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VCH

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Contents

9 Molecular Engineering of Liquid Crystalline Polymers*

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and Rudolf Zentel**

9.1 Introduction: Self Organizing Systems

Polymer science within the scope of the Sonderforschungsbereich 41 was, at its inception, devoted to classical problems in chemistry and physics of macromolecules, e. g. polymerization kinetics, solution properties and partially crystalline polymers. From this starting point, research in Mainz has evolved and expanded into the areas of material and life sciences. Polymeric liquid crystals and polymeric membrane models have played significant roles in this evolution. Investigations of these materials have led to a view of polymer science as an interdisciplinary field, with the areas of polymeric liquid crystals and polymeric membrane models (cellular liquid crystals) as two important research areas within this field. This relationship is schematically represented in Fig. 9.1.

Within the perspective of the Sonderforschungsbereich 41, the investigation of polymeric liquid crystals and membrane models was incorporated into the study of *self-organizing supramolecular structures*. These systems are unique in that they combine *order and mobility* as well as *function via organization* (see Fig. 9.2). Polymeric thermotropic liquid crystals and liposomes are the two extremes within this framework. These areas of investigation are linked by

Fig. 9.1: Polymer science as an interdisciplinary field.

the investigation of polymeric surfactants. Some of these surfactants are used to build mono- and multilayers, while others aggregate in solution to form micelles of different shapes and lyotropic liquid crystalline phases. Since investigations on polymeric amphiphiles have been reviewed quite recently [1], this chapter will concentrate on the synthesis, structures and properties of thermotropic liquid crystalline polymers.

9.2 Molecular Architecture of Liquid Crystalline Polymers

Liquid crystals [2–4] combine the properties of liquids and crystals – most characteristically, those of mobility and order. Liquid crystalline phases or mesophases ("meso" = inbetween, here the liquid and crystalline state) occur in a particular temperature interval between the well ordered crystalline phase and the mobile isotropic liquid. Whether a liquid crystalline phase is formed or not, as well as its type, is closely related to molecular structure. Typical of liquid crystalline molecules, also called mesogens, is their strong formanisotropy. They are in general composed of an inner rigid core which is rod-like or

SELF-ORGANIZING SYSTEMS
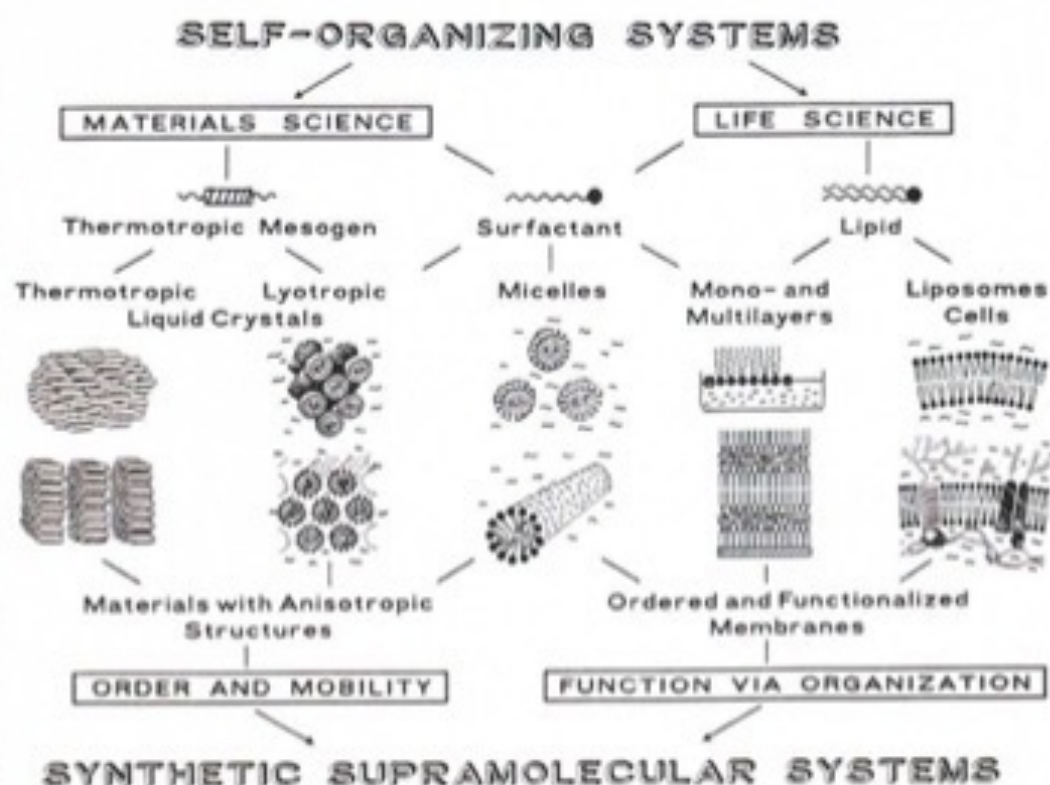
Fig. 9.2: Self-organization and supramolecular systems [1] in material science and life science. The supramolecular structures range from thermotropic liquid crystals to liposomes.

disc-like [5, 6] in shape and often substituted with alkyl chains (the so-called "tails" of the mesogen). Fig. 9.3 shows the formation of different thermotropic liquid crystalline phases starting from rod-like mesogens (for the formation of liquid crystalline phases from disc-like mesogens see section 9.2.2).

The *nematic phase* (n) is usually the high temperature phase. The mesogens are arranged in such a way that their centres of mass display a short range order and their long axes lie preferentially in one direction *(long range orientational order)*. This long range orientational order describes the characteristic difference with respect to the isotropic melt, where the centres of mass are also isotropically distributed but a preferred orientation of the molecules is not found over long distances. At lower temperatures different *smectic* phases may occur. The mesogens now arrange in layers. As in nematic phases, their long axes still lie preferentially in one direction (long range orientational order). Their centres of mass, however, are no longer isotropically distributed but ordered (in layers), giving the smectic phase an additional element of order with the *long range positional order*.

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formanisotropic molecules

mesogen   e.g.

$C_8H_{11}O$ —⟨⟩—⟨⟩— CN

↓

self-organization

↓

crystal   **thermotropic liquid crystal**   liquid

smectic   nematic

order   **order and mobility**   mobility

↑

temperature →
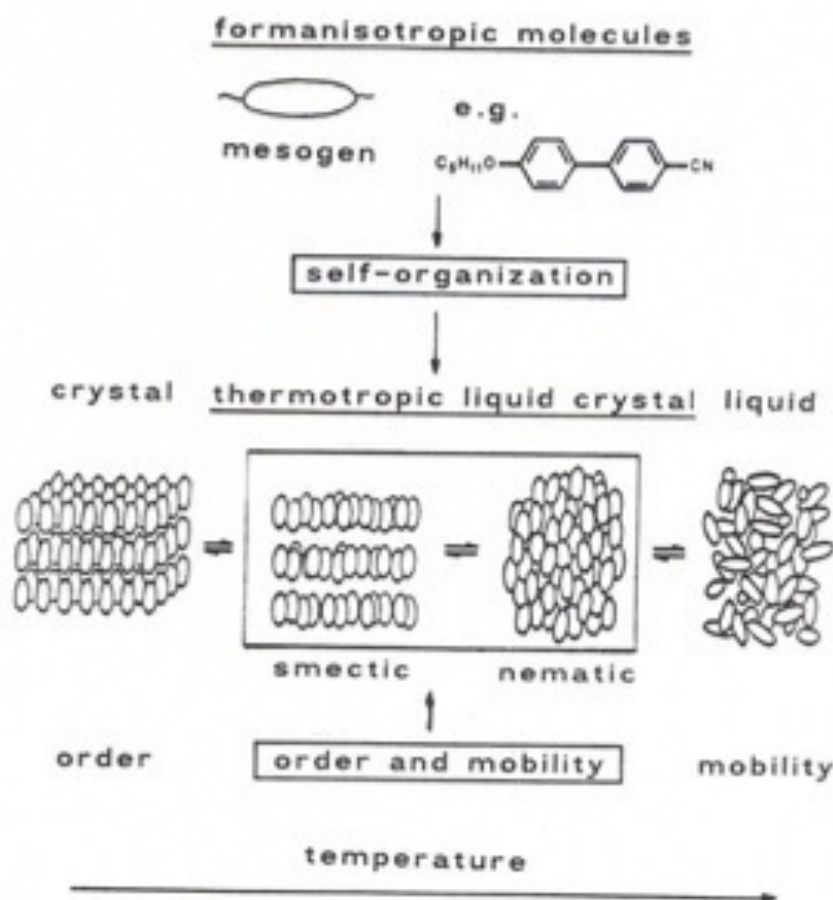
Fig. 9.3: Structure and phase behaviour of thermotropic liquid crystals from rod-like molecules.

Eleven types of smectic mesophases have been identified, ranging from smectic A (S_A) to smectic K (S_K). These differ in the arrangement of the mesogens within each individual layer (e.g. no order within the layer in S_A, hexagonal order in S_B) and/or their orientation within the layer plane (e.g. orthogonal in S_A, tilted in S_C) [7].

Rapid developments in the field of liquid crystalline (LC) polymers [8] occured after the realization of *rigid rod macromolecules* in which the main chain, as a whole, functions as the mesogen. Such polymers form liquid crystalline phases either in solution (lyotropic) [9] or in the bulk at high temperatures close to the decomposition temperature (thermotropic) [10]. At present they are used as high tensile strength fibers (e.g. Kevlar®) or as thermoplastically processable, self-reinforcing plastics (e.g. Xydar®, Vectra®, Ultrax®).

Parallel to these industrial developments, numerous studies have been carried out in areas of basic research during the past fifteen years. The original goal was to prepare thermotropic LC polymers which form liquid crystalline

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phases at moderate temperatures, primarily for kinetic investigations in oriented systems [11]. For this purpose, rod-like mesogenic groups, well known from low molar mass liquid crystals, were incorporated into flexible polymers. The crucial point in the systematic synthesis of these polymers was the combination of two opposing tendencies: Formanisotropic mesogens with their tendency towards an anisotropic arrangement had to be linked to polymer chains with the tendency to adopt a statistical coil conformation. This problem was solved by the use of a *flexible spacer* [12, 13] to ensure a *partial decoupling* between polymer chains and mesogenic groups (see Fig. 9.4).

Starting from the first – recognized as "classical" – liquid crystalline (LC) polymers prepared according to this concept (the side chain polymers *A* and the main chain polymers *B*, shown in Fig. 9.5), the *molecular architecture* of liquid crystalline polymers has been varied extensively [14]. This is illustrated schematically in Fig. 9.5.

On the one hand, it is possible to realize discotic phases, known from low molar mass liquid crystals, by using disc-like mesogens in side group [15] (type *C*) and main chain [16] (type *D*) polymers. On the other hand, it is, of course, also possible to incorporate rod-shaped mesogens in ways different from the two classical types *A* and *B*: examples are side group polymers [17–18] (type *E*) as well as main chain polymers [18] (type *F*) with laterally fixed mesogens. Contrary to expectations, these strange-looking architectures do not prevent the formation of liquid crystalline phases. As far as polymers of type *E* are concerned, the limited rotation of the mesogenic groups around their longitudinal axes leads to the formation of biaxial nematic phases [17]. A third type of structural variation makes use of a principle that is well known in polymer chemistry but has rarely been used in the field of liquid crystalline materials: the combination of different structural elements and different building principles within one molecule. This includes different combinations of rod- and disc-shaped mesogens [19–22] (types *G*, *H* and *I*) and the combination of structural principles of the two classical types of liquid crystalline polymers (type *A* and *B*) in combined main chain/side group polymers [23–24] (types *J* and *K*).

Furthermore, polymers containing cross-shaped mesogens [18] (type *M*) should be noted, as well as the idea of combining laterally and terminally connected mesogenic groups (type *L*).

Parallel to this variation in molecular architecture, LC polymers have been *functionalized* in different ways. For this purpose, dye containing groups [25, 26], groups undergoing chemical [27] or photochemical reactions [28, 29] and groups carrying chirality and strong dipole moments [30, 31] (see section 9.2.3 and Fig. 9.6) have either been incorporated into the mesogens or were added into the polymer chain as comonomers.

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STATISTICAL ARRANGEMENT
OF CHAIN SEGMENTS
- RANDOM COIL -

ANISOTROPIC ARRANGEMENT
OF MESOGENIC UNITS
- ANISOTROPIC PHASE -

PARTIAL DECOUPLING
BY FLEXIBLE SPACERS
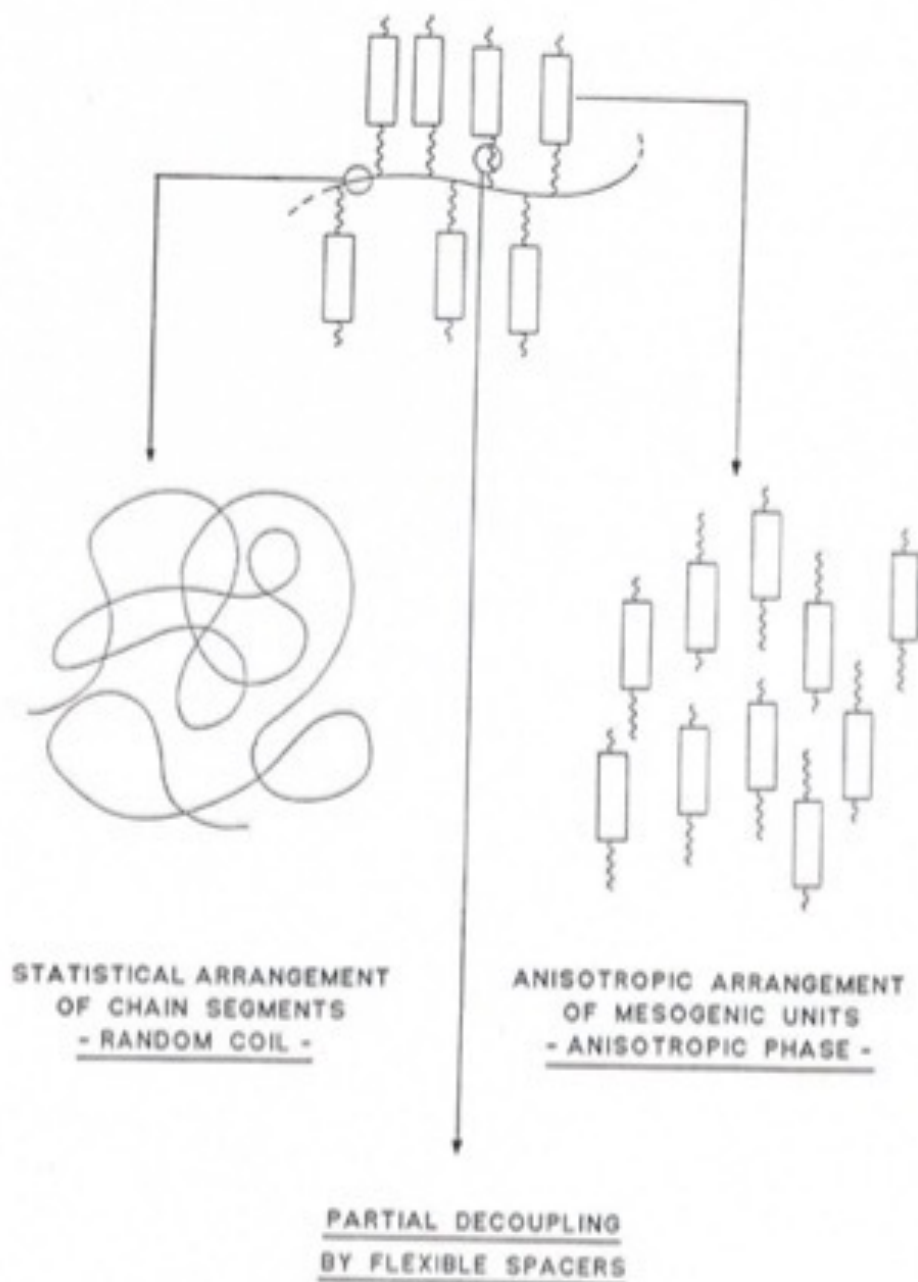
Fig. 9.4: The concept for the synthesis of LC polymers: Mesogens with their tendency towards anisotropic arrangement and polymer chains with their tendency towards random coil formation are partially decoupled via flexible spacers.
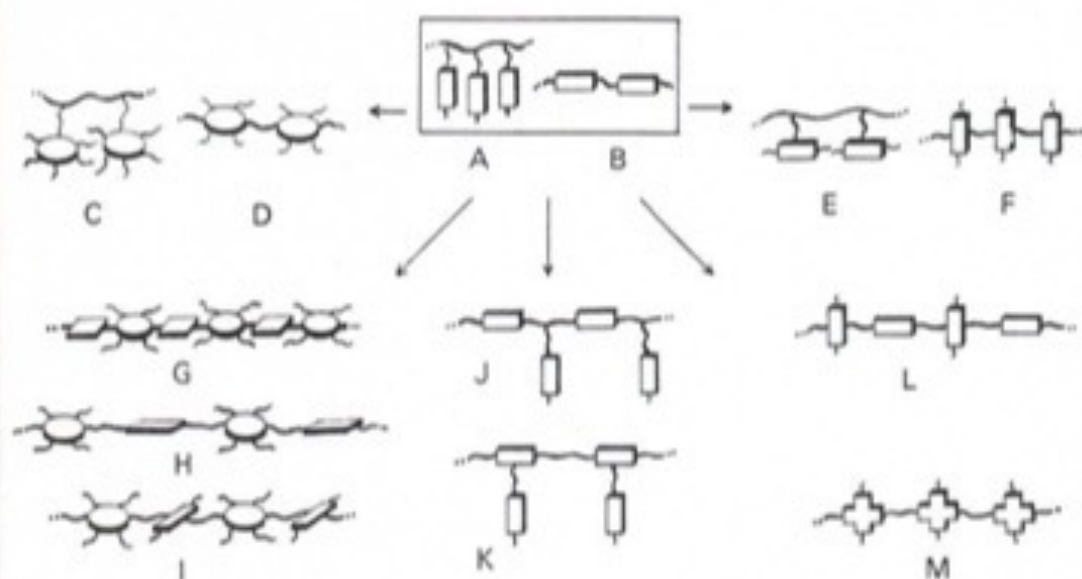
Fig. 9.5: Molecular architecture of polymeric liquid crystals: Variation of shape and arrangement of the mesogens.

