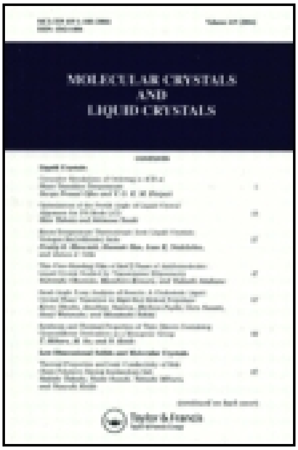

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Liquid Crystalline Elastomers—Characterization as Networks

M. Brehmer [a] & R. Zentel [a]

[a] Institut f. Organische Chemie, Universität Mainz, Becher-Weg 18-20, D-55099, Mainz, Germany

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Liquid Crystalline Elastomers—Characterization as Networks

M. BREHMER and R. ZENTEL†
Institut f. Organische Chemie, Universität Mainz, Becher-Weg 18-20, D-55099 Mainz, Germany

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This paper summarises the properties of archiral and chiral liquid crystalline (LC) elastomers, the latter of which have found interest due to their piezoelectric properties. In addition the formation of new LC elastomers by a radical polymerization of acrylate groups covalently linked to LC polymers was investigated. This was done concerning the progress of the crosslinking reaction, concerning the influence of the crosslinking on the LC phases and concerning the network properties (swelling ratio and elastic modulus) of the resulting elastomers. It turns out that the networks prepared in this way are very soft and their crosslinking density is low. This can be explained assuming that the radical polymerization of the acrylates leads only to short oligomers, due to steric restrictions. Photo crosslinking initiated by a photoinitiator in the LC phase creates a memory of the orientation before crosslinking.

Keywords: chiral LC elastomers, crosslinking reaction, network properties, mechanical properties, photocrosslinking

1. INTRODUCTION

1.1. LC Elastomers

Liquid crystalline (LC) polymers, in general, possess all of the properties that are typical of low molar mass liquid crystals, and in addition the properties of polymers.[1-3] From this situation new property combinations may arise,[4] which cannot be found in low molar mass liquid crystals. The polymer nature of LC polymers allows, for example, a "locking in" of the LC orientation either below T_g^5 or by the formation of a densely crosslinked network.[6] Alternatively, slightly crosslinked LC polymers (LC elastomers) offer the possibility of combining the rubber elasticity of polymer networks with LC phases[7,8] (see Figure 1).

In these systems a macroscopic deformation of the crosslinked sample leads to a corresponding equilibrium deformation of the polymer chains. Different degrees of orientation of the polymer chains can be achieved by stretching the macroscopic sample to different degrees. Afterwards an orientation of the mesogenic groups

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† To whom all correspondence should be addressed.

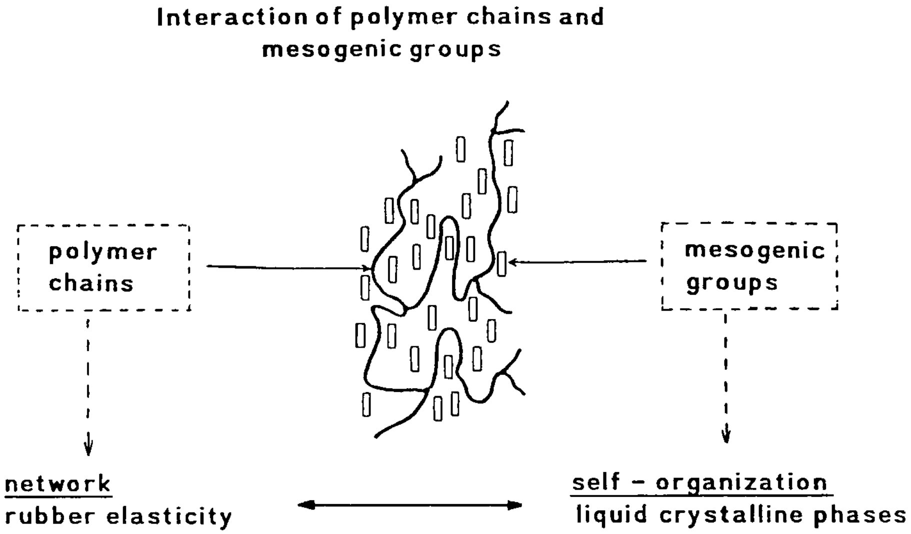


FIGURE 1 Schematic representation of a crosslinked LC elastomer. The linkage between polymer chains and mesogenic groups is not yet specified.

