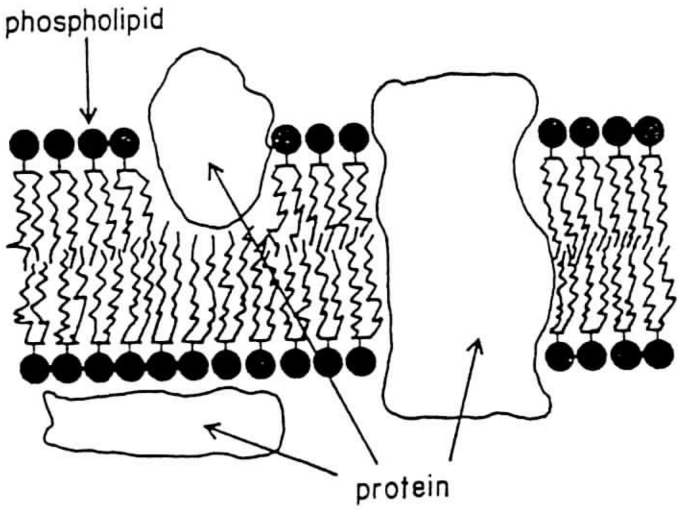


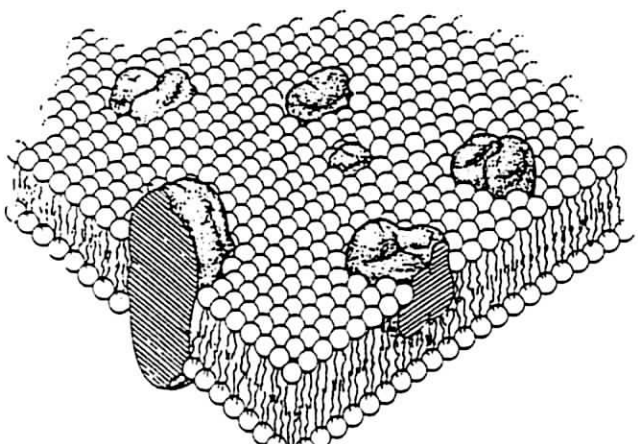
(b)

- **phospholipids:**

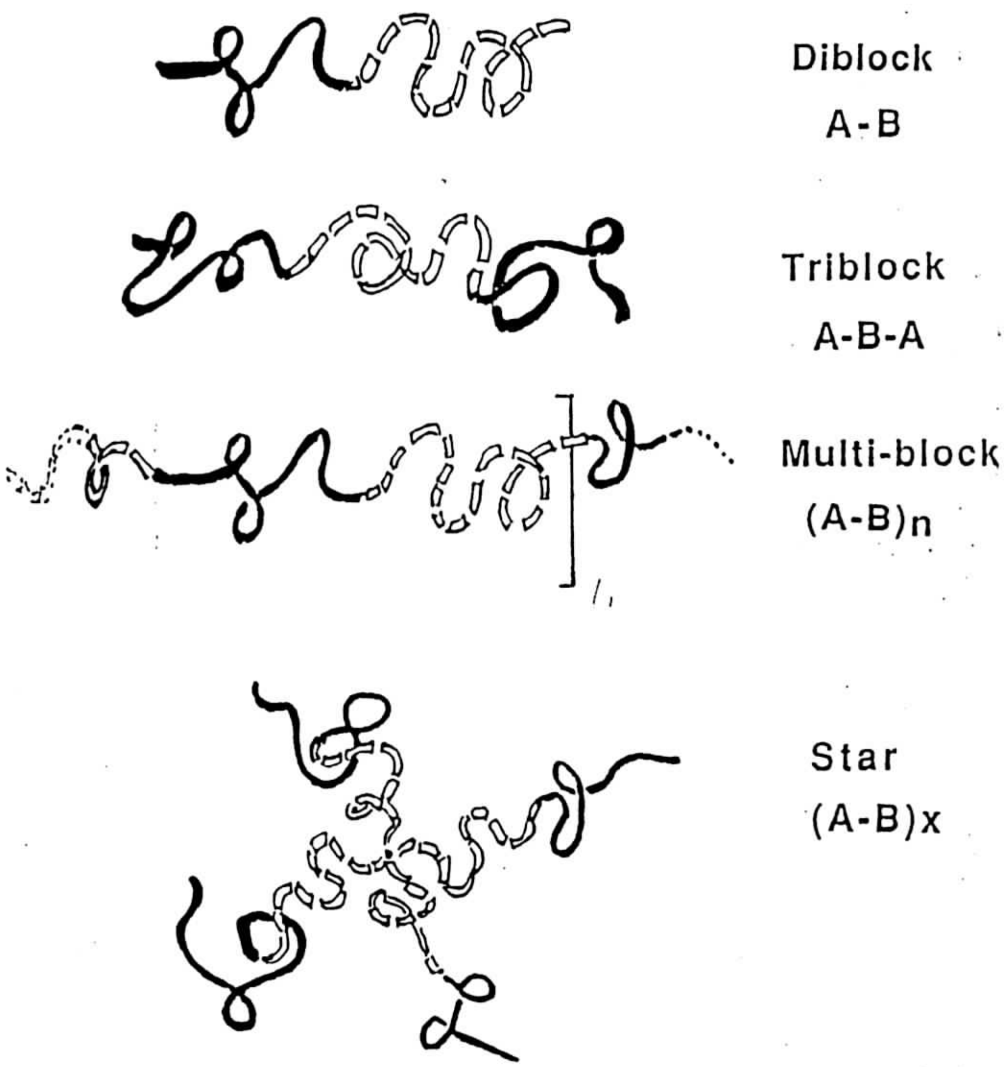
  a) diphosphatidylcholine

  b) diphosphatidylethanolamine





BLOCK COPOLYMER ARCHITECTURE



Block and Graft Copolymers:

- phase separation with domain size 20 - 50 nm
- uniform size distribution
- self organization ⟶ supramolecular structure

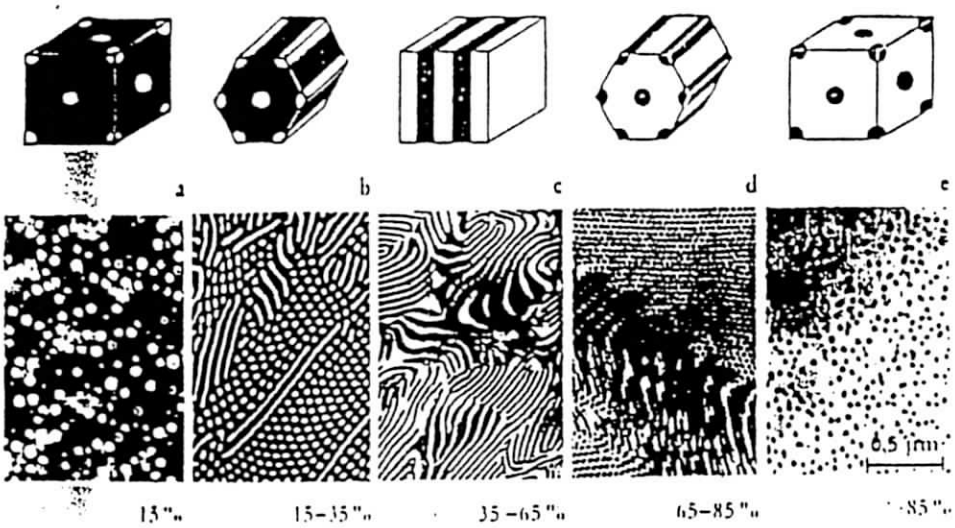


Table 1. Variants of Polymorphism

monomorphism	N	trimorphism	B A N
	A		C A N
	B		G A N
	C		B C N
	E		E B A
			B C A
dimorphism	A N		C D A
	B N		F C A
	C N		G C A
	G N		G B A
	B A		
	C A	tetramorphism	B C A N
	E A		G C A N
	C D		G F C A
	B C		G B A N
	E B		E B A N
		pentamorphism	G B C A N