Molecular Engineering of LC-Polymers

Molecular Architecture

Variation of Geometry

Shape of Mesogens
e.g.

Arrangement
e.g.

Functionalization

Function Incorporated in

Mesogens
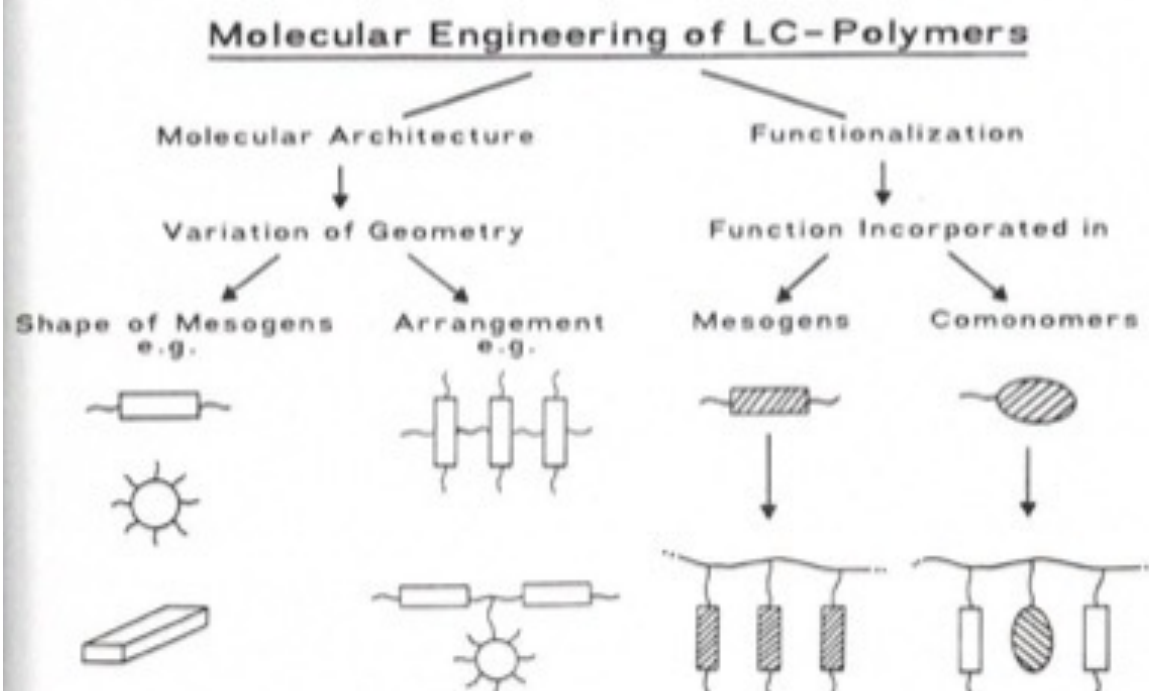
Comonomers

Fig. 9.6: Molecular engineering of LC polymers can be achieved either by varying the molecular geometry or by incorporating functionalized groups in mesogens or comonomer units.

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9.2.1 Liquid Crystalline Polymers with Rod-like Mesogens

9.2.1.1 Synthesis and Structure-Property Relations of LC Side Group Polymers
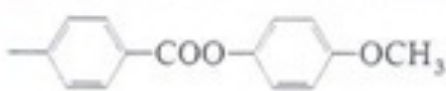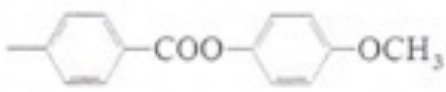
The concept of linking mesogenic groups via a flexible spacer to the polymer chain to produce LC side group polymers (type *A* of Fig. 9.5) was first realized with polymethacrylates using benzoic acid phenylesters as mesogens [12] (see Table 9.1). Later, biphenyls [32, 33], phenylcyclohexanes [25, 34] and phenyl-pyrimidines [35] were also used – in Mainz – as mesogens, with polyacrylates [36], polysiloxanes [33, 37], polychloroacrylates [38], and polyitaconates [34] as polymer chains. For a comprehensive summary of the systems synthesized so far see references [39] and [40]. The structural variation of polymer subunits – mesogenic groups, spacer groups, and polymer chains – enables the influence of each of these constituents on the properties of the liquid crystalline polymers to be determined. The influence of variations of the mesogenic groups and the spacer length on the phase behaviour is summarized in Table 9.1.

The *influence of varying the mesogenic structure* is demonstrated by comparing polymer *1* and *2*. A polyacrylate with 6 methylene units as a spacer and benzoic acid phenylester as mesogen (polymer *1*) shows a glass transition temperature at 35°C, a smectic A phase up to 97°C and a nematic phase that becomes isotropic at 123°C. A change of the mesogenic group, in this case the exchange of the benzoic acid phenylester with a phenylcyclohexane (polymer *2*), keeping the rest of the polymer structure constant, leads to drastic changes in the phase behaviour: The glass transition temperature drops to −10°C and only a nematic phase is found for this polymer. This is in accordance to what is known from low molar mass liquid crystals: the phenylcyclohexanes [41] are known for their low viscosities, low melting temperatures and a preference for nematic phases. The influence of a decrease in spacer length while keeping the mesogen constant is revealed by a comparison of polymer *1* and polymer *3*. In this case, the glass transition temperature rises and only a nematic phase is observed for the polymer with the short spacer. This again is not astonishing because a decrease in the spacer length corresponds to a decrease in the length of the tails of the mesogens and it is well-known from low molar mass liquid crystals [3–5, 7] that this favours the formation of nematic phases. In conclusion, the main effect of varying the mesogenic groups and spacer length is both a change in the mesophase type and the clearing temperature as the upper limit of the liquid crystalline phase.

In contrast, the main *influence of varying the polymer chain* is summarized in Table 9.2 [37].

All three polymers in Table 9.2 show, independent of the polymer chain, a nematic phase. However, the glass transition temperatures are very different.

Table 9.1: The influence of variations of the mesogens and the spacer length on the phase behaviour demonstrated by comparing polymers *1–3* [34, 36].

$$CH_2$$
$$CH-COO-(CH_2)_n-O-\boxed{R}$$
$$_x$$
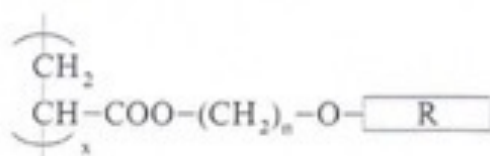
No.	n	R	Phase transitions/°C
1	6	—◯—COO—◯—OCH$_3$	g 35 s$_A$ 97 n 123 i
2	6	—CO—◯—◯—C$_3$H$_7$	g −10 n 20 i
3	2	—◯—COO—◯—OCH$_3$	g 62 n 116 i

They are as high as 97°C for the polymethacrylate *4*, and only 15°C for the polysiloxane *5*. This certainly reflects the different mobilities of polymethacrylate, polyacrylate and polysiloxane chains (T$_g$-values are 105°C for PMMA, 10°C for PMA and −120°C for PDMS homopolymers, respectively [42]). The fact that the glass transition of the polysiloxane *5* (15°C) is still much higher than the glass transition temperature of the pure polymer backbone (−120°C), demonstrates that the mobilities are, of course, modified by the mesogenic groups. Nevertheless, the main effect of a variation in the polymer chains is a variation of the mobility and the glass transition temperature as the lower limit of the liquid crystalline phase.

So far, the discussion has focused on structure-property relations of LC-polymers. *Characterization of the liquid crystalline phases* is addressed in the next section. The polymers prepared so far show different liquid crystalline phases, which can be classified in complete analogy to low molar mass liquid crystals [39]. In this way, nematic, cholesteric [43], and different smectic phases can be clearly identified. They show the optical textures typical for low molar mass liquid crystals and the corresponding X-ray patterns [44–47]. The order parameter of the mesogenic groups was determined, for example, by ESR- (see Fig. 9.7) and ^{2}H-NMR-spectroscopy [48a–c, 49] (see Spiess and Sillescu,

Table 9.2: The influence of variations of the polymer chain on the phase behaviour demonstrated by comparing polymers *3–5* [33, 36, 37].

$$\text{--}(\!-\!M\!-\!)_x\!-$$
$$(CH_2)_n\text{--}O\text{--}\bigcirc\text{--}COO\text{--}\bigcirc\text{--}OCH_3$$

No.	M	n	Phase transitions/°C
4	~(~ CH$_2$–C~)~ (CH$_3$ top, COO~ bottom)	2	g 97 n 120 i
3	~(~ CH$_2$–CH~)~ (COO~ bottom)	2	g 62 n 116 i
5	~(~ O–Si~)~ (CH$_3$ top, CH$_2$~ bottom)	2	g 15 n 61 i

Chapter 12, this Volume) and has been found to be in good agreement with the values measured for low molar mass liquid crystals. The results of ^{2}H-NMR-measurements [48a] proved, for example, that all mesogens participate in the liquid crystalline ordering. That means these polymers do not show a partial "degree of liquid-crystallinity" in analogy to partially crystalline polymers [48d]. Fig. 9.7 summarizes the results of ESR-measurements with a spin-probe on the polymers *1* (nematic and smectic) and *3* (nematic) of Table 9.1 [49]. For both polymers, the order parameter jumps at the clearing temperature from 0 (isotropic phase) to a finite value in the nematic phase. With decreasing temperature, it increases continuously, until it becomes constant around the glass transition temperature. For polymer *1* the transition from the nematic to the smectic A phase is accompanied by an additional jump of the order parameter. For this polymer an order parameter as high as 0.9 is frozen in the glassy state.

Well oriented samples of the LC polymers can be obtained by using electric and magnetic fields [39, 46–52] as well as mechanical stretching [16, 23, 27, 39, 44, 45]. Because of their orientability in electric fields, these polymers
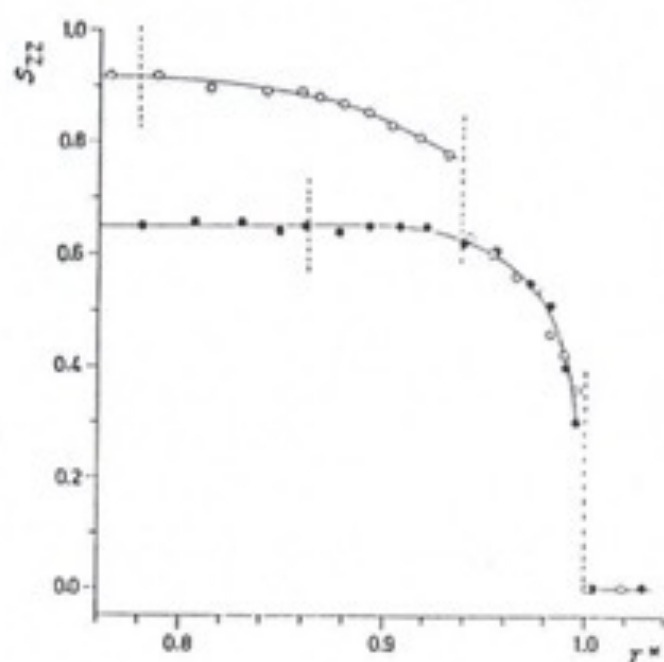
Fig. 9.7: Order parameters [49] of the liquid crystalline polyacrylates *1* (○) and *3* (●) (see Table 9.1) as function of the reduced temperature $T^* = T/T_{ni}$. (T_{ni}: transition temperature nematic-isotropic). The dashed lines indicate the phase transitions.

have been tested for use in liquid crystal displays (see Fig. 9.8). Fig. 9.8 shows schematically the reorientation of the mesogenic groups upon application of an electric field. Without an electric field, the mesogens are oriented parallel to the glass plates, giving rise to a birefringent texture which transmits light between crossed polarizers. Upon application of an electric field, the mesogens orient perpendicular to the glass plates and give rise to a pseudoisotropic, dark texture. Fig. 9.8 shows the switching behaviour for one polymer [50]. With rise and decay times around 200 msec, this polymer switches fairly fast, but only at high temperatures. As the measuring temperature approaches the glass transition, the reorientation times increase to infinity.