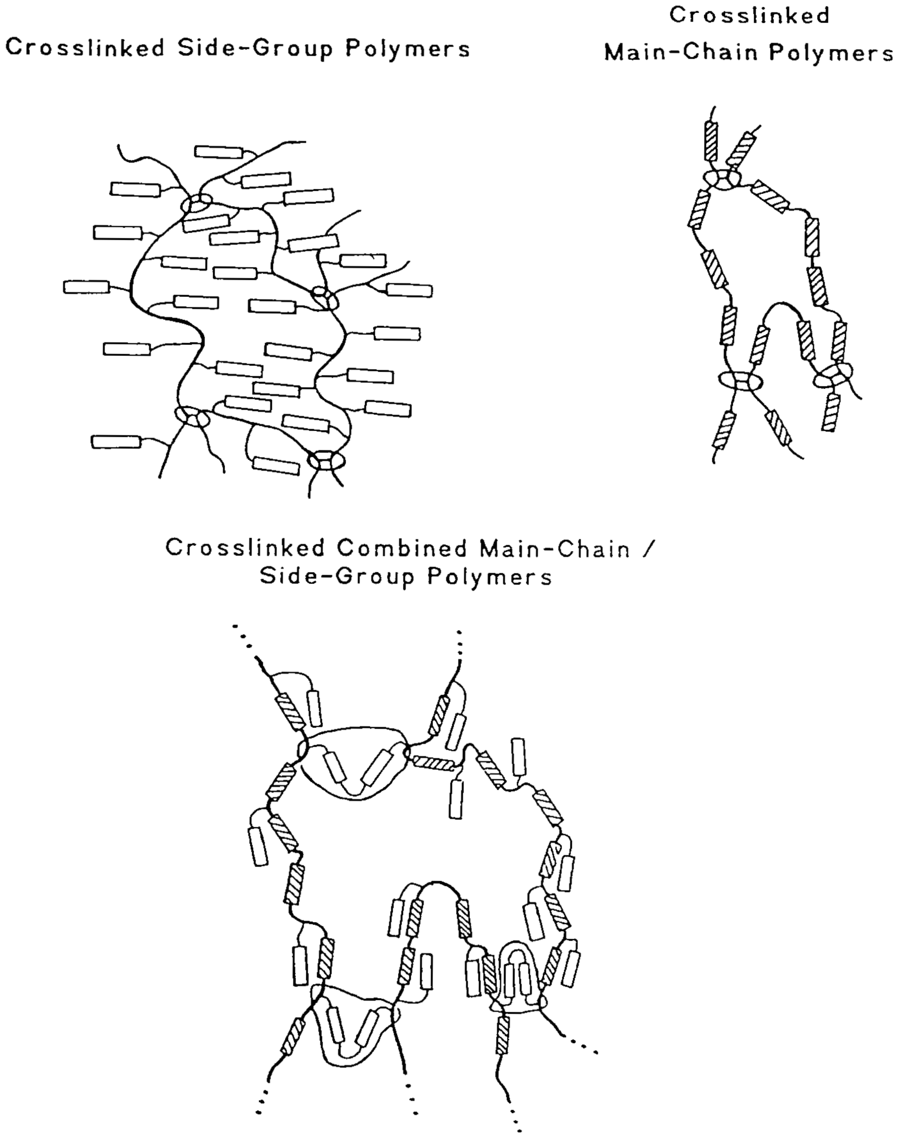
can be determined under equilibrium conditions. Therefore LC elastomers seem to be ideal systems, in which to investigate the interaction of the orientation of the polymer chains (induced by mechanical fields) and that of the mesogenic groups (induced by electric fields).

The use of differently structured LC elastomers (see Figure 2) is interesting in this respect, because the behaviour of the two "subsystems" (network of polymer chains-mesogenic groups) should be different in each case. For crosslinked side group polymers the orientation of the mesogenic groups is relatively free with respect to the polymer chain, since they are decoupled by a flexible spacer. In crosslinked main chain polymers, however, the mesogenic groups are directly incorporated into the polymer chains. Crosslinked "combined" polymers may behave in an intermediate manner because one half of the mesogenic groups is incorporated into the polymer chains, while the other half is linked to the polymer backbone as side groups via a flexible spacer. Both types of mesogens must, however, interact cooperatively to form an LC phase (both types of mesogens orient parallel to each other) (Figure 2).[9]

1.2. Properties of Achiral LC Elastomers

The LC phase is retained for the crosslinked elastomers. X-ray measurements performed with the uncrosslinked and the slightly crosslinked polymers show the same LC phases.[9-11] Thus the crosslinking reaction, which transforms a soluble polymer into a soft solid does not influence the LC order. As long as the crosslinking density is low, the phase transition temperatures are not shifted significantly.[7-12] Only a slight increase or decrease (± 5 K) is observed by DSC-measurements.