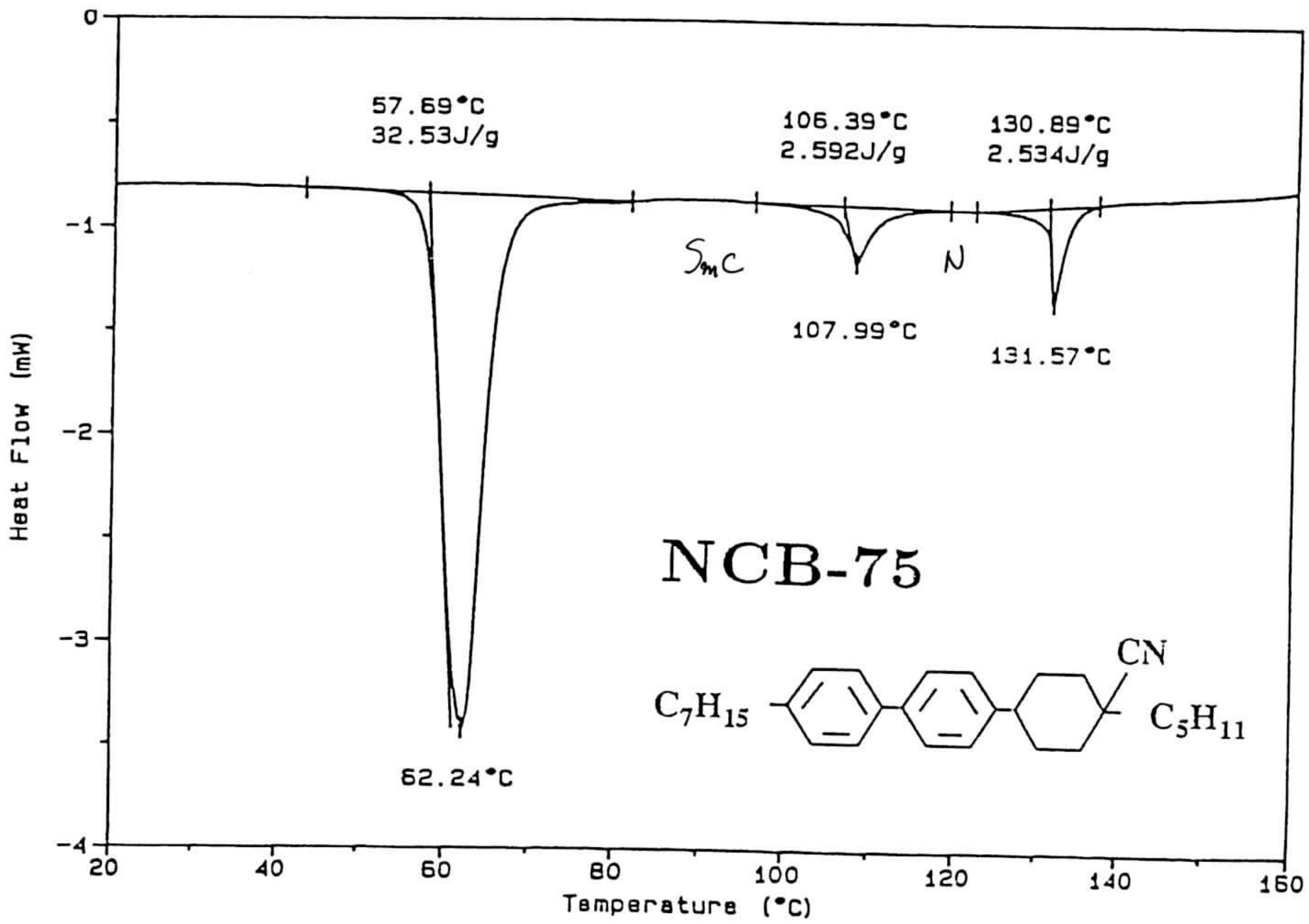
N = nematic (or cholesteric for chiral compounds)

A, B...G = smectic A, B...G

Demus, Dietrich and Richter, Lothar, *Textures of Liquid Crystals*, Verlag Chemie, Weinheim, New York, 1978.

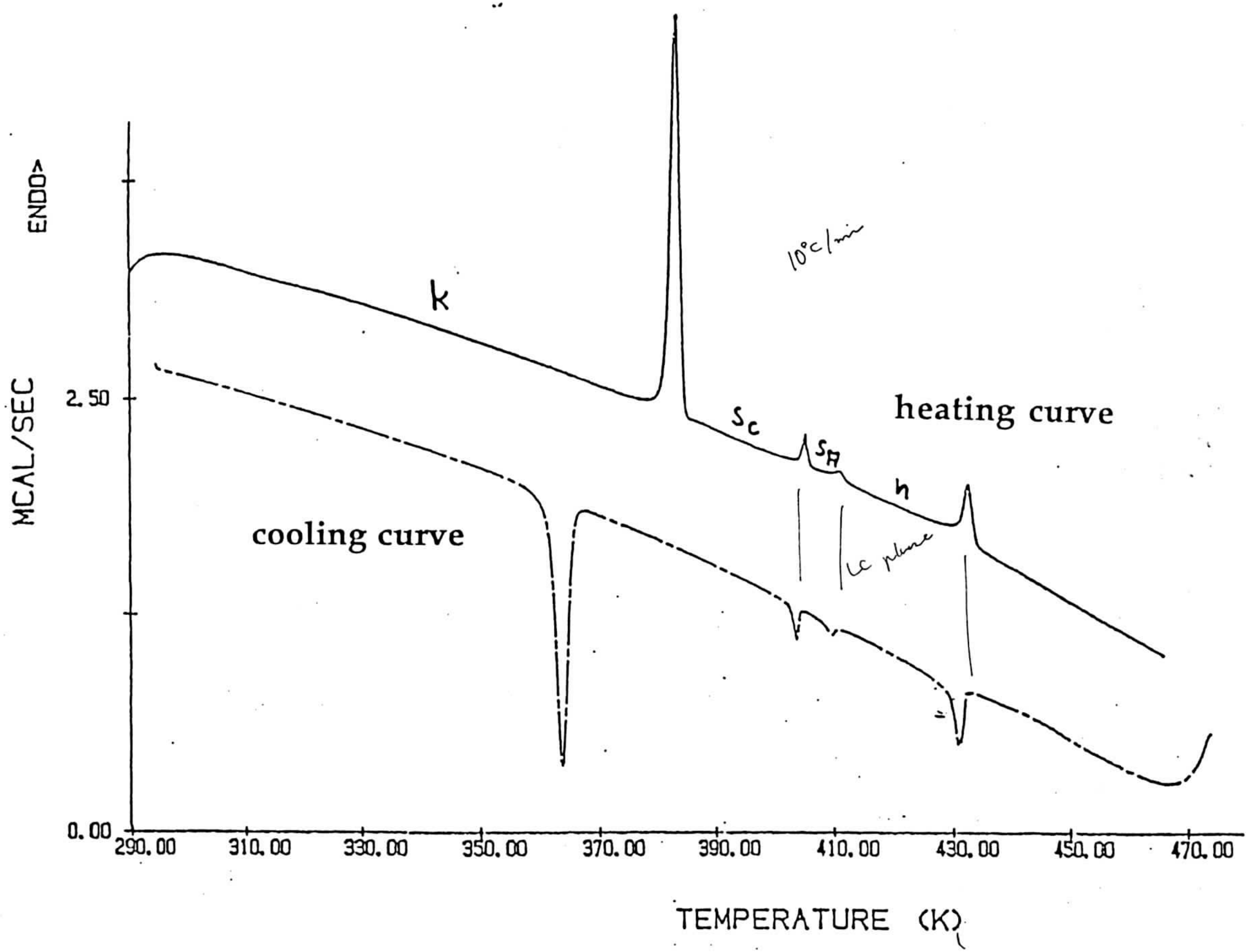
Transition	Number of cases	Transition enthalpy (kJ/mol)
n/i	202	0.84 – 9.6
c/i	79	0.84 – 3.8
s_A/i	93	2.9 – 12.6
s_C/i	21	10 – 42.7
s_D/i	1	10.5
s_A/n	65	0.21 – 4.6
s_A/c	26	0.42 – 1.9
s_B/n	1	8.8
s_C/n	17	0.67 – 9.6
s_C/c	2	2.1 – 4.6
s_B/s_A	55	0.42 – 4.6
s_B/s_C	12	1.84 – 10.5
s_C/s_A	59	$<$0.04 – 2.8
s_C/s_D	2	2.85 – 4.2
s_D/s_A	1	6.7
s_E/s_A	2	6.2 – 7.9
s_E/s_B	28	0.5 – 1.84
s_F/s_C	3	0.17 – 0.5
s_G/s_C	1	2.34
k/i (melting)	391	7.1 – 117

Kelker, Hans and Hatz, Rolf, *Handbook of Liquid Crystals*, Verlag Chemie, Weinheim, Deerfield Beach, Florida, Basel, 1980.