Properties of LC side group polymers and low molar mass liquid crystals differ mainly in the dynamic aspects mentioned above. This is demonstrated also in dielectric relaxation behaviour [53–57]. Dielectric relaxation measurements show both the dynamic glass process of the polymer chains (α-relaxation) and 180° jumps of the long axes of the mesogens (δ-relaxation: see Fig. 9.9) [54]. The δ-relaxation is orders of magnitude slower than in low molar mass liquid crystals and freezes at the glass transition temperature. In addition, up to 3 local relaxation processes are found below the glass transition temperature (see Fig. 9.9) which can be attributed to relaxations of the mesogenic groups (β), the spacer (γ_1) and the end group (γ_2) [54]. The results obtained for polymer *1* of Table 9.1 are presented in Fig. 9.9b. It is interesting

Relative Intensity
(Brightness)

turn on time
150 ms

turn off time
200 ms

$\oplus$

$\ominus$

1 2 3

t_{on} t_{off} $t\,/_{sec}$

Polymer :

CH_2
$CH-COO-(CH_2)_6-O--COO--CN$

0.3

CH_2
$CH-COO-(CH_2)_6-O--COO---OCH_3$

0.7
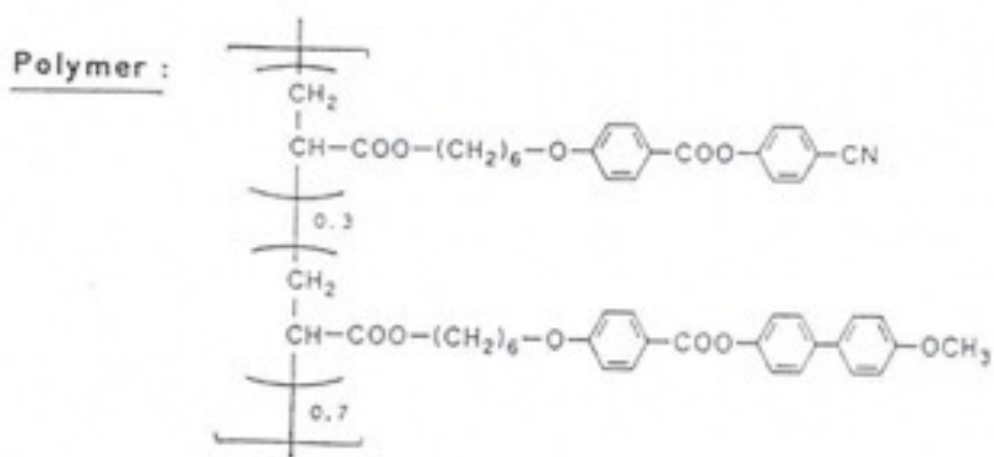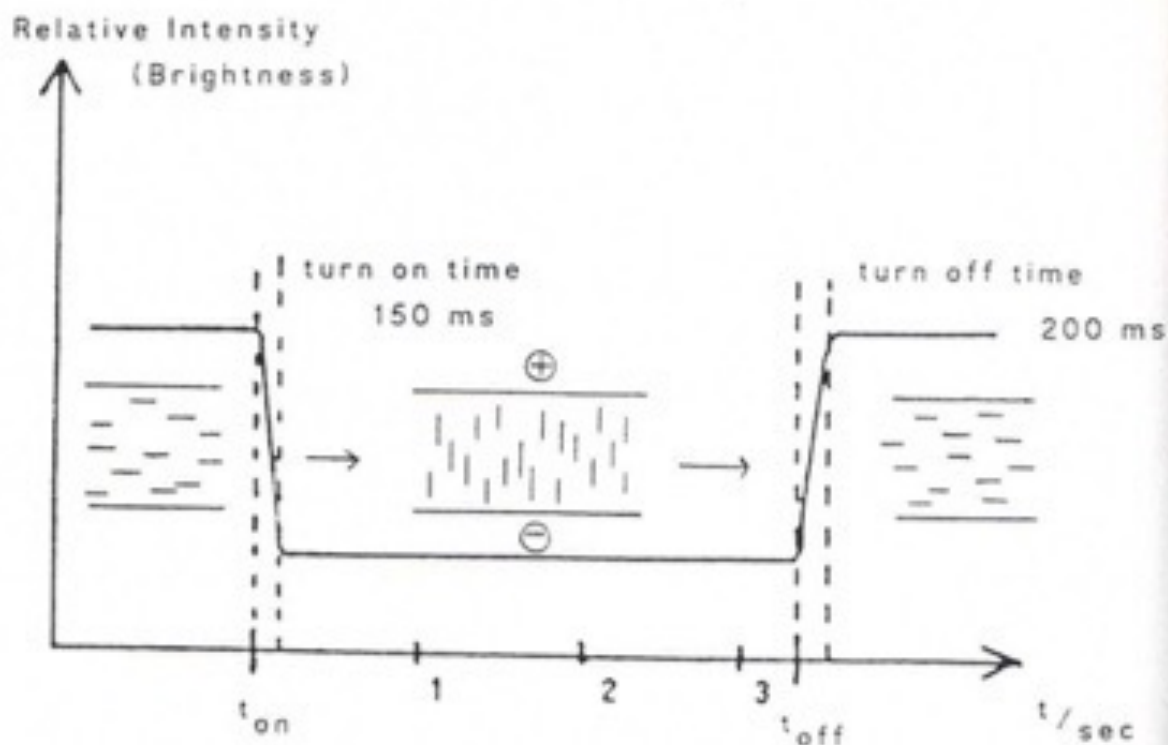
g 29 s 172 n 209 i

Conditions : 186 °C ; 20 V ; 500 Hz

Fig. 9.8: The switching of a liquid crystalline polymer in an electric field [50] changes the transmittance of the sample between two crossed polarizers.

222
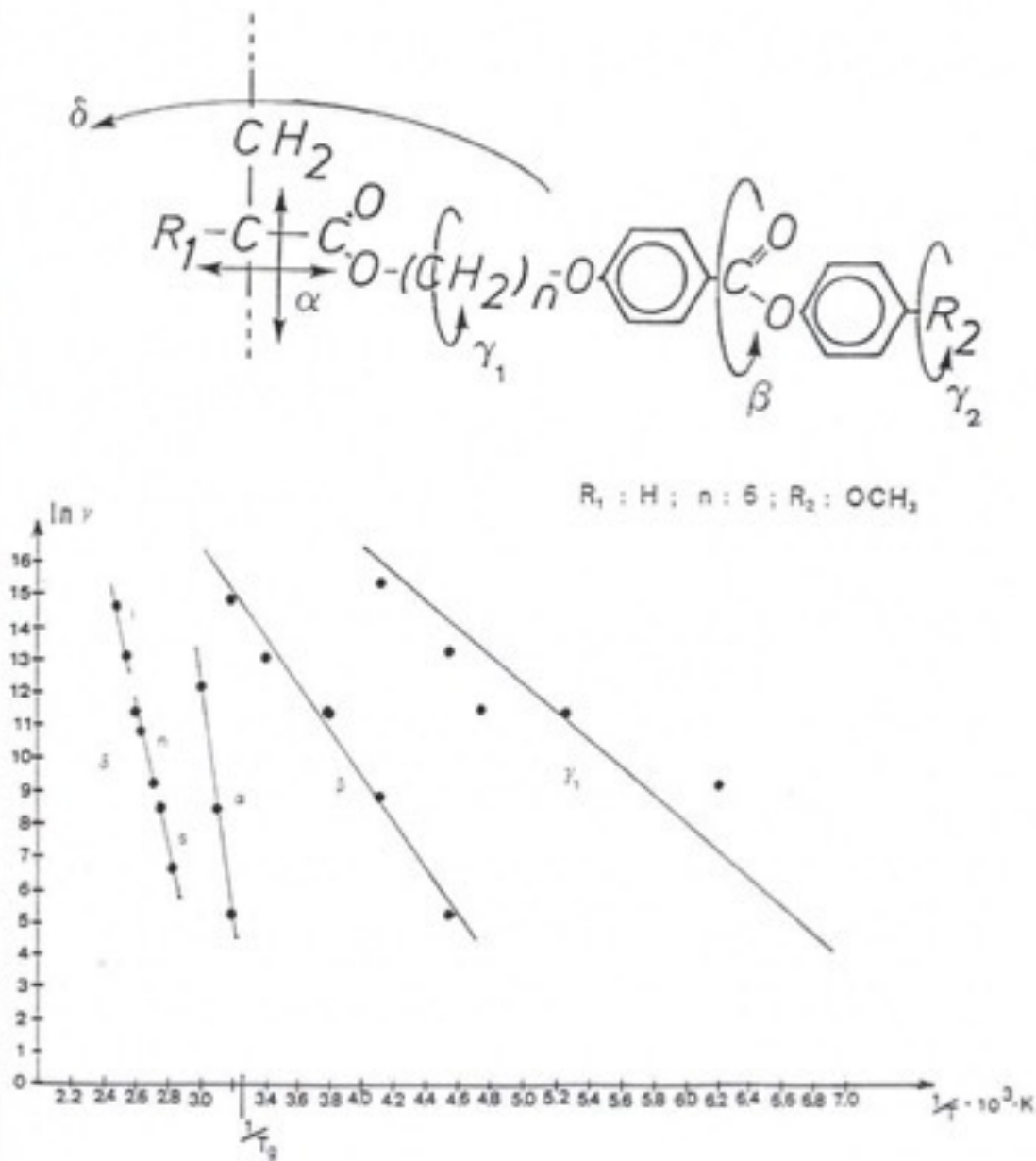
Fig. 9.9: Dielectric relaxation measurements [54] have revealed 5 different relaxation processes for LC polyacrylates (a). The plot of the natural logarithm of the relaxation frequency versus $1/T$ (b) shows the temperature dependence for 4 of the relaxation processes for polymer I (see Table 9.1).

to note that the ß-relaxation of the polymers *1* and *3* agrees completely with the dynamics of 180° phenylflips determined for the same polymers by ²H-NMR-spectroscopy [48c] (see Spiess and Sillescu, Chapter 12, this Volume).

9.2.1.2 Synthesis and Structure-Property Relationships of Main Chain Polymers

Classical rigid-rod polymers [10] show thermotropic liquid crystalline phases only at very high temperatures close to the temperature of thermal decomposition. The incorporation of flexible spacer segments, however, allows the synthesis of semiflexible main chain polymers (type *B* of Fig. 9.5) that show liquid crystalline phases at moderate temperatures [13]. Within the scope of the Sonderforschungsbereich 41, the research interests in semiflexible main chain polymers was aimed at a further decrease of the lower limit of the liquid crystalline temperature range by the use of very flexible spacer segments. For this purpose siloxane spacers were used. Fig. 9.10 shows the results obtained for one series of these siloxane spacer-containing main chain polymers [58]. With increasing length of the siloxane spacer, the glass transition temperature drops drastically and is as low as −100°C at a spacer length of 13 repeating units, while the phase width of the liquid crystalline phase is kept constant.

9.2.1.3 Molecular Engineering of LC Polymers: Side Group and Main Chain LC Systems

In connection with the structural variation of side group polymers, it was especially interesting to *vary the number of mesogenic units per repeat unit* in the polymer chain. In order to increase the concentration of the mesogens, polyitaconate diesters and polysiloxanes substituted with allylmalonic acid diesters (*"dimesogenic" polysiloxanes*, see Figs. 9.11, 9.12) were utilized [34]. Both systems allow the fixation of two mesogens per repeat unit. In order to decrease the concentration of the mesogens, copolysiloxanes were used in which only some of the siloxane units carried mesogenic groups.

These copolymers have found interest for preparation of LC polymers with low glass transition temperatures. If, in these copolymers, each mesogen is fixed separately to the polymer chain, then the liquid crystalline phase is lost at a ratio of 1 mesogen per more than 5 dimethylsiloxane units (see Fig. 9.12). If, however, „dimesogenic" polysiloxanes are used [34, 59], then the ratio can be as low as two mesogens (fixed together) per more than 30 dimethylsiloxane units (see Fig. 9.12). These copolymers show low glass transitions and broad liquid crystalline phases, the phase width of which is comparable to the homopolymers.
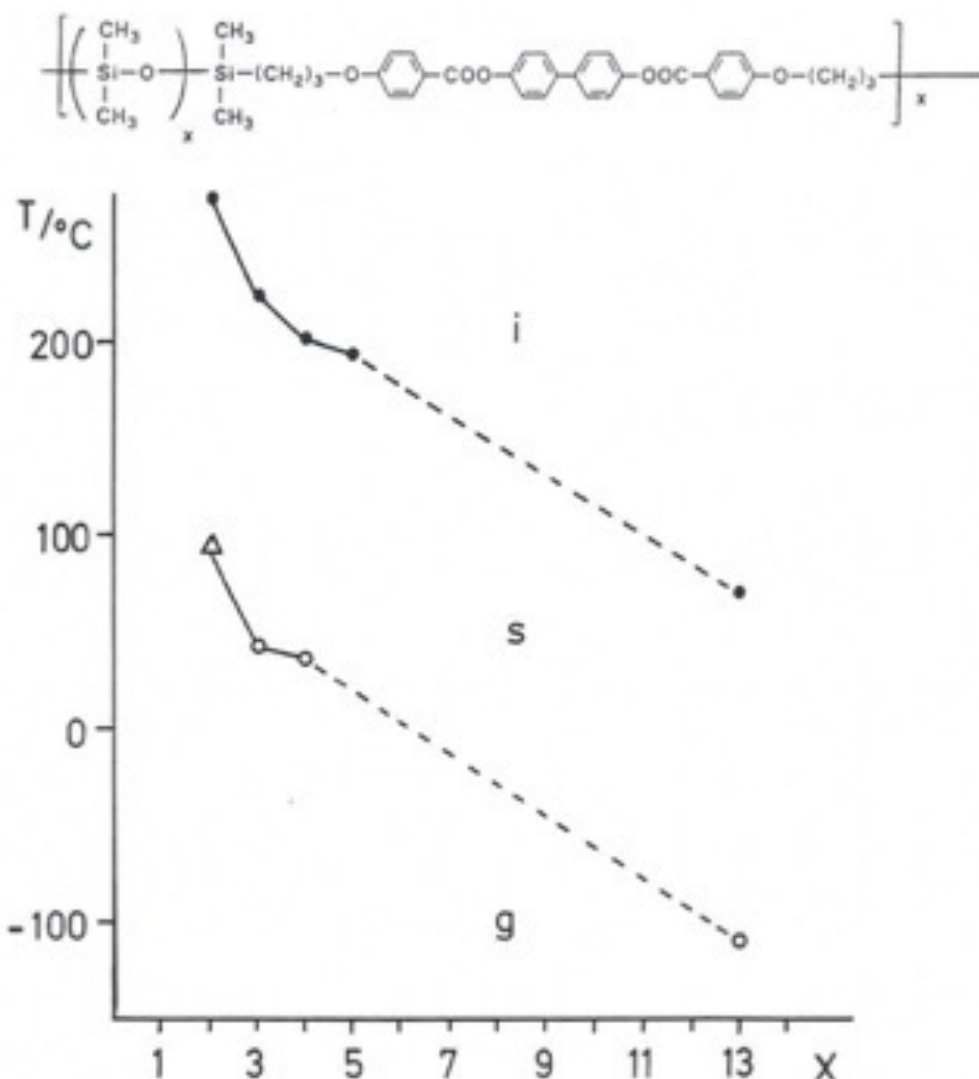
Fig. 9.10: Dependence of the transition temperatures of semiflexible LC main chain polymers on the length of the siloxane spacer [58].

The fact that „dimesogenic" polysiloxanes form liquid crystalline phases, even if only each 30th repeating unit is linked to mesogens, can be understood with a model derived from X-ray measurements of homologous series of these polymers [59] (see Fig. 9.13). The model assumes that mesogenic groups pack densely and reject the polysiloxane chains, which are incompatible with them. Thus, two sublayers are formed (microphase separation), one consisting of the disordered polysiloxane chains and the other of the mesogenic groups, which are in a smectic A arrangement.