The most prominent property of all LC elastomers is their rubber like elasticity


Crosslinked Side-Group Polymers

Crosslinked Main-Chain Polymers

Crosslinked Combined Main-Chain / Side-Group Polymers

FIGURE 2 Schematic representation of different types of LC elastomers.

and their mechanical orientability.[7,8,10,11,13-16] Small strains (about 20%) are enough for the reversible formation of an LC monodomain. Recently a threshold stress could be determined for the reversible orientation of LC elastomers.[15] Also a small shift of the phase transition temperatures of about 2 K can be induced by stretching.[8,14] The mechanical orientability of the LC elastomers is due to the anisotropic conformation, which the polymer chains adopt in the LC phase[17] (see Figure 1). Therefore the average distance between two crosslinks in a network does not only depend on the length between them, but also on the orientation relative to the director of the LC phase. This leads to a coupling of the preferred orientation of polymer chains and mesogenic groups, which has been described theoretically by various authors.[18,19]

The mechanical orientability has been used quite recently for the preparation of single crystal LC elastomers,[20] performing a second crosslinking reaction on a mechanically oriented slightly crosslinked LC elastomer. In turn, the action of electric field on LC elastomers can lead to shape variations of the sample,[21,22] because the attempt of the director to reorient in the LC elastomer couples to the anisotropic chain conformation.

1.3. Properties of Chiral LC Elastomers

The special interest in chiral LC elastomers stems from the possibility to modify the helical superstructure of cholesteric or chiral smectic phases by mechanical forces[7,23–25] (see Figure 3) that is to use the mechanical field in elastomers in analogy to electric or magnetic fields in low molar mass liquid crystals.

Two concepts have been presented to use this possibility for the preparation of new piezoelectric materials. One concept started from the basic idea that a ferroelectric (chiral smectic C*) elastomer has to be piezoelectric[7,23] (see Figure 3). In this respect it is the advantage of the elastomer that it can support stress under equilibrium conditions, whereas uncrosslinked LC polymers and low molar mass materials are liquids, which relax shortly after a deformation.

The second concept was deduced theoretically.[26,27] A compression parallel to the helix axis should lead, for symmetry reasons, to a piezoelectric response of a cholesteric phase. This effect is likely to be observable only in cholesteric elastomers, because uncrosslinked systems are liquids, which cannot support an uniaxial compression.

These predicted piezoelectric properties could be proven quite recently for chiral LC elastomers of different structures.[24,25] The piezoelectric response of chiral smectic C* elastomers (see Scheme I) was demonstrated for a "combined" polymer[24] (see Figure 4). The piezoelectric response of cholesteric elastomers was demonstrated both for side group polymers[25] and "combined" polymers.[24]

The preparation of the piezoelectric elastomer (**1b**) of Scheme I was done by a radical polymerization of acrylate groups at the side group of polymer **1a**. It is the advantage of this method that the crosslinking can be performed in the bulk and specially in an oriented LC phase, whereas the LC elastomers described so far[7–16,20–23] have to be crosslinked in a (non LC) solution. The crosslinking by radical polymerization leads however also to the disadvantage that the crosslinking density and the functionality of the netpoints is less well defined and more complicated to control.

In the following we will describe the characterization of LC elastomers, prepared by radical polymerization, concerning this important polymer aspect that means, concerning the progress of the crosslinking reaction and the characterization as elastomer. In addition a comparison with elastomers prepared from the same polymers by a reaction with a bifunctional crosslinking agent in solution will be done. Since chirality is not important for these network properties, the investigations were done mostly with achiral LC polymers.