Birendra, Bahadur, *Liquid Crystals Applications and Uses*, Vol. 1, World Scientific Publishing, Singapore, New Jersey, London, Hong Kong, 1990

DSC - CURVES OF A POLYMORPHIC LIQUID CRYSTAL

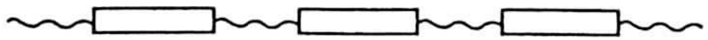


Liquid Crystal polymers

- Two basic (classic) categories:

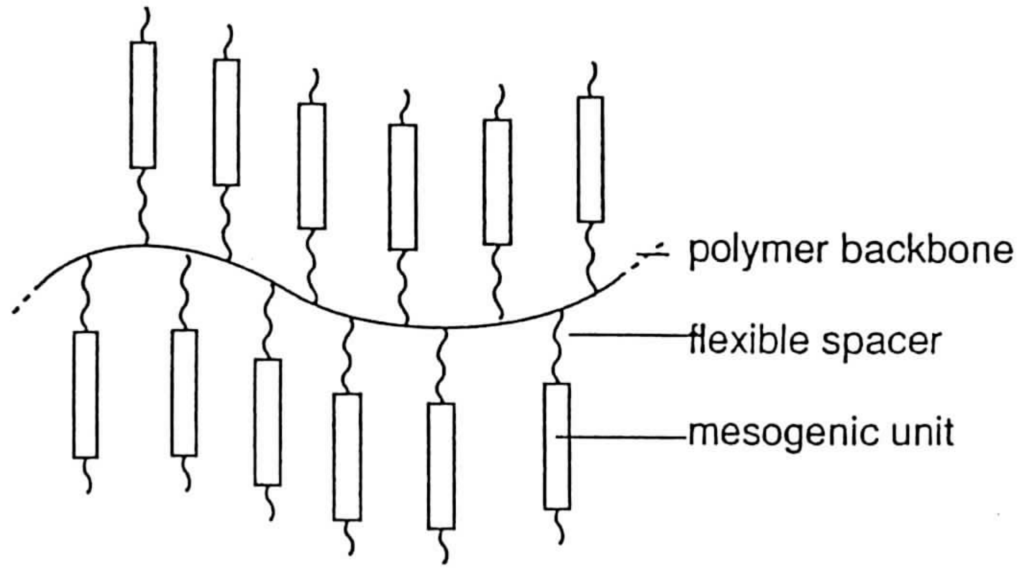
Main Chain LCPs

(rod-like)



(semi-flexible)

Side Chain LCPs



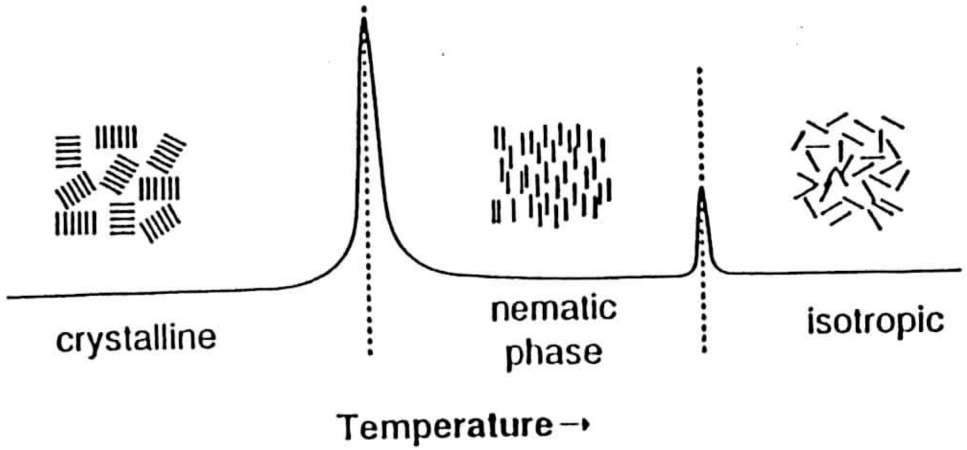
Structural materials

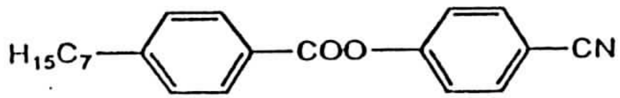
- High modulus, high strength fibers
- Engineering thermoplastics
- Additives in polymer blends

Functional Materials

- Anisotropic glasses
- Opto-electronic
- Optical information storage

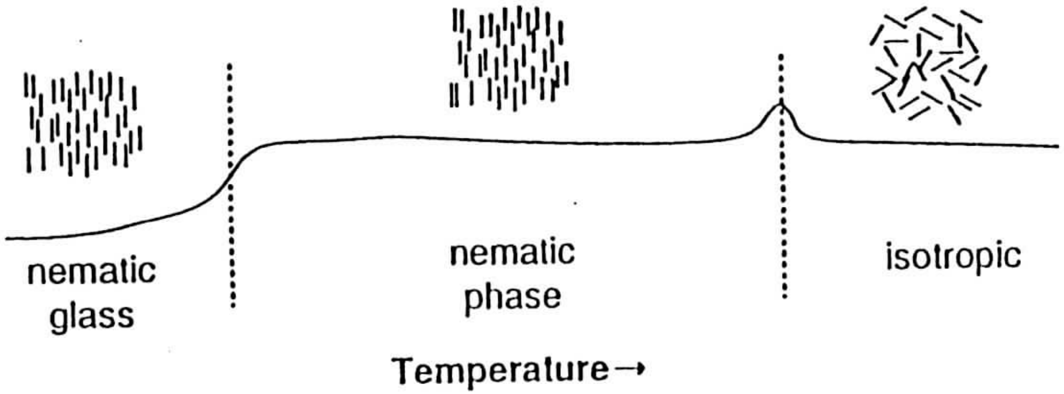
Low Molar Mass LC

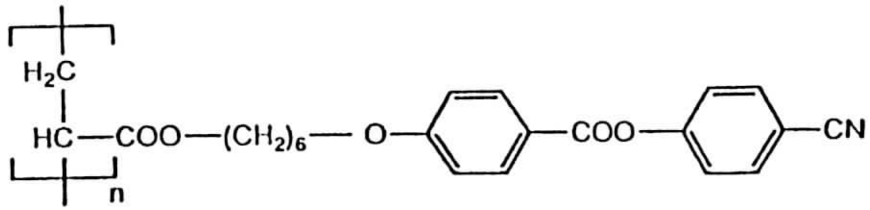




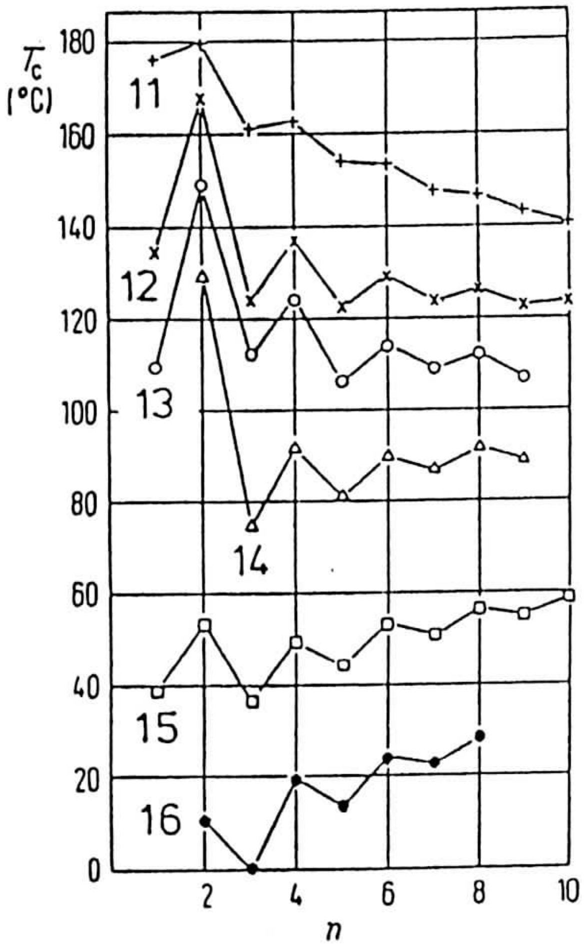
k 44 n 56 i

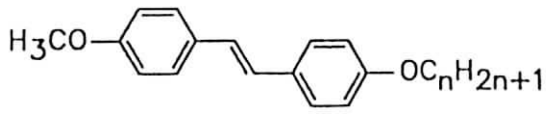
Side Chain LCP





g 30 n 126 i





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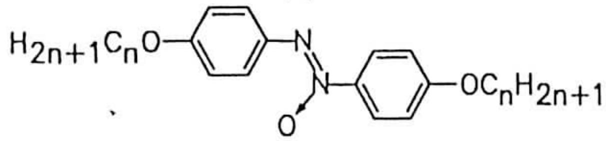