However, if each mesogen is linked to the polymer chain separately, or if the polymer chains are more compatible (e.g. polyacrylates) with the mesogens,

HOMOPOLYMERS   COPOLYMERS
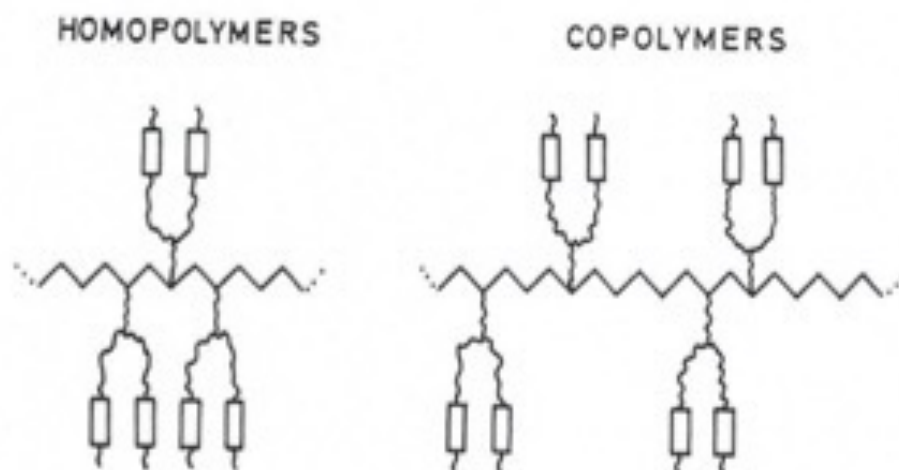
Fig. 9.11: Schematic structure of "dimesogenic" polysiloxanes. In the case of the homopolymers, two mesogens are fixed per each repeating unit. In the case of the copolymers, the mesogens are statistically distributed along the polymer chain.

then the tendency towards microphase separation is reduced. In these cases, the incorporation of nonmesogenic units into the polymer chain reduces the interaction among the mesogens and destroys the liquid crystalline phase.

Another structural variation of LC polymers led to the synthesis of *combined main chain/side group polymers* [23, 24] (types J and K of Fig. 9.5) that combine the structural principles of the „classical" main chain and side group polymers (types A and B of Fig. 9.5). These polymers show very broad liquid crystalline phases that are, in most cases, broader than the liquid crystalline phases of the corresponding pure main chain or side group polymers. This suggests that the mesogenic groups in the main chain and the side groups are not oriented perpendicular to each other as suggested by the chemical formula in Fig. 9.14. They orient parallel to each other (see Fig. 9.14) to produce an uniaxial mesophase, as confirmed by X-ray measurements on oriented fibres [60]. This structure, in which both types of mesogens are oriented parallel to each other, can also explain the differences in the phase behaviour of polymers of type J and K [24]. For polymers of type J, a smectic layer structure is preformed locally and consequently mostly smectic phases are observed. For polymers of type K, however, the fixation of mesogenic side groups to the middle of the mesogenic groups in the main chain favours nematic phases (see Fig. 9.14).

By the use of chiral end groups, polymers of type J with cholesteric and chiral smectic C* phases can be prepared [30, 31] (see also Fig. 9.29 in Section 9.2.3.3). As far as the dynamics of these „combined" polymers is concerned, it is especially interesting that the reorientation of the long axes of the mesogenic side groups (δ-relaxation, see Fig. 9.9) is still possible [61].
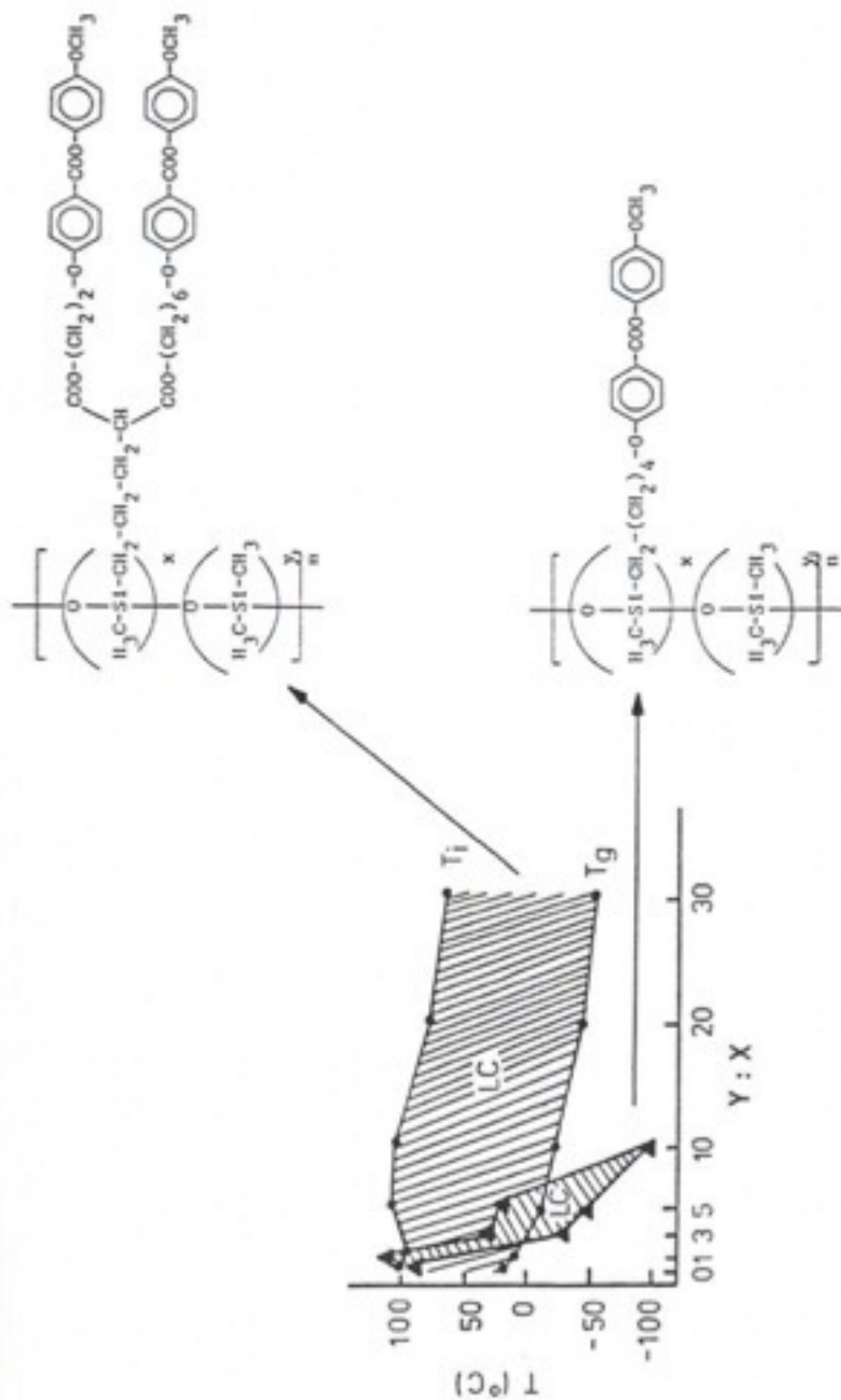
Fig. 9.12: Phase behaviour of "monomesogenic" and "dimesogenic" copolymers versus the ratio of repeating units carrying no mesogens (Y) to units carrying mesogens (X). For the "dimesogenic" copolymers the lc-phase width remains broad and constant up to 30 dimethylsiloxane units per "dimesogenic" unit (Y : X = 30). In contrast, for the "monomesogenic" copolymers the lc-phase width shrinks and is lost above 10 dimethylsiloxane units per "mono-mesogenic" unit (Y : X ≥ 10).
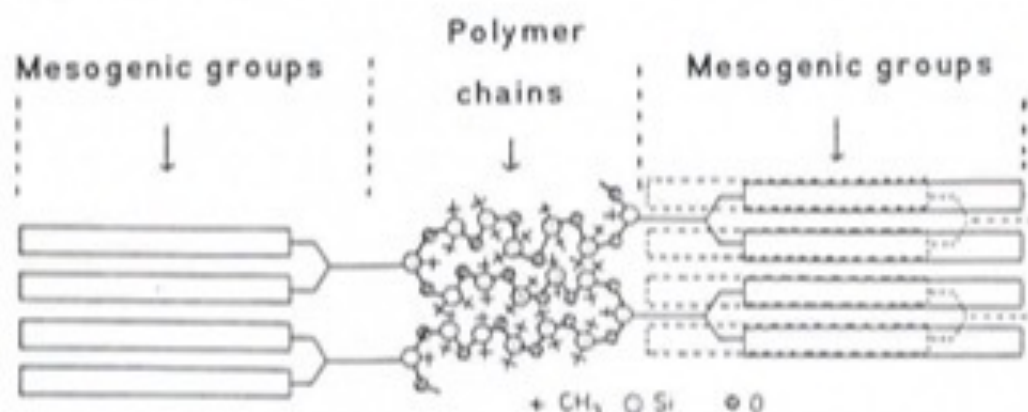
Fig. 9.13: Schematic model of the layer structure for "dimesogenic" polysiloxanes [59]. The mesogenic groups drawn in dashed lines are positioned above the drawing plane.

9.2.2   Liquid Crystalline Polymers with Disc-like Mesogens

Calamitic mesophases formed from rod-like mesogens are well-known and have been realized in many polymeric systems. This is not the case with discotic mesophases formed from disc-like mesogens. Predicted theoretically in 1974 [2] discotic mesophases remained undiscovered until 1977 [5] (see Fig. 9.15).

Analogously to calamitic phases which are divided into nematics (n) or smectics (s), discotic mesophases [62] can be either nematic-discotic (N_D) involving long range orientational order of the mesogens only, or columnar (e.g. D_{ho}) involving both long range orientational and long range positional order. In the latter columnar phases disc-like molecules are stacked, regularly (ordered) or irregularly (disordered), in columns. These arrange in various lattices of which the hexagonal lattice is most commonly observed (D_{ho} = discotic hexagonal ordered mesophase). As with calamitic systems, *discotic polymers* of both the side group [15] and main chain type [16] have been synthesized analogously by linking disc-like mesogens through flexible spacers (see Fig. 9.16).

A third type of fundamentally different molecular structure is a board-like shape (see Fig. 9.15). Boards do not show rotational symmetry about any axes at all, neither about the long axis as for rods nor about the short axis as for discs. Molecular (polymeric) engineering has recently succeeded in making board-like structures by linking disc-like mesogens rigidly in a main chain polymer (see Fig. 9.16). For the resulting *sanidic polymers*, both phase types, sanidic nematic [66] and the higher ordered sanidic phases [19, 69], are found.

J

k 129 s$_C$ 153 s$_A$ 162 n 181 i

K

g 41 n 221 i
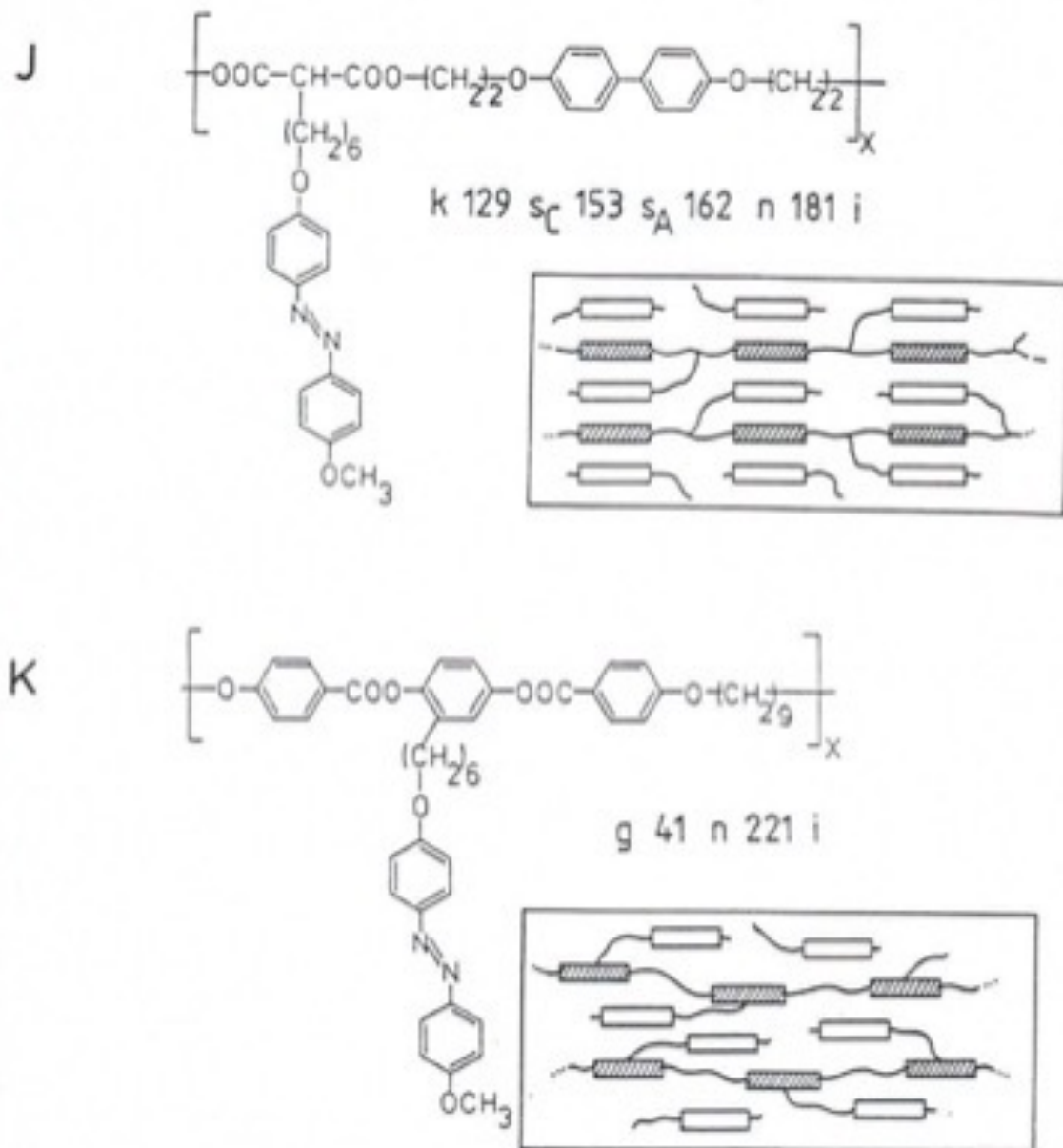
Fig. 9.14: Chemical structure, phase behaviour and structural models of the meso-phases of combined main chain/side group polymers [24].