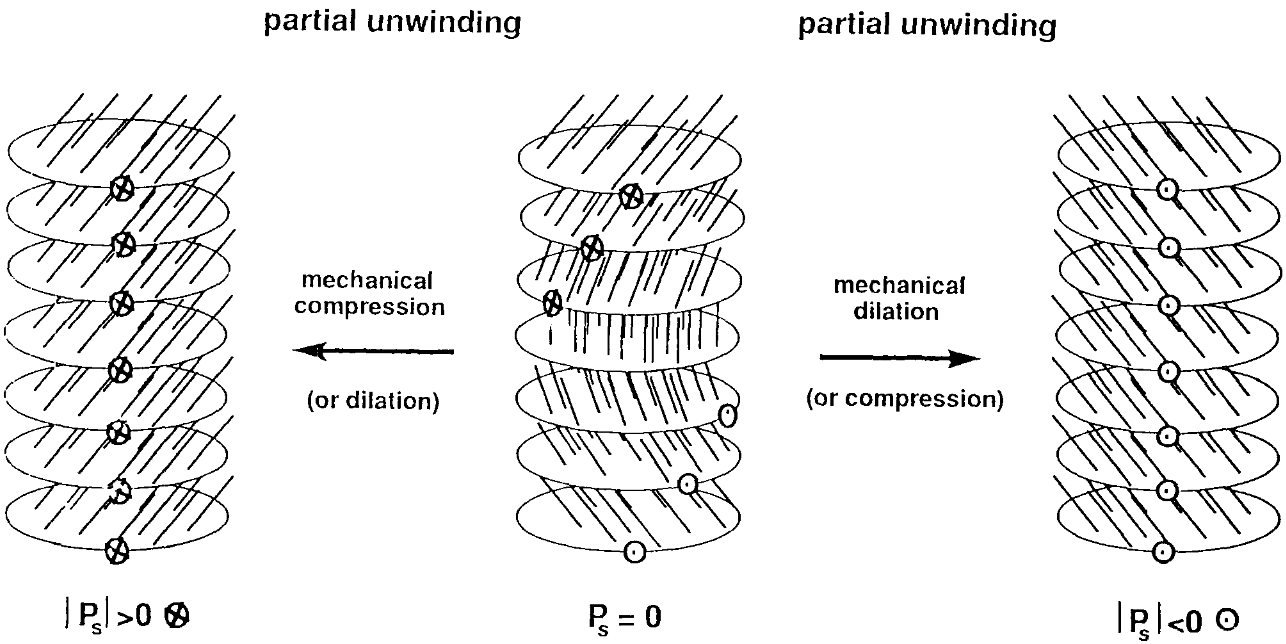
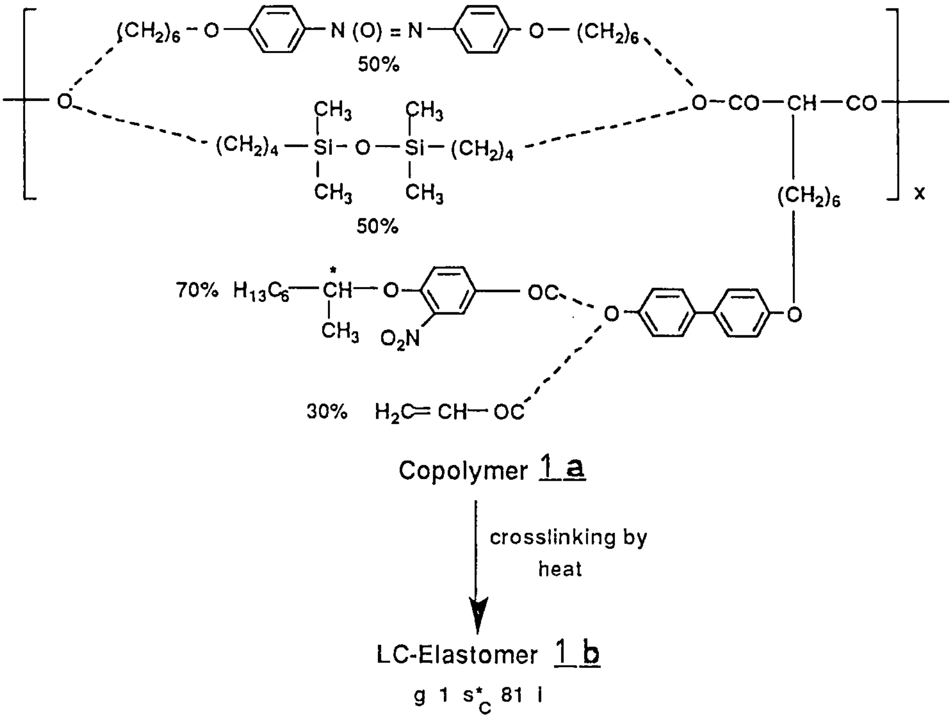


FIGURE 3 Idealized presentation of the orientation process, which leads to piezoelectricity in chiral smectic C* elastomers (only the mesogens are shown). The deformed states with a partially unwound helix (left and right) are prepared from the ground state with a helical superstructure (middle) by mechanical forces. (⊗ and ⊙: direction of the spontaneous polarisation in and out of the plane of drawing).