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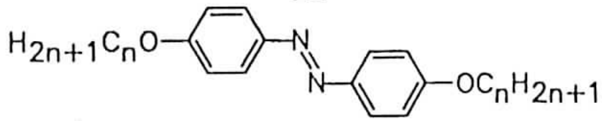

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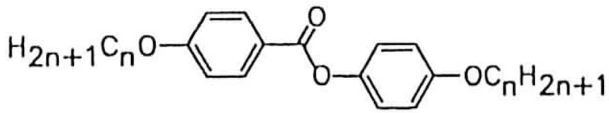

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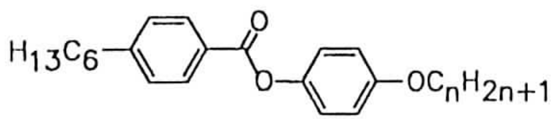

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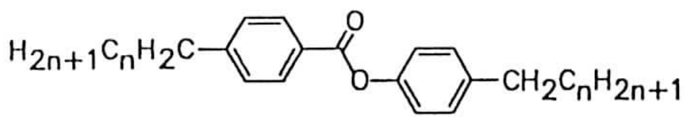
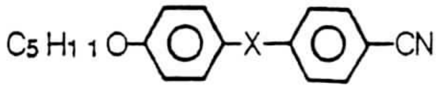
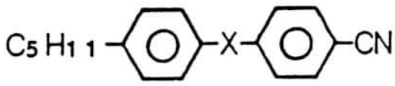


16

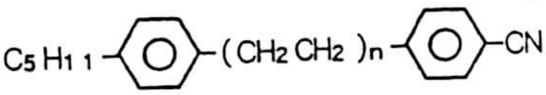
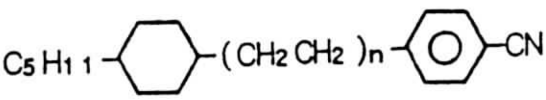


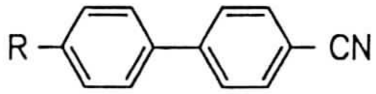
X	C-N(°C)	N-I(°C)
-N=N(O)-	93*	142.6
-N=N-	92	139
-CH=CH-	97	126
-COO-	87	96
-C≡C-	78	94
-CH=N-	62	93
Single bond	53	67.5

* a smectic A phase also occurs up to 107.2°C



X	C-N(°C)	N-I(°C)	Δn
$-CO_2-$	64.4	(55.4)	0.18
-C=C-	79.5	(70.5)	0.29

	N-I(°C) (n=0)	N-I(°C) (n=1)
	35	-24
	55	51



	R	
17a	$H_{11}C_5$	K 22.5 N 35.0 I
17c	$H_{15}C_7$	K 28.5 N 42.0 I
18a	H_5C_2O	K 48.0 N 69.0 I
18b	H_7C_3O	K 102.0 N (90.5) I
18c	$H_{11}C_5O$	K 71.5 N (64.0) I

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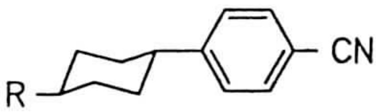
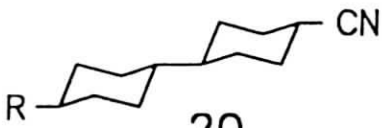


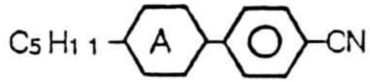
19

	R	
19b	H_3C	K 38 N (−25) I
19d	H_7C_3	K 42 N 46 I
19e	$H_{11}C_5$	K 30 N 55 I
19c	$H_{15}C_7$	K 30 N 57 I

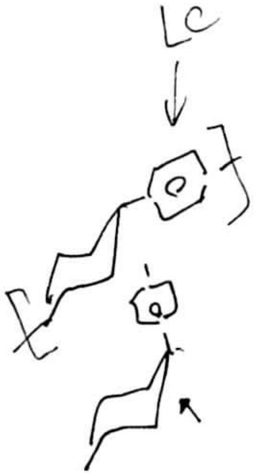


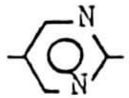
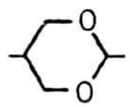
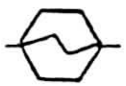
20

	R	
20a	H_7C_3	K 58 S_1 (18) S_2 (44) S_3 (57) N 80 I
20b	$H_{11}C_5$	K 62 S_1 (43) S_2 (52) N 85 I
20c	$H_{15}C_7$	K N 83 I

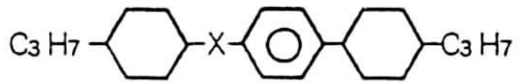


(53)

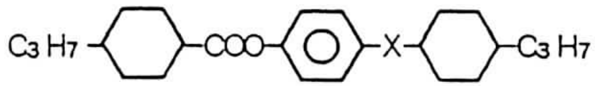


A	C-N(°C)	N-I(°C)	Δn	Δε	k_{33}/k_{11}	
	22.5	35	0.18	11.5	1.3	(53a)[6]
	31	55	0.1	9.7	1.6	(53b)[5]
	71	52	0.18	19.7	1.2	(53c)[92]
	56	52	0.09	13.3	1.4	(53d)[93]
	62	100	–	–	–	(53e)[94]