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Molecular Structure	Type of Mesophase
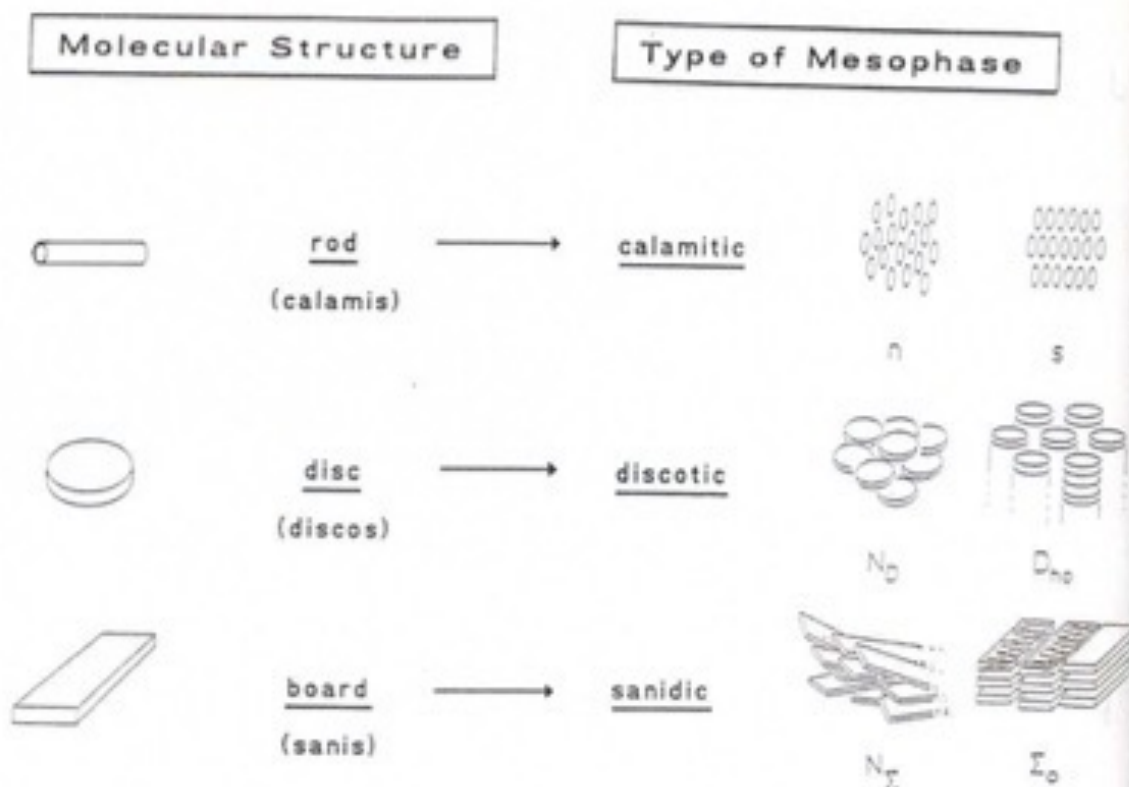
Fig. 9.15: Relationship between molecular structure and mesomorphic structure for rod-like, disc-like and board-like mesogens. The greek expressions are in brackets.
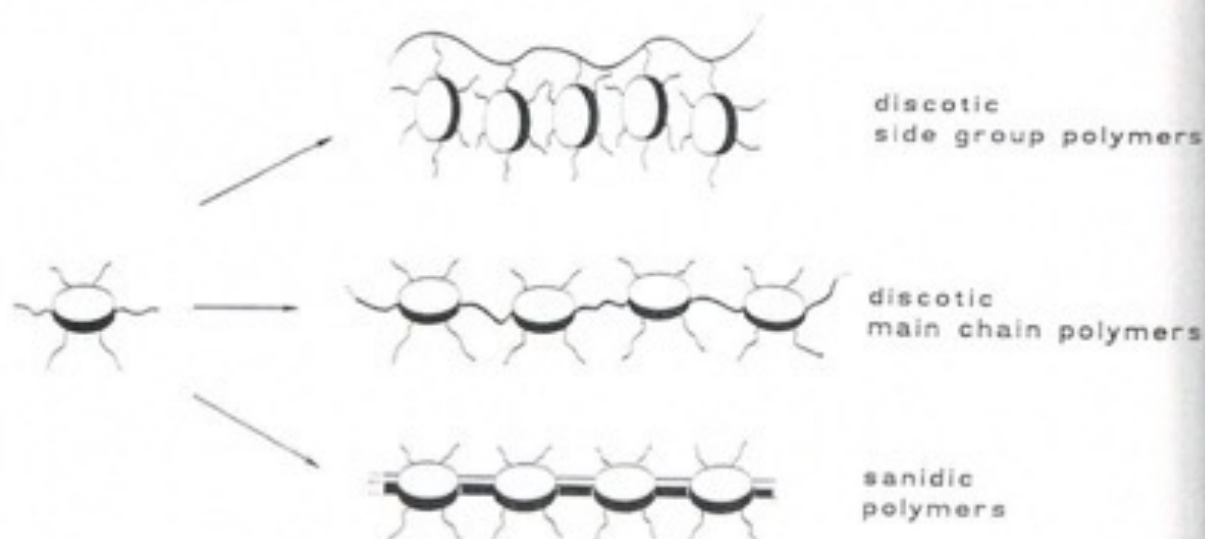
Fig. 9.16: Different ways to prepare discotic and sanidic polymers.

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9.2.2.1 Polymers with Discotic Phases

Linking disc-like molecules through *flexible* spacers leads to discotic polymers, i.e. polymers with discotic mesophases. The first discotic polymers were side group systems incorporating hexapentyloxytriphenylene as the disc-like mesogen [15]. More recently some more polymers with disc-like mesogens [16, 64a–d] have been synthesized. Structural variations, however, are still restricted and not to be compared to those of calamitic polymers. The disc-like mesogens so far incorporated are triphenylene ethers [15, 16, 64a–d] and benzene esters [16a], all highly substituted with six long alkyl chains; and alkylated phthalocyanines [65] (only rigid main chain polymers). The backbones are polysiloxanes [15], polymethacrylates [64a], polyacrylates [64c], and polymalonates [64b] for side chain polymers and polyphenylesters [15, 16, 64a–d] for main chain polymers.

Molecular engineering of discoid polymers has so far indicated some *differences with respect to calamitic polymers*. Polymerization generally increases or stabilizes the order for rod-like mesogens, bringing about, for example, smectic phases from nematic monomers or thermodynamically stable nematic mesophases from monotropic nematic monomers (monotropic mesophase = metastable mesophase only observed on cooling). This is not necessarily the case for disc-like mesogens: The discoid side group polymethacrylate in Fig. 9.17, for instance, is not liquid crystalline and amorphous ($T_g = 30°$ C), the preceding monomer, however, shows a highly ordered monotropic D_{ho}-mesophase. Likewise, the influence of the spacer in calamitic and discoid polymers is different. Long spacers do not prevent the formation of smectic mesophases for calamitic polymers, but lead to non liquid crystalline amorphous systems for discoid polymers [16a, 64a]. Thus, the discoid main chain polyester in Fig. 9.17 exhibits a D_{ho} – mesophase for spacer lengths n = 10 and n = 14, but is non liquid crystalline and amorphous for the higher spacer length n = 20.

Recent experiments have shown that if the intracolumnar interactions are enhanced, such as through charge-transfer interactions, discoid polymers can stand more variations of molecular structure (longer spacers, bulkier polymer backbones) without loosing the liquid crystalline phase. In this way, many amorphous discoid polymers with electron rich triphenylene mesogens can be transformed into liquid crystals by adding electron acceptors: e.g. the amorphous side group polymethacrylate and the amorphous main chain polyester (n = 20) in Fig. 9.17 by adding 2,4,7-trinitrofluorenone [64c].

To discuss a general *relationship between polymeric structure and mesomorphic properties*, the number of discotic polymers is far too small. For hexapentyloxytriphenylene containing polymers the following relationships are found. Polymerization or a change in polymeric structure do not bring about any change in the phase type but influence the mesomorphic ranges, clearing temperatures and lower transition temperatures (melting point or glass-transi-
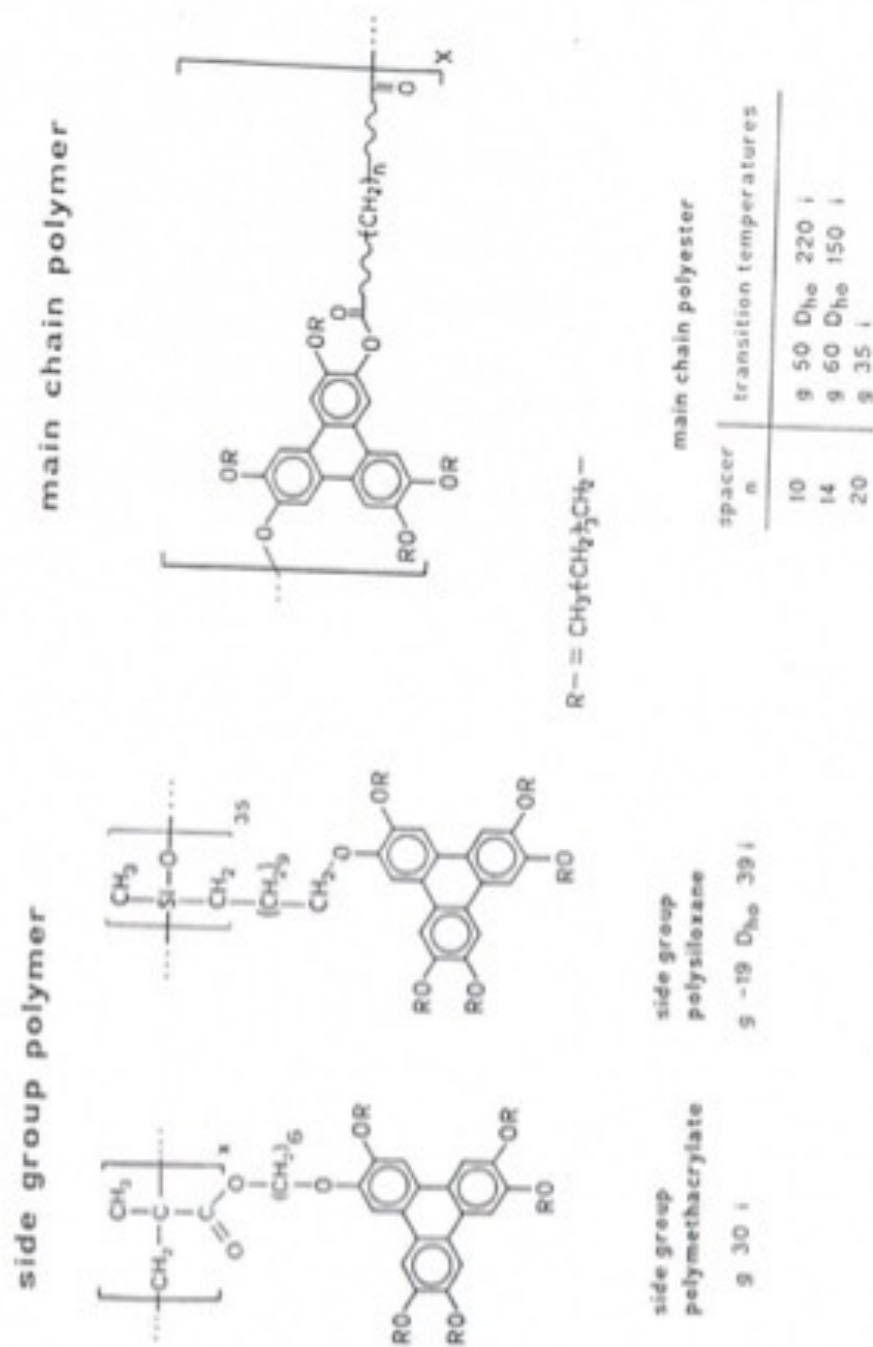
Fig. 9.17: Structure and phase behaviour of discotic polymers with triphenylene as mesogen [15, 16a, 64a]. For comparison: hexapentyloxytriphenylene (low molar mass model compound): c 69 D$_{ho}$ 122 i.

tion) [15, 16a–c] (see Fig. 9.17). The hexapentyloxytriphenylene, its side group polysiloxane and its main chain polyester in Fig. 9.17 all exhibit one identical mesophase type. The temperature range of the D$_{ho}$-mesophase however varies from 50° C for the hexapentyloxytriphenylene to 70° C for the side group polysiloxane and 170° C for the main chain polyester (n = 10). The clearing

temperature is the lowest for the side group polysiloxane ($T_c = 39°$ C) and the highest for the main chain polyester ($T_c = 220°$ C).

The side group polysiloxane and main chain polyester also differ in the intermolecular distances between the mesogens in their liquid crystalline state and most distinctly in their *alignment upon stretching* [66, 16a] (see Fig. 9.18). The side group polysiloxane orients like low molar mass discotics with the column axes *parallel* to the direction of strain [66], whereas the main chain polyester (n = 14) orients in the opposite way with the column axes directed *perpendicular* to the direction of strain [16a]. Which factors are responsible for the orientation of the main chain polyester is not fully investigated yet. Probably, the alignment results from the arrangement of the polymer chain which links discs of neighbouring columns rather than those of the same column. This is supported by ^{2}H-NMR measurements of core- and tail-deuterated derivatives of the main chain polyester, the corresponding dimer and the monomer [67]. There are further factors which may also play an important role in the alignment of main chain discotic polymers, such as molecular weight (as found for smectic polymers [60]) as well as the relative flexibility of backbones and mesogenic tails.

In order to answer the above and many additional open questions in the field of discoid polymers, the scope of structural variations has to be expanded. This will be one task for the synthetic chemist in the near future. The major tasks, though, will be to synthesize functionalized and less viscous polymeric discotic systems, and also to look at some potential applications that have so far only been discussed for low molar mass discotics [68] (e.g. as one-dimensional conducting materials, as stationary phases for liquid chromatography). To lower the viscosity, polymer backbones and side chains can be modified, or polymers with highly fluid nematic-discotic phases should be made. To introduce functionality, many approaches are possible; one of the easiest is certainly by inserting functionalized low molar mass dopants [64c].

9.2.2.2   Polymers with Sanidic Phases

Linking disc-like mesogens *rigidly in the main chain* leads to sanidic polymers, i.e. polymers with sanidic mesophases. The first sanidic polymer was a fully aromatic polyamide obtained through condensation of tetrasubstituted p-phenylenediamine and disubstituted terephthalic acid dichloride [19a]. The mesomorphic structure, as determined by X-ray investigations of oriented fibres, is neither calamitic nor discotic, but shows characteristics of both systems: the well defined layered structure of smectic (calamitic) phases and the one-dimensional packing in stacks of columnar (discotic) phases (see Fig. 9.19). The layer spacing (2.85 nm) corresponds to the maximum cross-section of the macromolecules perpendicular to their backbones.

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side group polymer   main chain polymer

stretching

direction of strain

halo
intracolumnar spacing
intercolumnar spacing

X-ray beam
parallel   perpendicular
to strain direction

X-ray beam
perpendicular
to strain direction
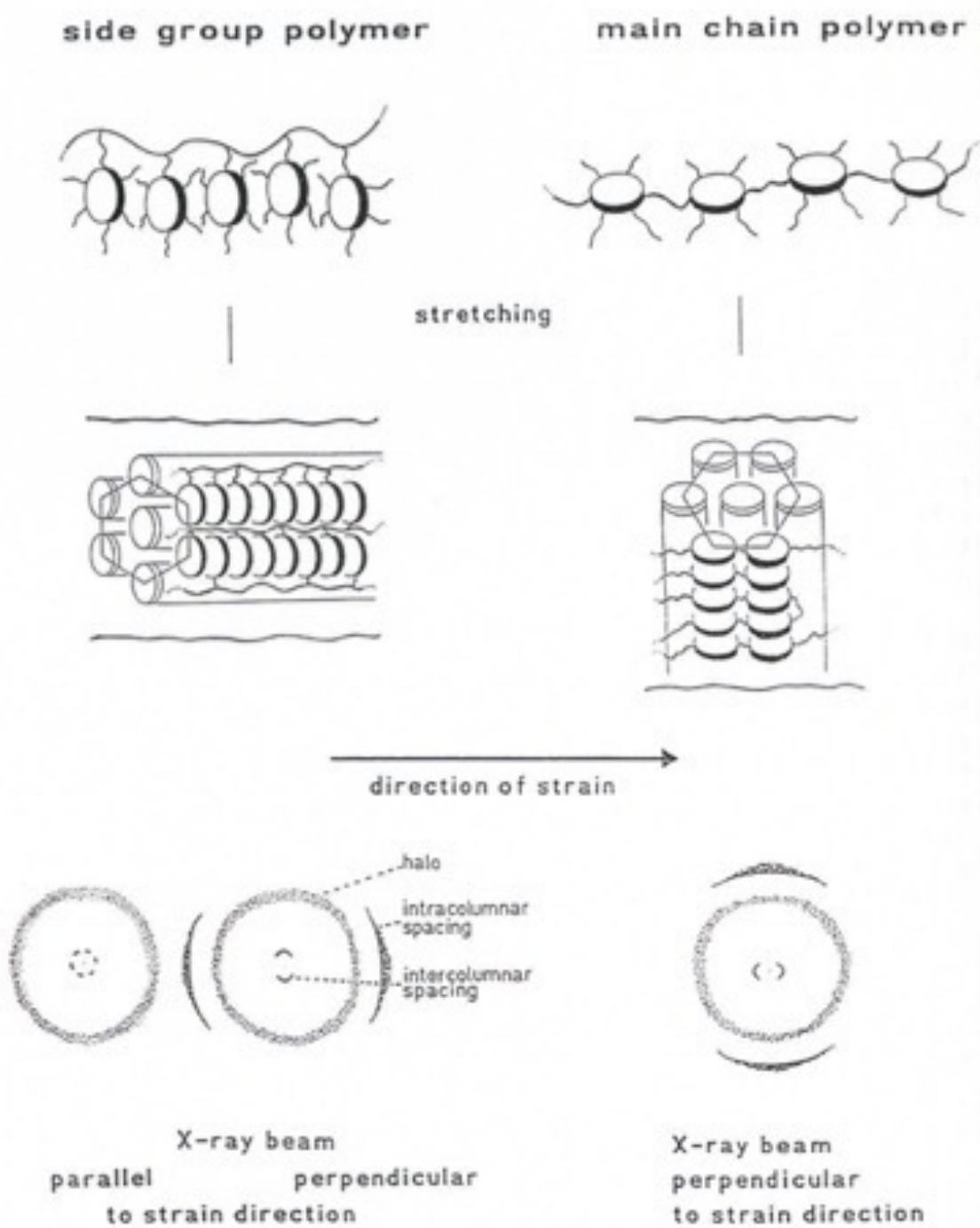
Fig. 9.18: Alignment of a discotic side group polysiloxane [66] and a discotic main chain polyester [16b] on stretching.