SCHEME I

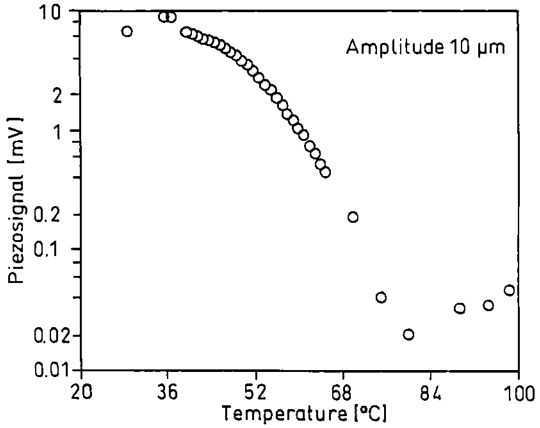
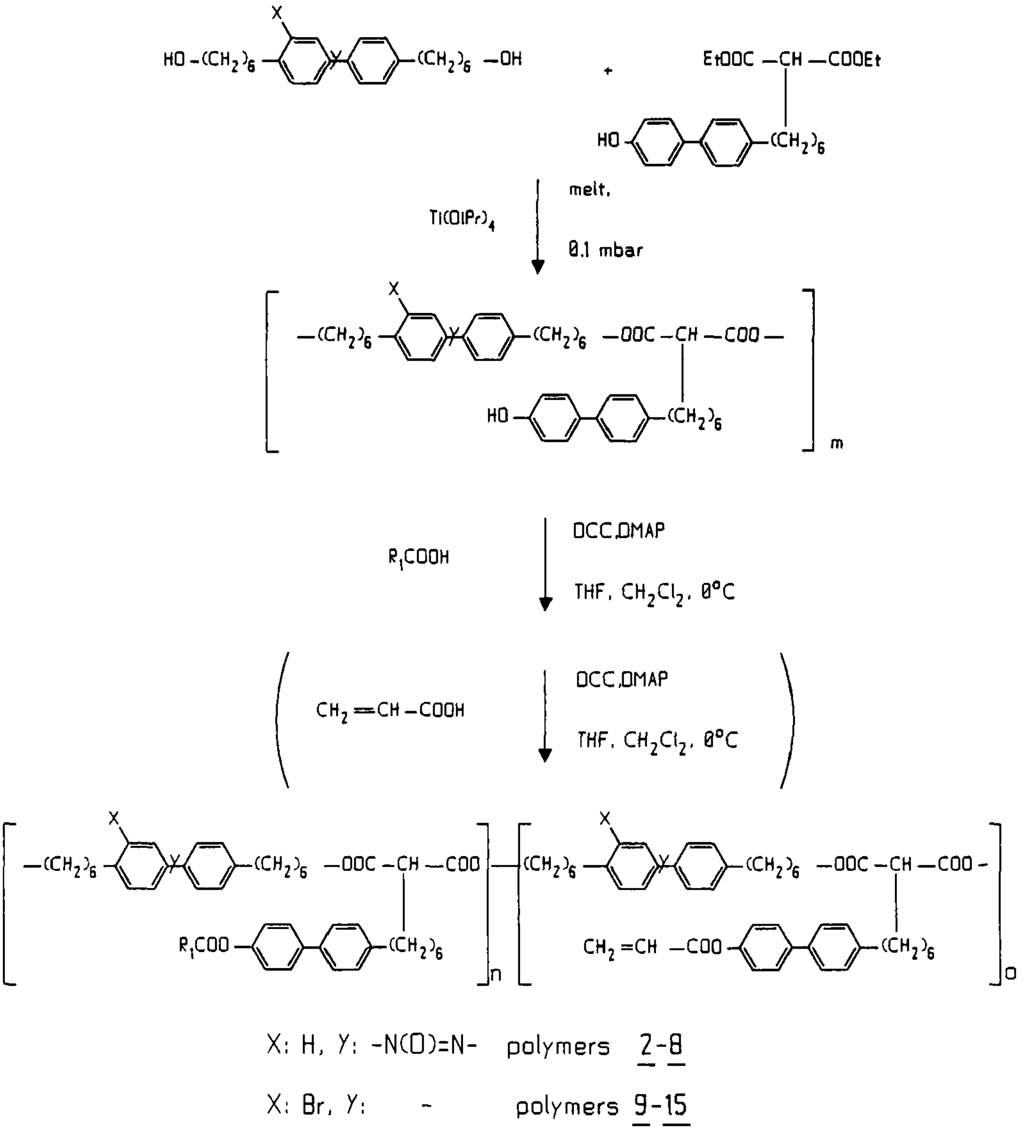


FIGURE 4 Log_{10} piezosignal versus temperature for elastomer **1** (amplitude about 10%).

2. GENERAL PART

2.1. Crosslinkable Polymers

2.1.1. Selection of polymers and synthesis. Recent investigations on chiral combined polymers have revealed many structure property relations.[23,28] For the



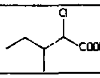
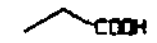
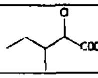
SCHEME II

preparation of crosslinkable polymers, some of the chiral tails of the mesogenic side groups have to be exchanged by acrylate groups (see Scheme I and II). In order to correlate the effect of this substitution to differences in the molecular shape between "original" tail and acrylate group, homopolymers with tails of different geometries should be used (see Tables I and II).

Propionic acid is of the same size as acrylic acid, whereas palmitinic acid contains a much longer alkyl-chain *S*(–)2-chloroisovalerianic acid is chosen as chiral acid, because lateral substituents may have an influence too. As mesogenic core two systems were selected: Azoxybenzene gives rise to broad LC phases (see Table I).

TABLE I

Characterisation of the Azoxypolymers **2–8** (see Scheme II)

polymer	R_1	$n^{a)}$	$M_W{}^{b)}$	phase-transitions/°C $^{c)}$	d/nm$^{d)}$
2		0	25 000	g 39 n 139 i	
3		1	26 000	g 30 s_A 93 n 150 i	2.47
4		1	27 000	g 28 s_A 93 n 138 i	2.56
5		1	26 000	g 12 s 108 n* 116 i	2.51
6		0.5	26 000	g 28 s_A 80 n 150 i	2.49
7		0.5	27 000	g 20s_A 50 n 124 i	2.57
8		0.5	26 000	g 11 s_A 65 n* 115 i	2.52

a) mol. fraction of R_1 as determined by ^{1}H-NMR, the mol. fraction of acrylic acid (copolymers **6-8**) is 1-n

b) determined by GPC in THF against polystyrene standards

c) g: glassy, s_A: smectic A, n: nematic, s: smectic C* or smectic a, not further determined, n*: cholesteric, i: isotropic

d) smectic layer spacing as determined by X-ray-diffraction

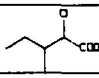
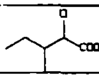
However, it's colour makes a photochemically initiated crosslinking impossible. Bromobiphenyl (see Table II) is transparent in the near UV-region. However, the temperature range of the LC phases is rather small. Both mesogens suppress a crystallization at low temperatures and increase thereby the temperature range of the LC phase.[28]