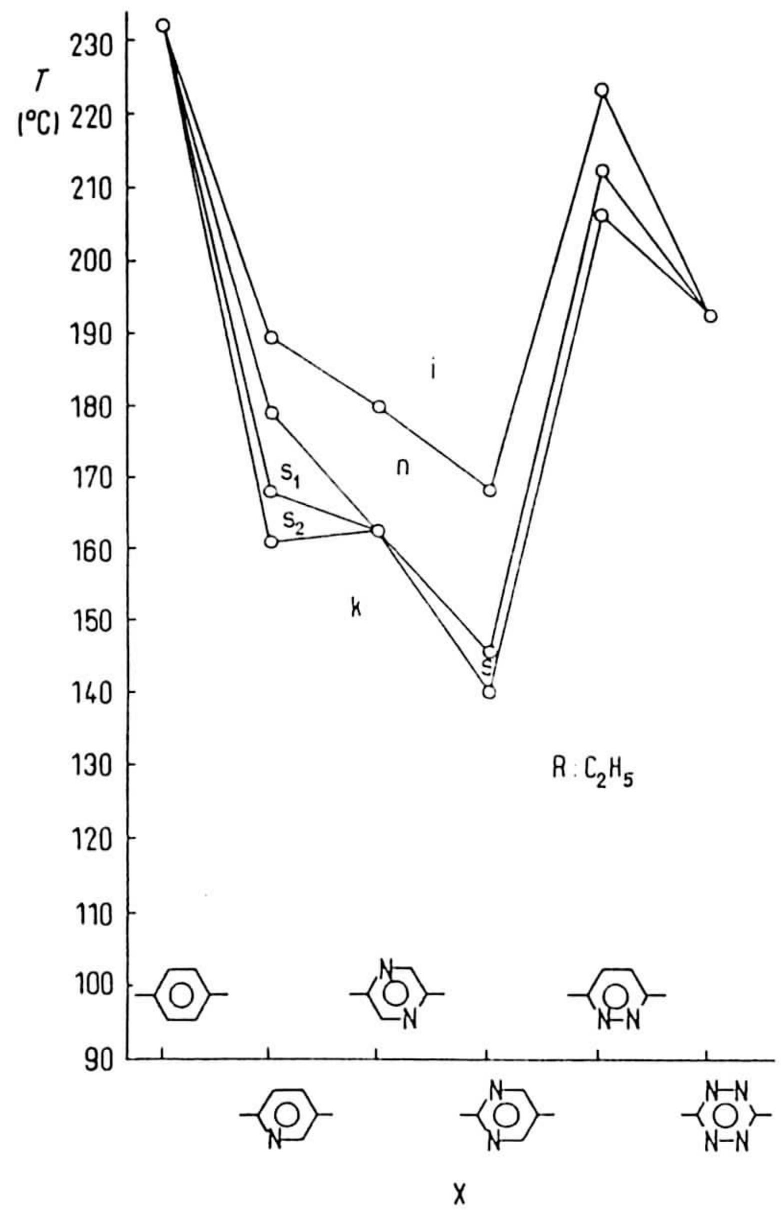
← display



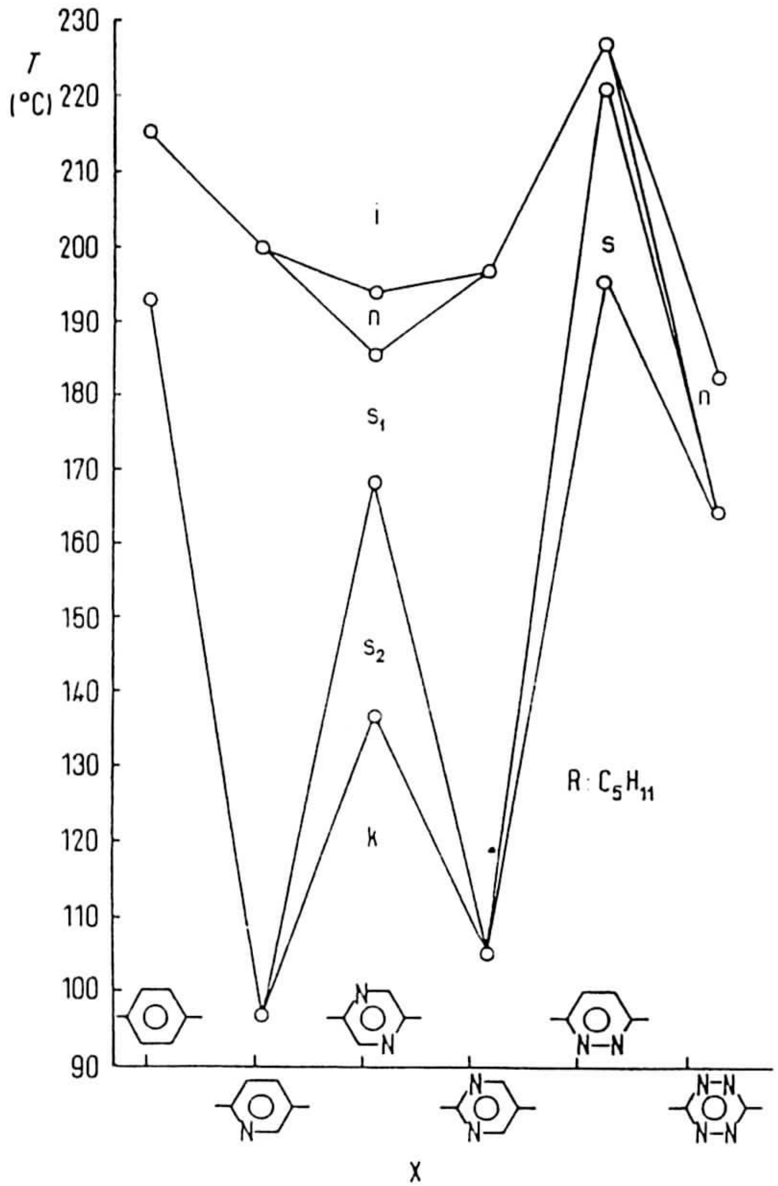
X	$-CH_2CH_2-$	$-CH_2O-$	$-COO-$	$-OOC-$
N-I(°C)	131	140	190	158
Visc 20°C(mm^2/s)	17	48	44.2	103
Birefringence	0.101	0.105	0.112	0.116



X	$-CH_2CH_2-$	—	$-OCH_2-$	$-COO-$
N-I(°C)	163	190	169	219
Visc 20°C(mm^2/s)	34	44.2	132	117



T
(°C)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
i
n
s1
s2
k
s
R : C2H5
X



T
(°C)
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k
R : C5H11
X

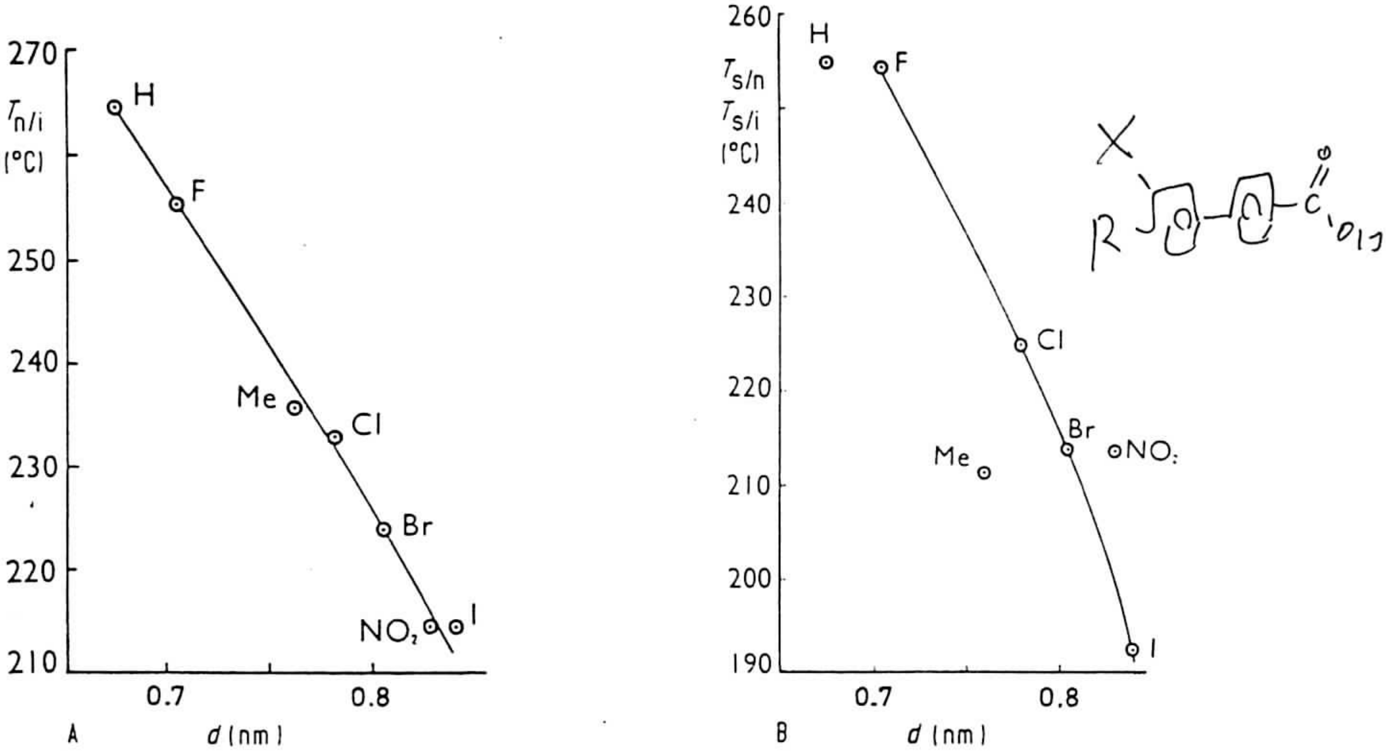
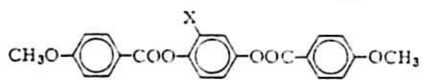