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fibre axis

X-ray pattern
2.85 nm = layer spacing
0.63 nm = regularity of the stiff backbone

$R_1 = -\overset{O}{\overset{\|}{C}}OC_{12}H_{25}$

$R_2 = -OC_{12}H_{25}$

$c\ 17\ \Sigma_{d_1}\ 70\ \Sigma_{d_2}\ 130\ i$
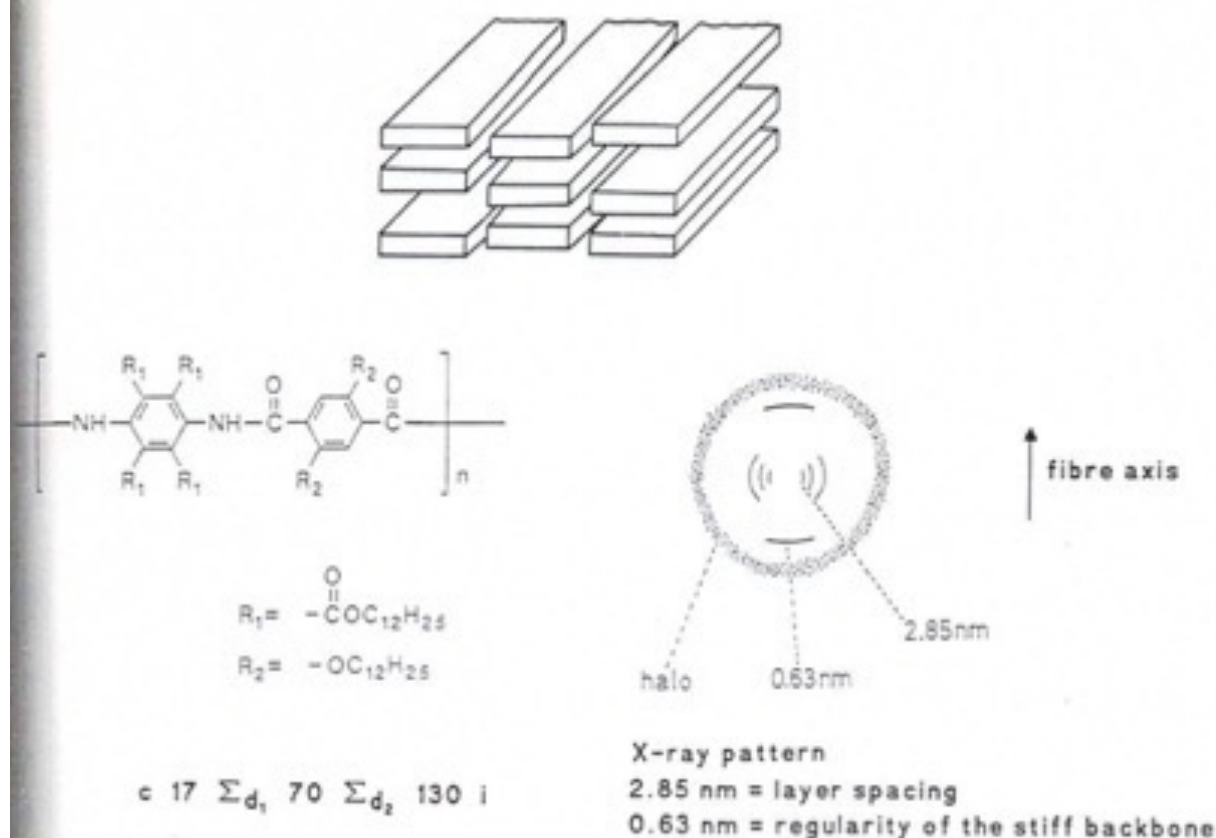
Fig. 9.19: Chemical structure, X-ray pattern and structural model for a sanidic disordered phase Σ_d of a fully aromatic polyamide [19a].

This new mesomorphic structure called *"sanidic disordered phase"* has also been found for many similarly structured polyamides and -esters [19b, 20, 22]. It is explained by the new geometric shape of the mesogens acquired only through polymerization. This is a board-like structure on the average since the long densely packed alkyl chains hinder rotation around the main chain axis and thus prevent the macromolecule from adopting a rod-like shape.

Meanwhile, molecular engineering has produced two further types of sanidic phases: the higher ordered *"sanidic ordered phase"* [69] and the less – merely orientationally ordered – *"sanidic nematic phase"*. The former differs from the *"sanidic disordered phase"* (in Fig. 9.19) in that the spacing between the boards of each layer is constant. The latter is obtained for a polyamide dissymmetrically substituted with ethylene oxide chains [63] (see Fig. 9.20).

The sanidic nematic phase is of special theoretical interest due to its simultaneous nematic and biaxial character. Contrary to the ordinary uniaxial nematics, orientational order now exists in two directions, giving the phase

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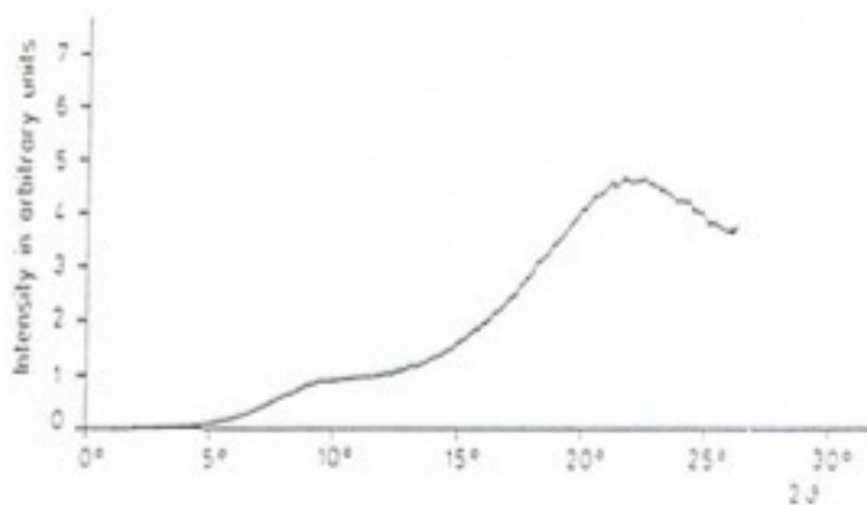
wide-angle X-ray diagram of
the biaxial nematic phase

R= $-O(CH_2CH_2O)_2CH_3$

R'= $-OCH_3$
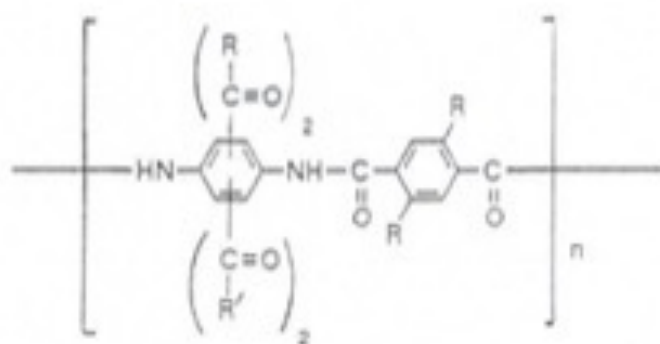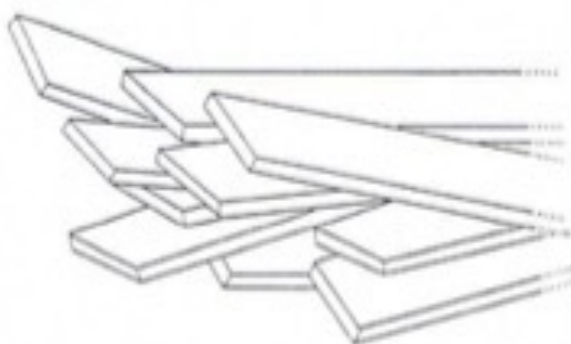
c 131 N_Σ 216 i

two directors. Biaxiality has already been reported for some other nematic systems [17b,c, 70], however, only on the grounds of conoscopic investigations. For the sanidic polyamide [63] further evidence for present biaxiality is provided by X-ray investigations (see Fig. 9.20): two halos are found, one corresponding to the packing of the boards along their normal, the other corresponding to the packing in a direction perpendicular to both their normal and their main chain axis.

Future work on sanidic polymers will certainly, as is the case for discotic polymers, concentrate on introducing functionality to make the sanidics more attractive to applied chemists.

9.2.3   Functionalized Liquid Crystalline Polymers

Besides the variations in molecular architecture of liquid crystalline polymers which has led to the use of mesogens of different shape (rods, discs and boards) and to different arrangements of mesogens (see Fig. 9.6), *functionalized LC polymers* have been synthesized and investigated. These polymers were functionalized by dye containing groups [25, 26] (see section 9.2.3.1), or by mesogens undergoing photoreactions [28, 29]. This can lead subsequently to a formation or destruction of the liquid crystalline phase (see section 9.2.3.2). Alternatively liquid crystalline polymers were functionalized by groups capable of undergoing chemical reaction [27] and by chiral groups [30, 31]. This led to the formation of chiral LC elastomers (see section 9.2.3.3).

9.2.3.1   Dye Containing Polymers

The incorporation of dichroic dyes into liquid crystalline polymers enables the formation of coloured LC copolymers [25]. Due to the covalent linkage of dyes and mesogens via the polymer chain, high dye concentrations can be obtained without a demixing, while in low molar mass liquid crystals the solubility of dyes is very limited. In these dye-containing polymers the dyes orient with a high order parameter parallel to the preferred orientation of the mesogenic groups [26]. Different orientations of the dyes along with the mesogens lead to different colours of the polymers if they are viewed with polarized light. The possibility of orienting and reorienting the dye containing LC polymers in electric and magnetic fields [50–52] makes these polymers very interesting as media for optical data storage and as additives for colour displays [26].

◄

Fig. 9.20: Chemical structure, X-ray diagram and structural model for a sanidic nematic phase of a fully aromatic polyamide with ethylene oxide chains [63].

It is found that the structure of the dye containing comonomer modifies the width of the liquid crystalline phase. This is schematically presented in Fig. 9.21. The incorporation of an anthraquinone dye, which is not mesogenic by itself, leads to a narrowing of the liquid crystalline phase, which is lost at high dye contents. Nevertheless, up to 30 % by wt of the dye can be incorporated into the copolymers while still retaining the liquid crystalline phase. For low molar mass liquid crystals the maximal concentration of anthraquinone dyes is limited to a few percent, due to the very low solubility of these dyes.

If, however, dyes of an elongated rod-like structure that resemble mesogens are incorporated into LC polymers, a totally different behaviour is found. This is presented for a tris-azo-dye in Fig. 9.21. The incorporation of this strongly mesogenic dye leads to a broadening of the liquid crystalline phase.

9.2.3.2 Photosensitive Liquid Crystalline Polymers

Photosensitive LC polymers (see Fig. 9.22) can be prepared by the use of mesogens with photocleavable lateral substituents [29], by the incorporation of photochromic dyes into the polymer [28], or by the use of mesogens that undergo photoisomerizations [71]. The endproducts of photoisomerizations or photoreactions of mesogenic molecules will have, in general, a higher or lower tendency towards liquid crystallinity than their precursors. Therefore, it is possible to stabilize or – in the more common case – to destabilize a liquid crystalline phase via a photoreaction.

The photoisomerizations of azobenzene [71] and of 1-iminopyridinium ylides [29] can be used for a *destabilization or destruction of the liquid crystalline phase*. The reversible isomerization of azobenzene is especially interesting in this context because it reversibly modifies the optical properties of azo-group containing polymers upon illumination with light of an appropriate wavelength [71]. The reason for this is that the rod-like trans-configuration of azobenzene is transformed into a non-rod-like, non-mesogenic cis-configuration. These changes are obvious from the UV spectra displayed in Fig. 9.23. They may occur even in the solid glassy state.

This trans-cis transition induces a variation in the anisotropic surroundings of the azobenzene unit and consequently, also of the optical properties. Strong changes are introduced both with respect to the extinction and the refractive index. An important finding is that these changes remain stable in the glassy nematic or smectic state even if the azobenzene experiences a thermal backrelaxation (see Fig. 9.23) into the trans-configuration.

This effect can be exploited for optical application such as holographic storage of information or the holographic manufacturing of optical components such as lenses. Fig. 9.24 gives an impression of the quality of the liquid crystalline films as storage materials. Results obtained on holographically induced cross gratings are shown: the resolution is better than 0.3 µm, corresponding
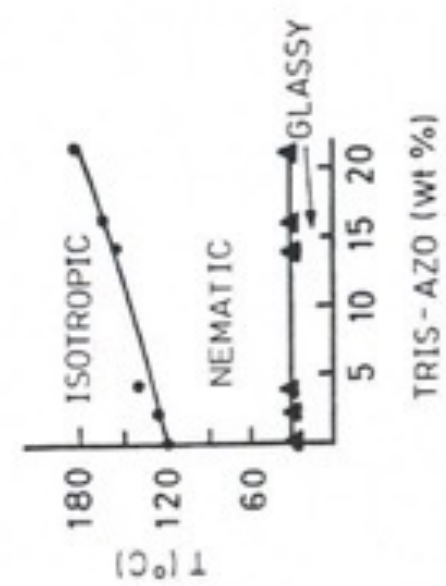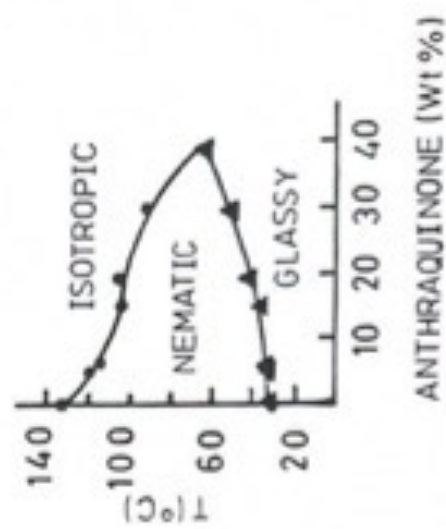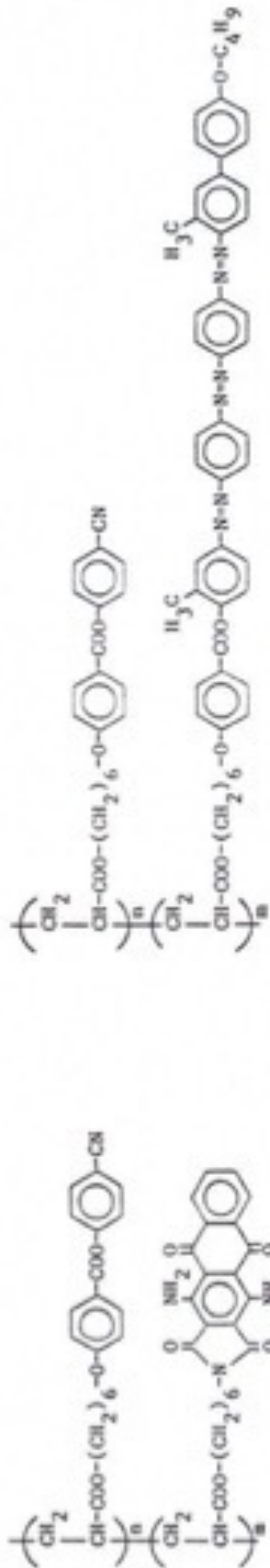
Fig. 9.21: Dependence of the width of the liquid crystalline phase on the dye content for copolymers with anthraquinone dyes or tris-azo-dyes [25].