The preparation of the polymers is done by a reesterification reaction according to Scheme II, starting from known compounds.[28] The introduction of the tails of the mesogens is done by an esterification with the help of DCC[28] (see Scheme II) in one or two steps. The structure of the polymers thus obtained is given in Tables I and II. ^{1}H-NMR proves that the conversion during the polymer analogous reaction is quantitative within the limits of accuracy (Figure 5). It was used in addition to determine the copolymer composition.

2.1.2. Phase behaviour. The phase assignment of the polymers has been done by a combination of polarizing microscopy (Figure 6), DSC (Figure 7), and x-ray measurements (see Figure 8). Due to the high viscosity of the polymers only in some cases characteristical textures could be found (see Figure 6). The results are compiled in Tables I and II. All polymers show smectic and nematic, resp. cho-

TABLE II

Characterisation of the Biphenylpolymers **9–15** (see Scheme II)

polymer	R_1	$n^{a)}$	$M_W^{b)}$	phase-transitions$^{c)}$	d/nm $^{d)}$
9	-	0	10 000	g 18 n 98 i	-
10		1	12 000	g 15 s_A 88 n 100 i	2.24
11		1	13 000	g 15 s_A 50 n 77 i	2.21 3.08
12		1	12 000	g 13 s 91 i	2.30
13		0.5	14 000	g 28 s_A 70 n 94 i	2.25
14		0.5	16 000	g 19 s_A 46 n 73 i	2.27 3.05
15		0.5	14 000	g 5 s 68 n* 85 i	2.32

a)-d) see footnotes in table 1

lesteric, phases. For the homopolymers the attachment of longer alkyl-chains or lateral groups leads to a decrease of the phase-transition temperatures.

The introduction of acrylate groups leads to a destabilization of the smectic phase in all copolymers. The magnitude of this effect depends on the difference of the length between the two different tails of the mesogen. For copolymers with large difference in the length (polymers **7** and **14**) both the clearing temperature and the transition smectic-nematic are reduced. For copolymers with two tails of nearly identical length (polymers **6** and **13**) the clearing temperature is nearly unchanged and only a small reduction of the transition smectic-nematic is observed.

X-ray measurements show that the variation of the length of the mesogenic tail has only a minor influence on the thickness of the smectic layers (e.g. 0.09 nm difference in thickness (polymers **3** and **4**) for 10 additional —CH_2-groups). A variation of the mesogenic core in the main chain (azoxybenzene instead of biphenyl) leads however to a pronounced increase of the thickness of the smectic layers of about 0.2 nm (compare Tables I and II). For the polymers **11** and **14** (Table II) two periodicities are observed, which are not higher orders of each other.

2.2. Crosslinked Samples

2.2.1. Network topologies and crosslinking reactions. Beside polymerizations, acrylate groups are able to undergo addition reactions. One of them is a reaction with thiols. Therefore, a network formation should be possible by the use of dithiols too. This reaction must be performed in solution (no LC phase) and it will produce netpoints with a defined functionality of four. In contrast to this the networks produced by polymerization should be polyfunctional with two different polymer