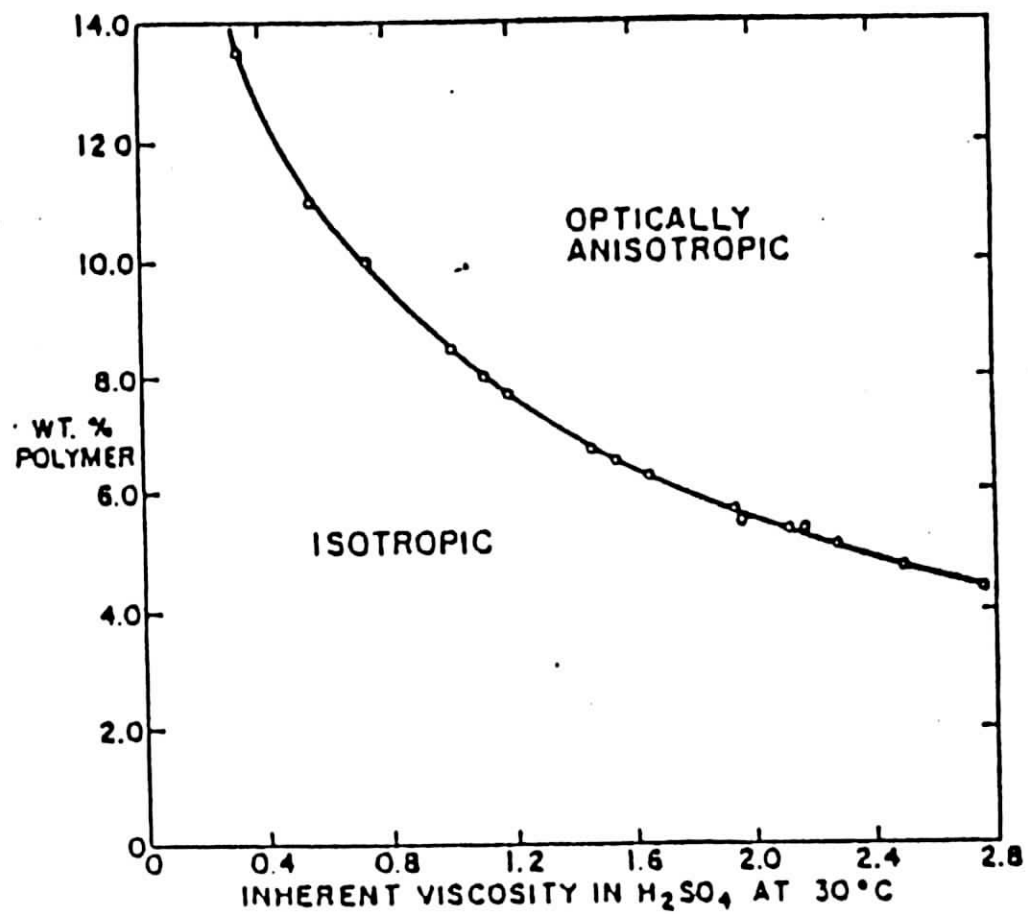
Fig. 2.12. Transition temperatures, $T_{n/i}$, (fig. A, the point for NO_2 in fig. A indicates the $T_{s/i}$), $T_{s/n}$ or $T_{s/i}$ (fig. B), as a function of molecular diameter, *d*, for different 3'-substituted 4'-*n*-alkoxybiphenyl-4-carboxylic acids (from [276]).

Table 2.6. Effect of molecular broadening on the thermodynamic parameters of the compounds.



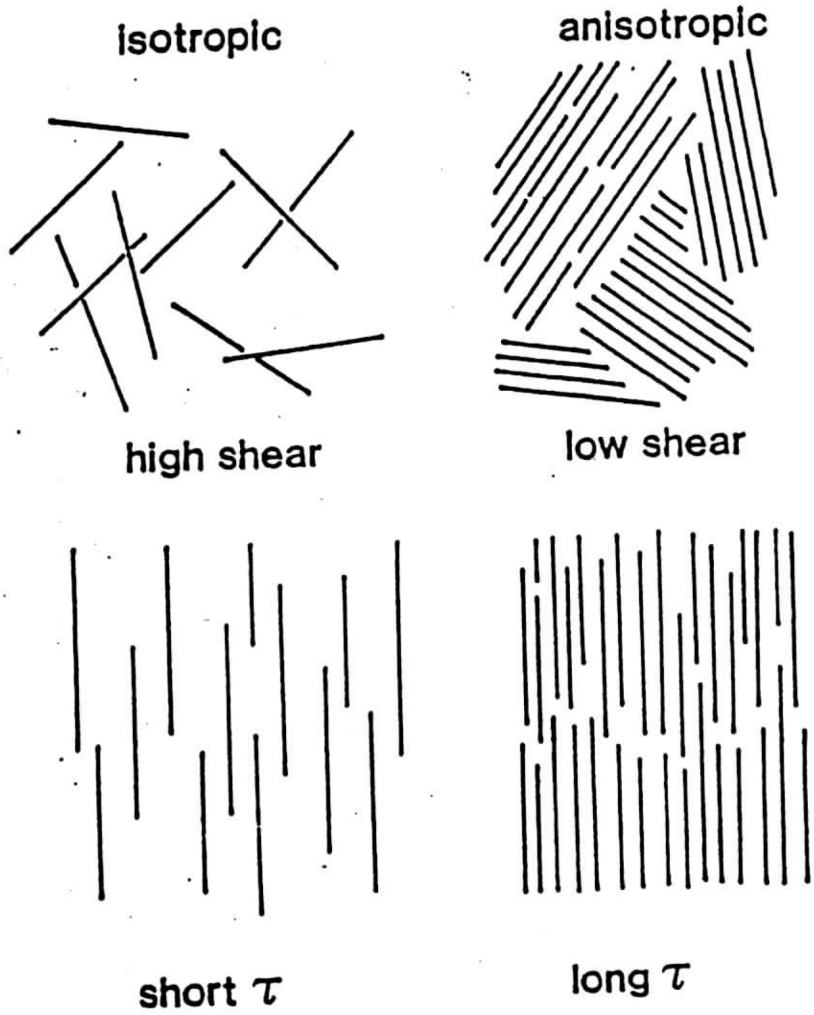
(ΔH: Heat of transition in kJ/mol, ΔS: entropy of transition in J/mol·K).

X	$r_{(x)}$	$T_{(n/i)}$	$\Delta H_{(n/i)}$	$\Delta S_{(n/i)}$
H	0.12	301	1.71	2.98
F	0.135	278.5	1.69	3.07
Cl	0.18	252.4	1.94	3.69
Br	0.195	241.1	2.04	3.97
I	0.215	222.9	2.07	4.16
CH_3	0.20	252.1	2.22	4.23



Effect of inherent viscosity on critical concentration for poly(1,4-benzamide) in DMAc–4% LiCl.