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Photosensitive LC-Polymers
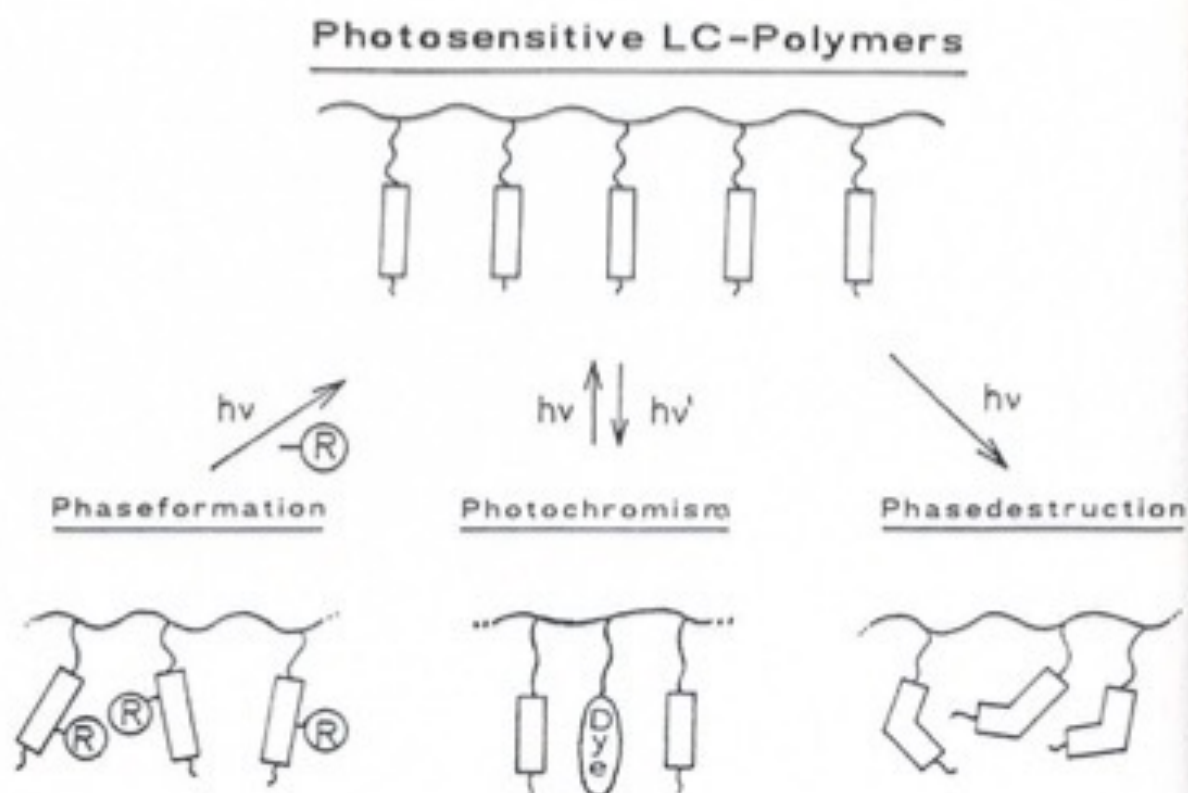
Fig. 9.22: Depending on the kind of photoreaction, the irradiation of photosensitive LC polymers can either lead to a phase formation, to photochromism or to a phase destruction.

to an information density of 1 Gbit/cm^2 and the efficiency, as defined by the ratio of the first order diffraction intensity and of the primary beam intensity, amounts to about 50 %. Recent experiments have shown that transmission and reflection holograms of real objects can be stored reversibly in such liquid crystalline films.

In contrast to the phase destruction of azobenzene containing polymers the *formation of a liquid crystalline phase* can be induced on irradiation. This is observed if mesogenic groups are modified with cleavable lateral substituents (see Fig. 9.25) [29]. The bulky lateral substituents suppress the formation of liquid crystalline phases, but after their cleavage, liquid crystalline phases can be formed. This cleavage can be induced photochemically via the formation of strong protic acids from sulfonium salts, which split off the labile lateral substituents (the TBOC-protective group in Fig. 9.25).
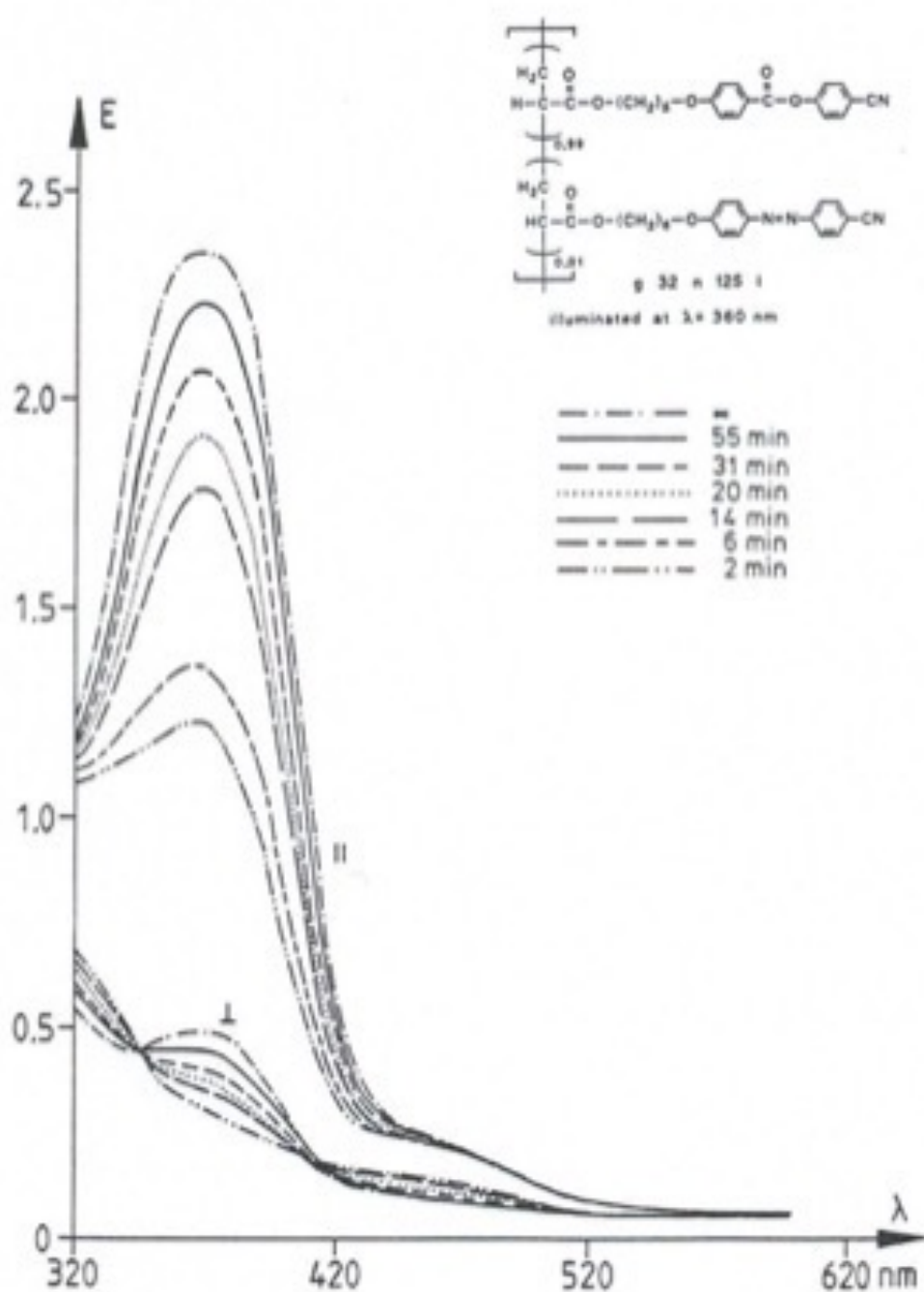
Fig. 9.23: UV spectrum of an azobenzene containing side chain polymer after irradiation measured parallel (ll) and perpendicular (⊥) to the director. Parameter is the time after the irradiation.
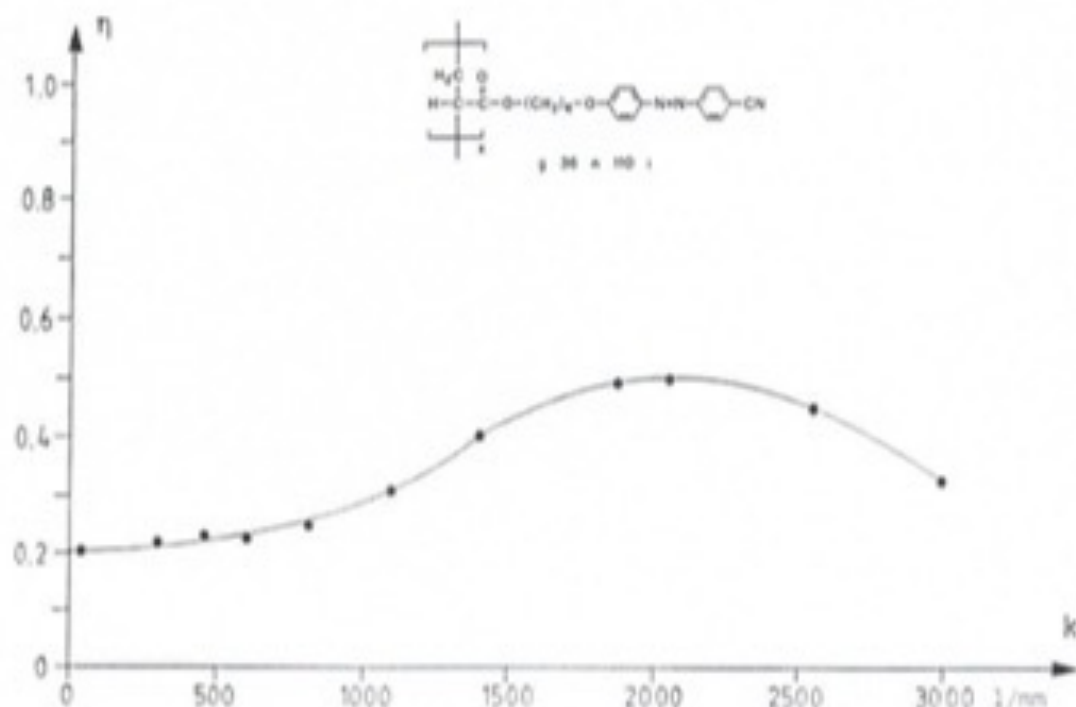
Fig. 9.24: Dependence of the diffraction efficiency on the spatial frequence, as obtained from grating experiments performed on a monodomain of a side chain liquid crystalline polymer. The gratings were obtained holographically.

9.2.3.3 Liquid Crystalline Elastomers

Another type of functionalized LC polymer is the LC elastomer. LC elastomers can be prepared in a one step reaction (see Fig. 9.26a), modifying a functionalized polymer backbone with mesogenic side chains and simultaneously cross-linking [72]. Alternatively, they can be prepared in 2 steps: First, soluble functionalized LC polymers are synthesized which are then cross-linked in a second step [27, 73] (see Fig. 9.26b). We have used this second method to prepare slightly cross-linked side group polymers, main chain polymers and combined main chain/side group polymers (see Fig. 9.27) with elastic properties. These polymers are especially interesting because of their good *mechanical orientability*. A strain of 20–40 % leads to a well oriented sample if it is applied in the liquid crystalline phase [60, 74, 75]. The same strain produces only a small orientation, if applied in the isotropic phase [75].

If liquid crystals are functionalized with chiral groups, then some liquid crystalline phases are transformed into *chiral phases* with a helical superstructure: In this way a nematic phase can be transformed into a *cholesteric phase* which shows *selective reflection* of light, and a smectic C phase can be transformed into a *chiral smectic C* phase* which has *ferro-electric properties* (see Fig. 9.28)

Photoinduced LC-Phase Formation in Polymers
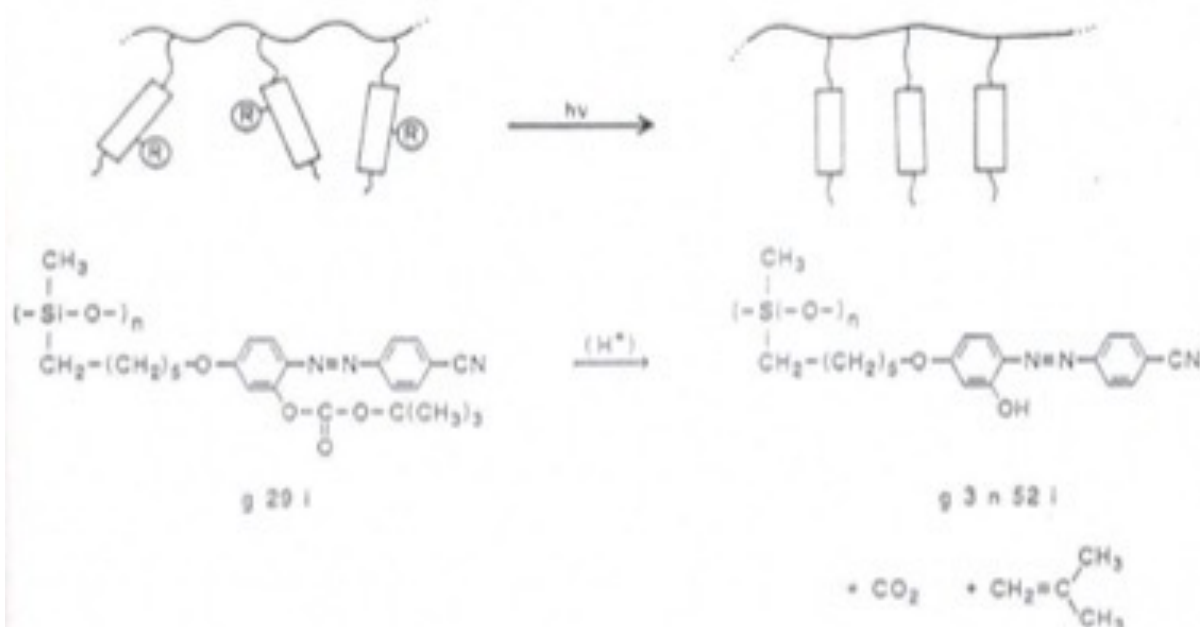
Photoinitiated Proton Formation:
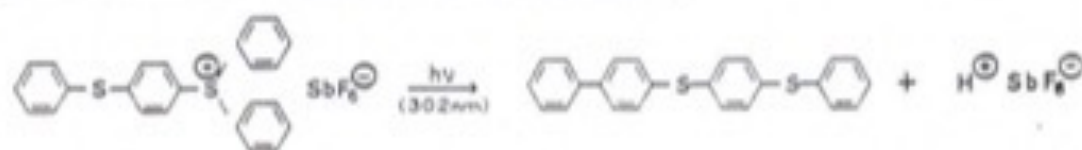
Fig. 9.25: Photoinduced phase formation via a photoinitiated proton formation [29].