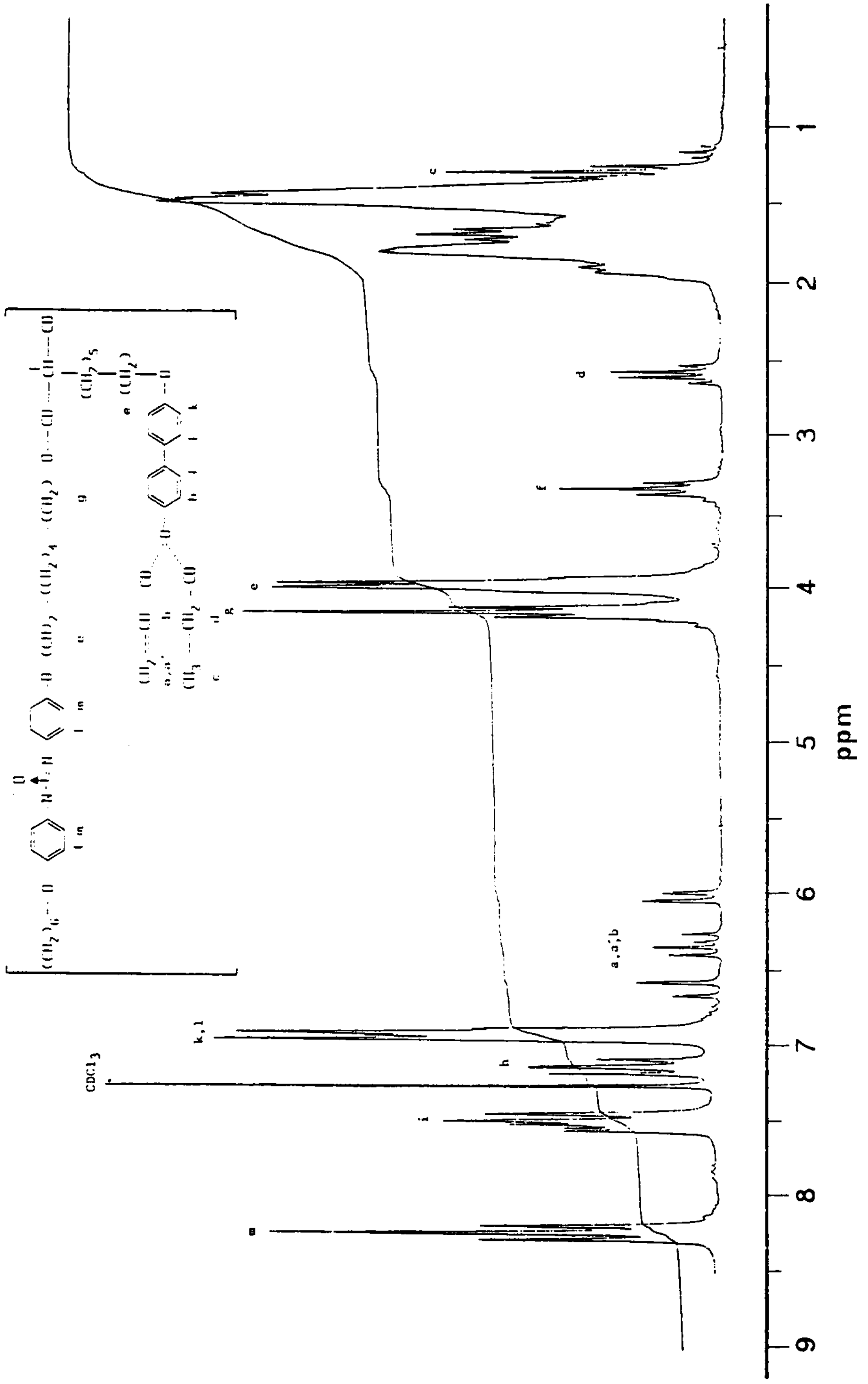


FIGURE 5 ^{1}H-NMR of **6**. The ratio from acrylate- to propionic-groups is represented by the ratio of signals *a*, *a'*, *b* to signal *d*.

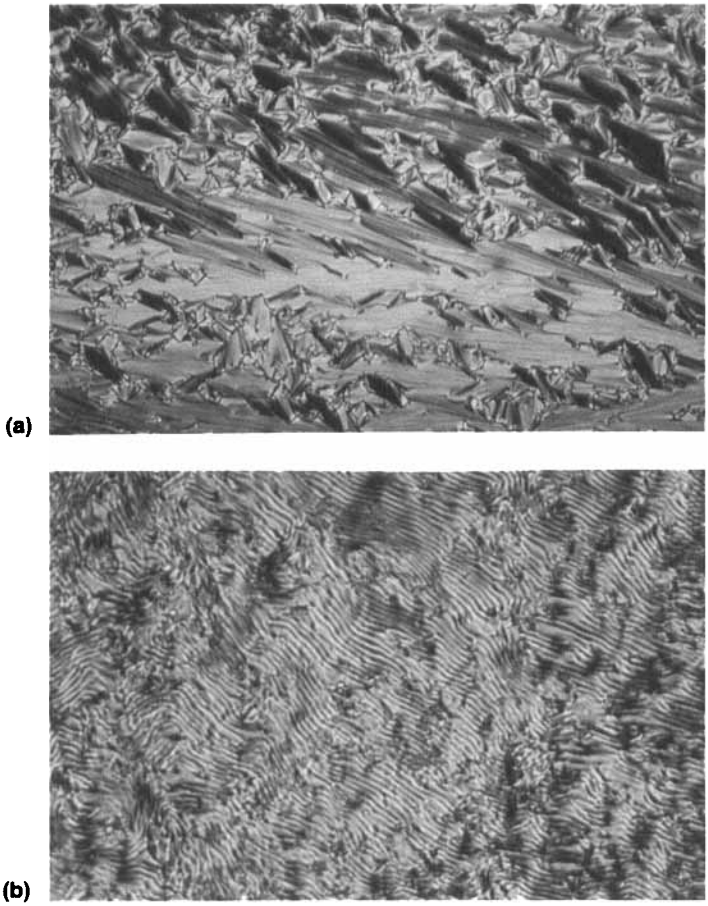


FIGURE 6 Optical textures of polymer **15**; a: smectic fan shaped texture, 65°C; b: cholesteric polygonal texture; 72°C magnification 200×. See Color Plate X.

chains. The different network-topologies that result from these two crosslinking reactions are presented in Scheme III.