RIGID CHAINS



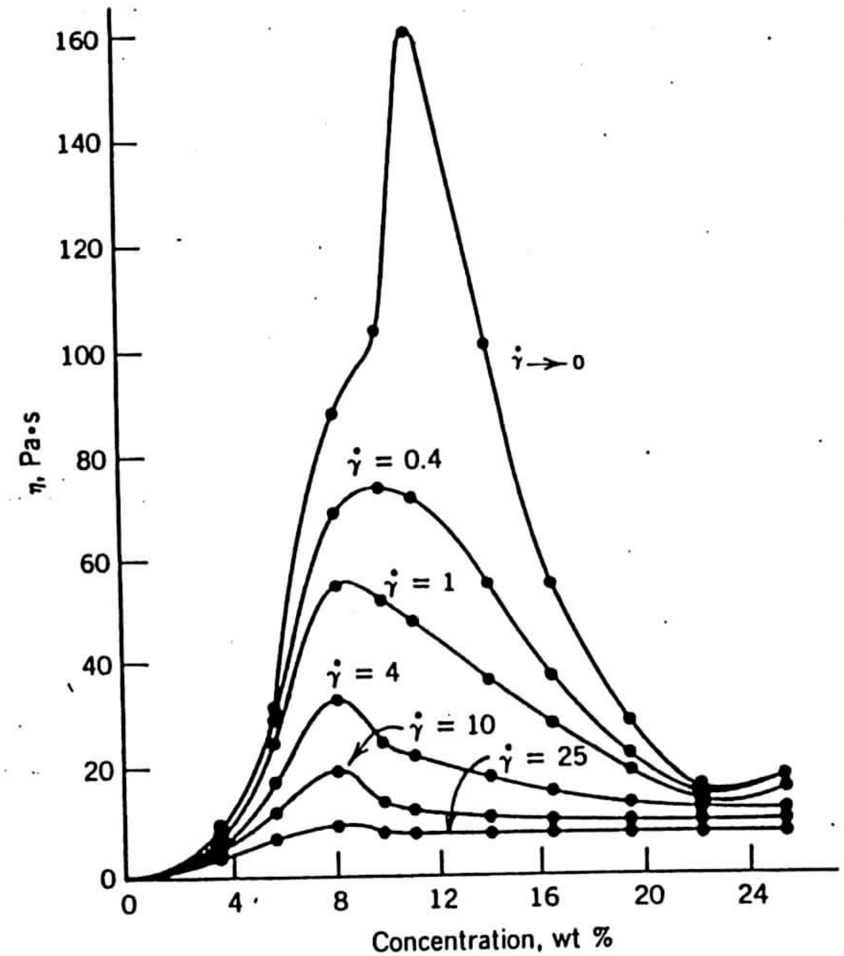
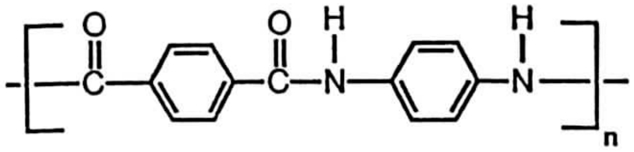


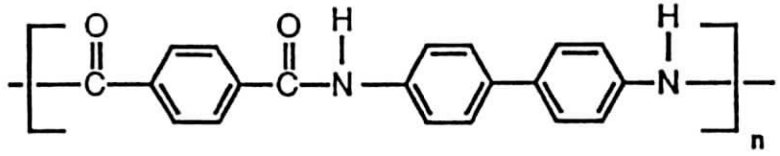
Fig. 6. Concentration dependence of steady-shear viscosity at several shear rates ($\dot{\gamma}$) for PBG in *m*-cresol (58). To convert Pa·s to P, multiply by 10.

(G. Kiss, R.S. Porter, J. Polym. Sci. Polym. Symp. <u>65</u>, 193 (1978)

- **Unsubstituted aromatic polyamides**



Poly-(1,4-phenylene terephthalamide)



Poly-(4,4'-biphenylene terephthalamide)

- limited solubility (solvent: sulfuric acid)
- limited temperature stability in solution
- high melting temperature (undergo decomposition)

- **Influence of structural modifications on:**

solubility properties:
- higher molecular weight polyamides
- higher concentrated solutions

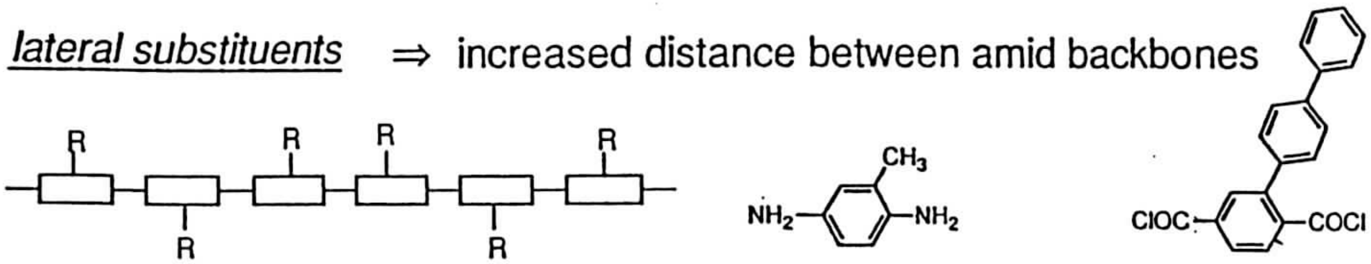
lyotropic liquid crystalline solutions:
- phase behavior
- critical concentrations

thermal properties:
- lower phase transition temperatures

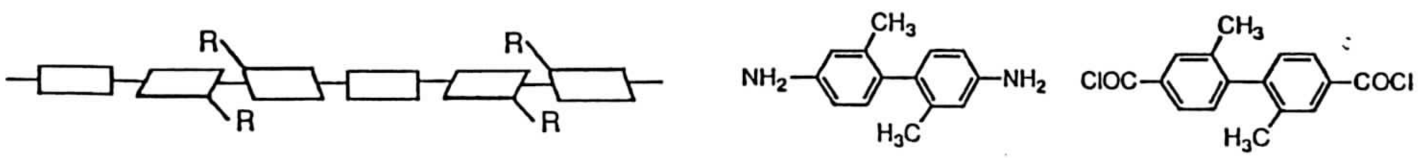
• Concepts of structural modifications for rodlike polyamides

-reduction of hydrogen bonding
-lower crystallinity

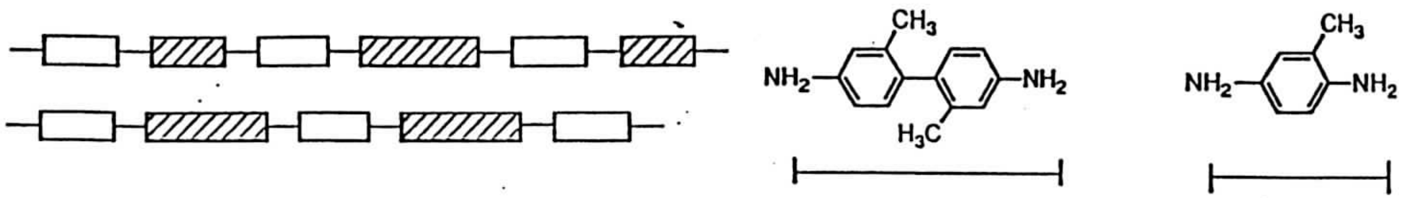
lateral substituents ⇒ increased distance between amid backbones



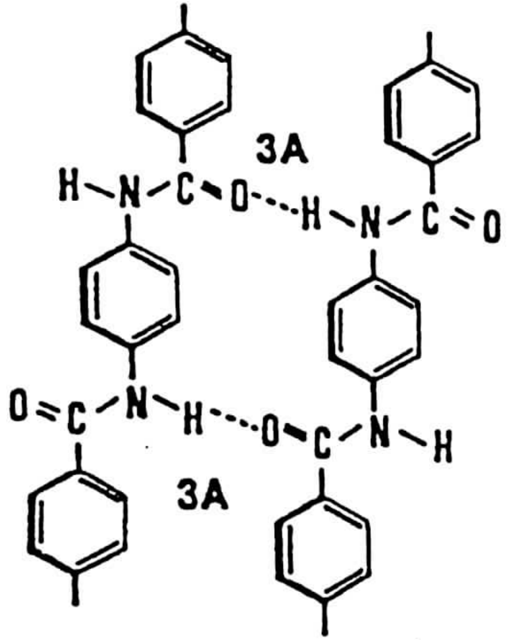
2,2'-disubstituted biphenylenes ⇒ non-coplanar structure



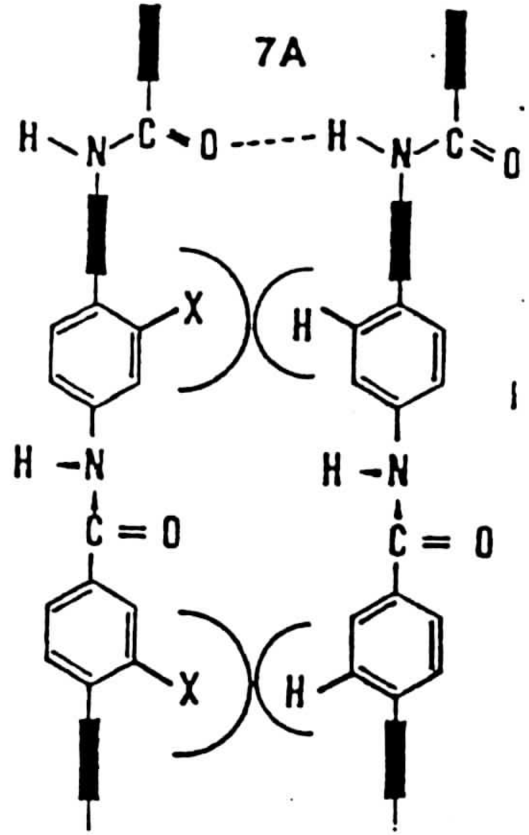
comonomers with different lenght ⇒ statistical incorporation