[2–4,7]. The properties of these chiral phases are linked to their helical super-structure. They can, therefore, be manipulated by a partial or complete untwisting of this helical superstructure, which is achieved for low molar mass liquid crystals by strong electric or magnetic fields. It seemed, therefore, interesting to investigate if similar effects – an untwisting of the helical superstructure – could be achieved in chiral LC elastomers by mechanical strains. If this is the case, then these chiral elastomers should act like a device that transforms a mechanical signal (the strain) into an optical signal (selective reflection of light for the cholesteric phase) or into an electric signal (spontaneous polarization for the chiral smectic C* phase) [76]. This is schematically illustrated in Fig. 9.28.

In order to prepare *chiral liquid crystalline elastomers*, two functions have to be combined in one polymer: chirality to obtain chiral phases and reactive groups for the cross-linking reaction. Since combined main chain/side group
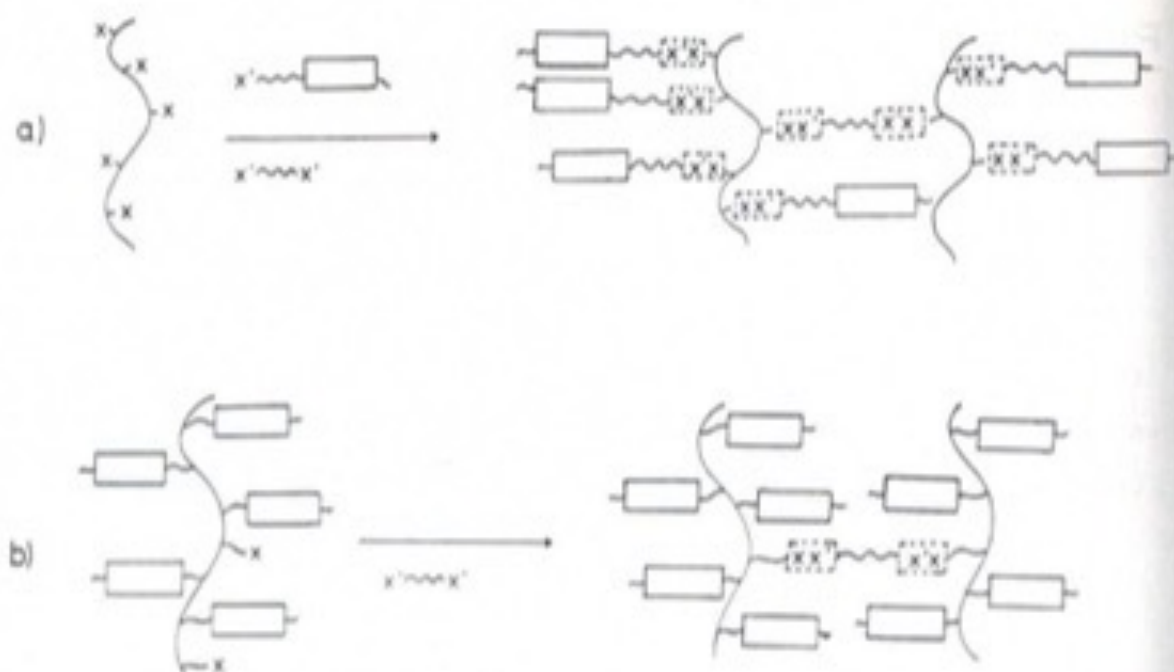
Fig. 9.26: Different ways to prepare LC elastomers in one (a) or two (b) steps [27, 72].

polymers form broad liquid crystalline phases which are often of the smectic C and nematic type, they seem especially interesting in this respect. Therefore, in a first step, noncross-linkable combined main chain/side group polymers with chiral groups have been prepared [30, 31] which show cholesteric and chiral smectic C* phases. The additional functionalization of these polymers with reactive groups can be achieved by the preparation of copolyesters (see Fig. 9.29) in which one half of the mesogenic side groups is functionalized with chiral tails, while the other half is functionalized with olefinic double bonds [76, 77]. These chiral copolyesters can be cross-linked by a hydrosilylation reaction between some of the olefinic double bonds and the Si-H bonds of a α-ω-dihydrooligo(dimethylsiloxane) as described for one example of cross-linked combined polymers (see Fig. 9.27) in Fig. 9.29.

First measurements on these chiral elastomers [76] show that the analogy between electrical (low molar mass liquid crystals) and mechanical fields (LC elastomers) really exists and that it is possible to untwist the helical super-structure by mechanical stretching, as presented in Fig. 9.28.

Crosslinked Side Group Polymers

Crosslinked Main Chain Polymers

Crosslinked Combined Main Chain / Side Group Polymers

Fig. 9.27: Schematic drawing of networks prepared from side group, main chain and combined main chain/side group polymers [27].

cholesteric phase
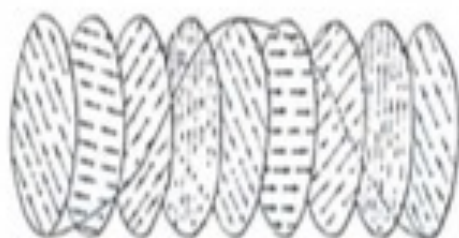
a) helical superstructure
(ground state)
selective reflection
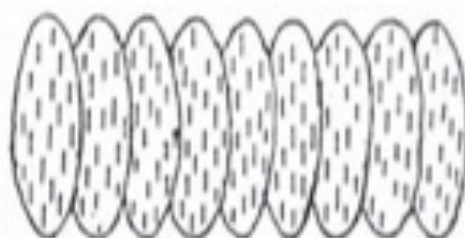
b) nematic arrangement
no selective reflection

chiral smectic C* phase
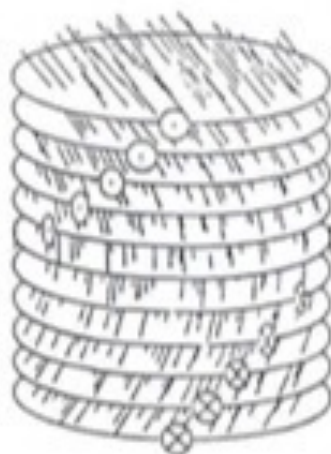
c) helical superstructure
(ground state)
no macroscopic polarization
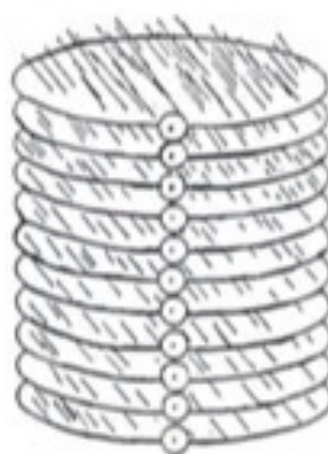
d) smectic C-like arrangement
macroscopic polarization

Fig. 9.28: Twisted (a and c) and untwisted (b and d) states of cholesteric and chiral smectic C* phases [76].

$$-[-[-O-\mathbf{A}-OOC-\underset{\underset{\mathbf{S}_1}{|}}{CH}-CO-]_{0.5}-[-O-\mathbf{A}-OOC-\underset{\underset{\mathbf{S}_2}{|}}{CH}-CO-]_{0.5}-]_2-$$

$\mathbf{A}: -(CH_2)_6-O-\bigcirc-N=N-\bigcirc-O-(CH_2)_6-$

$\mathbf{S}_1: -(CH_2)_6-O-\bigcirc-N=N-\bigcirc-O-(CH_2)_3-CH=CH_2$

$\mathbf{S}_2: -(CH_2)_6-O-\bigcirc-N=N-\bigcirc-O-CH_2-\overset{*}{C}H-C_2H_5$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\underset{CH_3}{|}$

Uncrosslinked Copolymer

g 20 s$_c$* 116 n* 151 i

$H-[-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-O-]_{6.5}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-H$ **10 mol %**

Crosslinked Elastomer
g 22 s$_c$* 110 n* 147 i
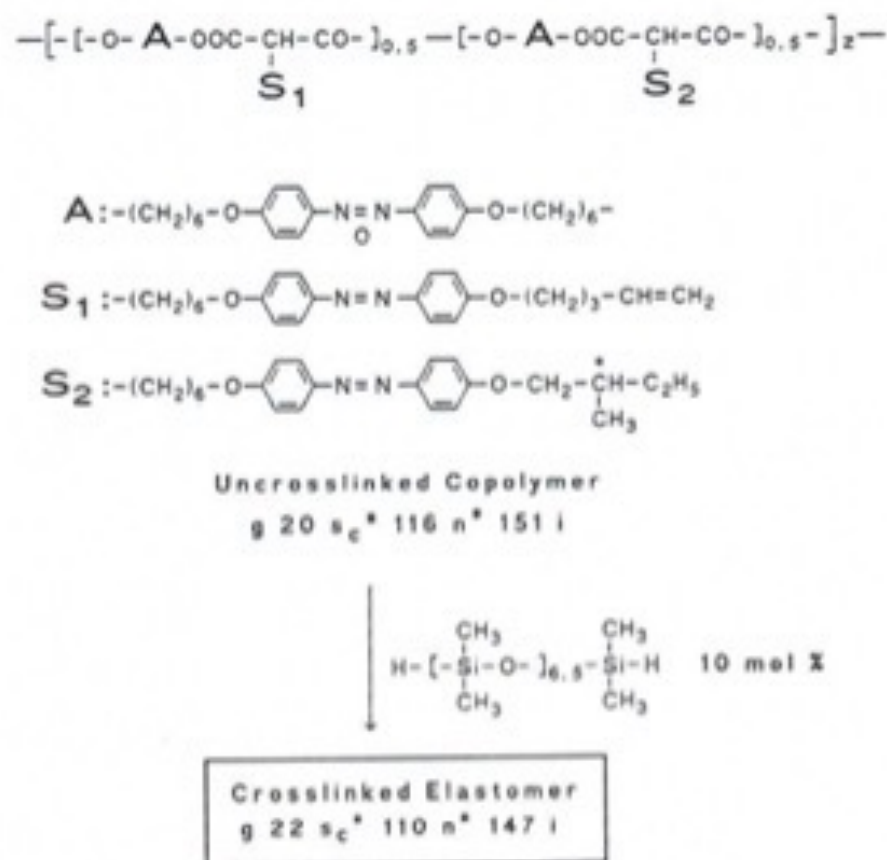
Fig. 9.29: Molecular structure of a chiral, uncross-linked copolymer and its transformation into a cross-linked elastomer (see Fig. 9.27) via a hydrosilylation reaction [76, 77].

9.3   Molecular Architecture and Physical Properties

9.3.1   The Amorphous, Crystalline and Liquid Crystalline State of Matter

Liquid crystals represent a state of matter which combines, in different ways, the properties of a crystal having long range positional and orientational correlations, with those of an amorphous material, having only short range correlations. This gives rise to a multitude of different macroscopic structures which have been extensively documented in the literature [78].

The molecular structure of liquid crystal polymers and the dynamical behaviour of individual molecules and groups of molecules is now being subjected

to increasing scrutiny because of their paramount importance in determining the physical properties of the system. Some of the topics in relation to liquid crystal polymers which are gaining increasing importance both in basic research as well as for their potential technological applications are:

a) Non-linear optical properties for application in optical data storage, b) electrical conductivity in precisely ordered structures by controlled charge transfer, c) collective phenomena involving long-range forces which influence the glassy state, d) the physics of critical phenomena, in order to understand and control segregation effects, with potential application for the fabrication of membranes with specific pore sizes and distributions, e) good orientability of main chain systems giving high tensile strength.

Future development in all these fields requires precise knowledge about the molecular structure of these materials and their defects.

Unfortunately nature does not divulge this information easily. The structure of matter as well as its time dependent fluctuations can be measured by various elastic and inelastic scattering techniques such as X-ray, neutron, electron and light scattering as well as by spectroscopic methods such as deuteron nuclear magnetic resonance.

All these experimental methods, as well as interpretation of the results, require specialized knowledge about the crystalline and the amorphous state which has been developed by various groups within the framework of this Sonderforschungsbereich. Only a fraction of the work on amorphous and semi-crystalline polymers which has been published in the specialized literature is indicated here. Thus an enormous research effort has been invested and experience gained in the investigation of the static properties such as polymer chain conformation [79–81], orientational order [82], correlation functions [83], morphology of the semi-crystalline state [84–86], density fluctuation [87] and on dynamic properties of molecules or groups of molecules from light [88] and neutron scattering [89] as well as ^{2}H-NMR-spectroscopy [90]. In the following, therefore, we indicate only a few examples of investigations which have been performed on liquid crystalline systems, specifically those which were introduced in the first part of this chapter.

9.3.2 Fluctuations in Liquid Crystalline Polymers

9.3.2.1 Defining Fluctuations

When discussing the characteristic structures of liquid crystalline phases, one tends to forget that molecular motions such as rotation or translations take place leading to molecular configurations which fluctuate rapidly as a function of time. The fact that the average orientational order parameter S = ½ $(3 \cos^2\theta - 1)$, for instance, is zero in the isotropic phase does not imply that

fluctuations of the order parameter about its mean value do not take place. This can lead to strong orientational correlations already in the isotropic fluid phase [91–94]. Statistical treatments, based on a consideration of particle distribution functions, particle correlation functions, and correlation parameters connect the fluctuations with thermodynamic, dynamic and structural properties.

It is for this reason that the experimental analysis of such fluctuations yields valuable information on macroscopic properties. Topics of great interest are, for instance – in view of the molecular design of liquid crystalline polymers – an investigation of the difference between the properties of low molar mass and polymeric liquid crystals and the detection of liquid crystalline phase transitions which are hidden below a glass transition (kinetically hidden) or below another liquid crystalline phase transition (thermodynamically hidden). Examples will be given below.

9.3.2.2 Kerr Relaxation Studies on Orientational Fluctuations

Orientational fluctuations, which occur in the isotropic phase near a nematic one, lead to strong electrooptical effects. The application of a static or dynamic electric field causes the induction of birefringence Δn, which depends linearly on the square of the electric field (Fig. 9.30). The Kerr constant K, defined by:

$$\Delta n = \lambda \, K \, E^2$$

is thus a measure of the extent of orientational fluctuations.

Kerr effect studies [91–94] have actually shown that, both in low molar mass and in polymeric liquid crystals, strong orientational order parameter fluctuations occur already in the isotropic phase, and that their magnitude increases with decreasing temperature. The reason for this is that the number of molecules or mesogenic units performing correlated reorientational motions, as reflected in the magnitude of the orientational correlation parameter g_2, increases and tends to diverge as a characteristic temperature T^* is approached. This temperature is located close to, but below, the transition temperature T_{ni} into the nematic phase. These features can be accounted for – as described in detail by Jungnickel and Wendorff (Chapter 13, this Volume) – on the basis of the phenomenological Landau de Gennes theory, which essentially states that the nematic-isotropic transition is a weak first order transition but only a weak one. Pretransitional fluctuations characteristic of a second order phase transition, therefore, must be expected. This can be exploited as follows, for the detection of hidden transitions.

Fig. 9.31 shows the results of Kerr effect studies which were obtained for a side group polymer in which liquid crystalline structures could not be detected: the isotropic phase is frozen in the glassy state at lower temperatures. The Kerr

Fig. 9.41: Image of dislocation after electronic zooming and clipping.

9.3.3.5 Conclusion

We have shown that high resolution electron microscopy combined with electron diffraction and dark field methods is a very powerful technique to monitor molecular level information. For the first time images of smectic planes and their defects have been demonstrated. Investigations on other polymer systems are in progress and it is hoped that certain general principles of structural organization applicable to liquid crystalline polymers can be derived. The techniques of image analysis and digital processing are being improved, so that aperiodic images can be reconstructed more reliably.

9.4 References

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