Hydrogen bonding in aromatic polyamides



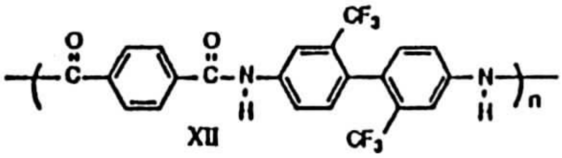
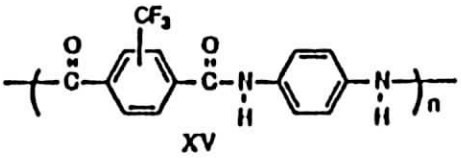
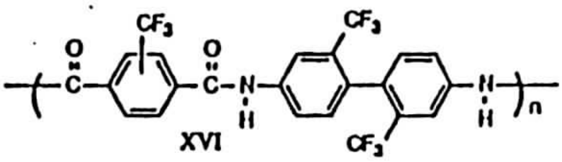
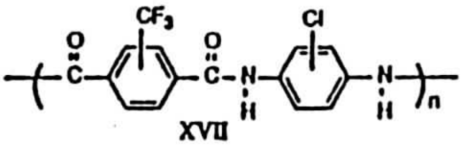
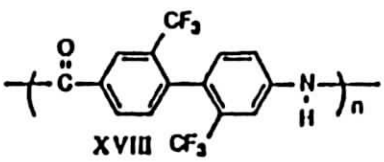
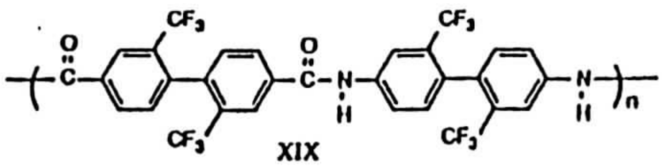
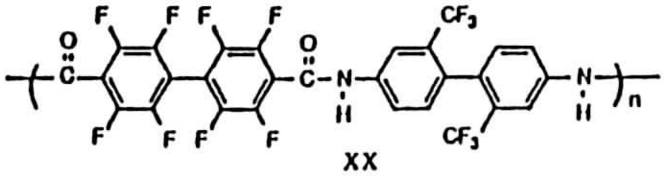
- hydrogen-bond distance: 3Å, (25-30 kJ/mol)



polyamides with substituted phenyl or biphenyl units:

- increased hydrogen-bond distance (7Å)
- less dense packing

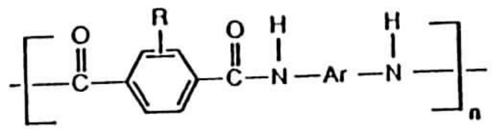
TABLE 2. Spectral properties of selected aromatic polyamides

Polymer	λ_{max}	Maximum chromophore length
 XII	310 nm[b]	3 rings
 XV	314 nm[a]	3 rings
 XVI	295 nm[a]	2 rings
 XVII	289 nm[a]	2 rings
 XVIII	295 nm[c]	2 rings
 XIX	290 nm[b]	2 rings
 XX	273 nm[b]	1 ring

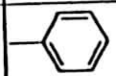
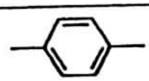
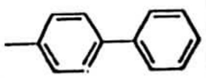
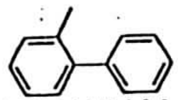
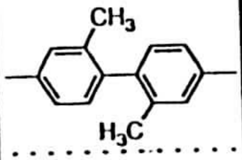
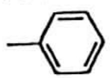
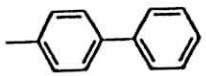
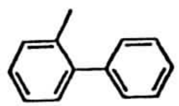
[a]DMAc.
[b]5% LiCl/DMAc (w/v).
[c]THF.

(from R. Gaudiana et al. Prog. Polym. Sci. 14,47 1989)

Solution properties



• **Homopolyamides**

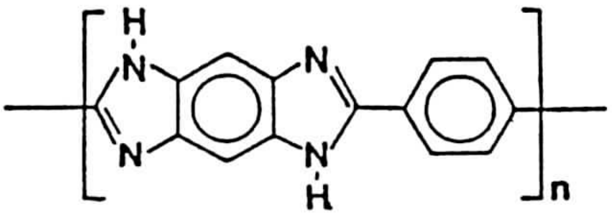
Nr.	R	Ar	Solubility a) H$_2$SO$_4$	DMAc/LiCl	DMAc	DMSO	inh. viscosity dl/g b)	c)
I			+	-	-	-	1.35	-
II		=	+	+	-	+	0.72	1.65
III		=	+	+	+	+	1.02	1.56
IV	H		+	+	-	-	-	4.07
V		=	+	+	up to 25%	-	-	3.82
VI		=	+	+	up to 30%	+	-	2.50
VII		=	+	+	up to 40%	+	-	2.42

a) + soluble, T=25°C
  - insoluble, T=25°C

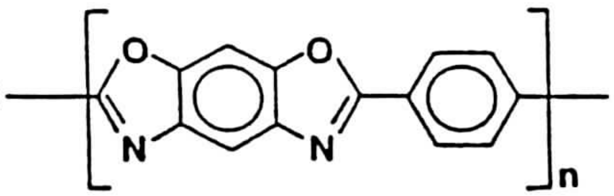
b) sulfuric acid (96%), 30°C, 0.5g/dl
c) DMAC/LiCl (4%, w/v), 25°C, 0.5g/dl

RIGID ROD POLYMERS

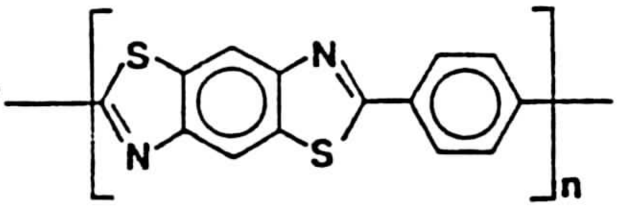
PBI

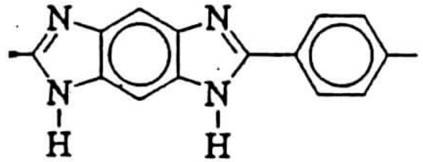
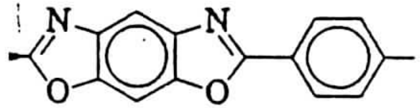
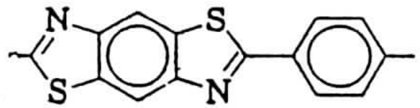
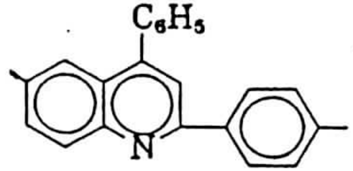
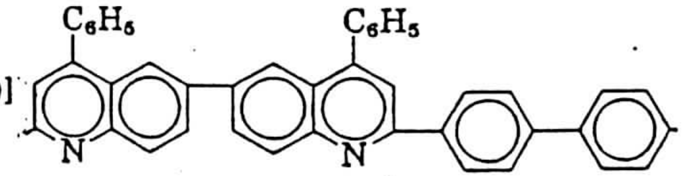


PBO



PBT



Compound	Structure	Lyotropic solution
poly(1,4-phenylene-2,6-benzobisimidazole)		methanesulfonic acid
poly(1,4-phenylene-2,6-benzobisoxazole) (PBO)		methanesulfonic acid chlorosulfonic acid 100% sulfuric acid
poly(1,4-phenylene-2,6-benzobisthiazole) (PBT)		5–10% in polyphosphoric acid methanesulfonic acid
poly[2,6-(1,4-phenylene)-4-phenylquinoline]		1.0–1.5% in *m*-cresol–di-*m*-cresyl phosphate
poly[1,1'-(4,4'-biphenylene)-6,6'-bis(4-phenylquinoline)]		>9% in *m*-cresol–di-*m*-cresyl phosphate

(from Kwolek et al. Encyclopedia of Polymer Science, Vol.9)