We have investigated the crosslinking reaction of polymer **6** in more detail. The performance of the reaction was controlled by GPC for soluble and by swelling experiments for geled insoluble samples (Table III).

As can be seen from Table III, the polymers can be crosslinked in the isotropic phase, even if there is no initiator added (see Reference 24 for comparison). This behaviour is probably caused by THF-peroxides, that are incorporated in the sample. It fails, if only CH_2Cl_2 is used as solvent during the preparation and purification of the polymers. Since the amount of accidentally introduced peroxides varies from sample to sample, it is difficult to control the network density in this way. In addition this method does not allow a crosslinking at lower temperature within the LC phases.

In order to perform crosslinking reactions at lower temperatures in the different LC phases, radical initiators are added. The use of different initiators allows cross-

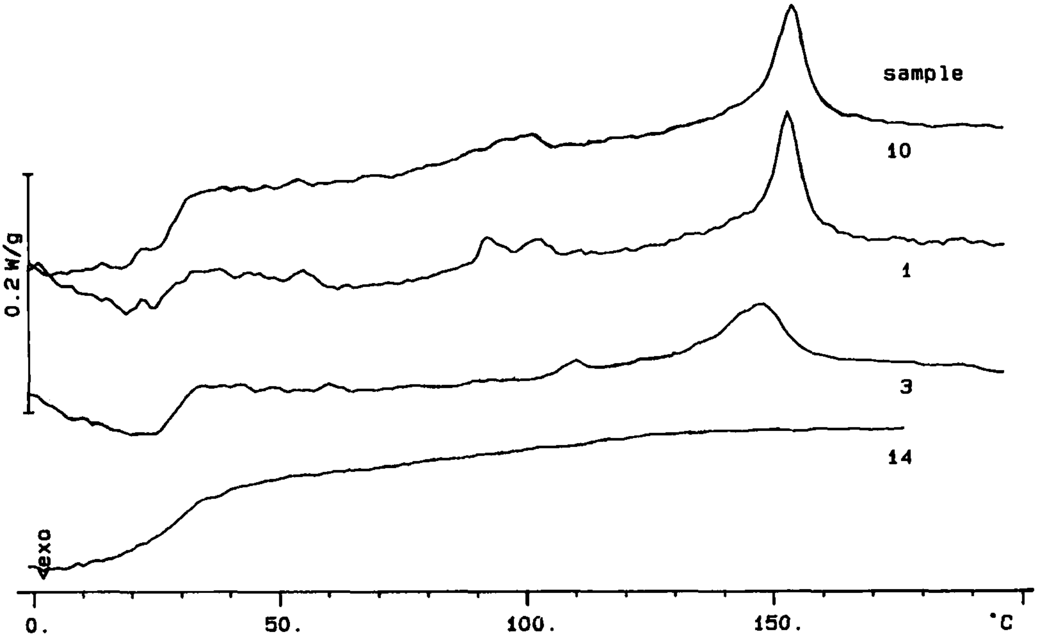


FIGURE 7 DSC-measurements on different crosslinked samples of **6**. Crosslinking-conditions of different samples according to Table III; sample 10 crosslinked for 8 h at 140°C without initiator.

linking at several temperatures. Azobisisobutyronitrile (AIBN) decomposes rapidly within the temperature range of the smectic phase. With it the crosslinking fails, presumably because of the sterical hindrance within the smectic A-phase and because of the vicinity to the glass transition temperature. Benzoylperoxide (BPO) and dicumylperoxide (DCP) decompose in the temperature range of the nematic phase. With both initiators networks are obtained. The crosslinking-effectivity rises with the decomposition-rate of the initiators. The half life time of BPO is 10 min. at 120°C whereas the value for DCP at 140°C is around 47 min.

Nearly all of the networks obtained in this way (Table III) swell highly and they contain still a lot of soluble polymer. Therefore the netpoint density is still rather low. This might be caused by a steric hindrance due to the direct attachment of the acrylic acid to the mesogenic core, and by the relatively low molecular weight of the crosslinking polymers. Only samples crosslinked with a high concentration of radicals (samples 4 and 5) give more densely crosslinked networks with a low sol content. A comparison with the sample crosslinked in solution during 8 hours with biphenyldithiol shows that the crosslinking density is rather low also in this case.

2.2.2. Influence of crosslinking on the LC phases. In order to elucidate the influence of the crosslinking on the LC phases, DSC- and x-ray measurements were performed (see Figures 7 and 8). DSC-measurements show (Figure 7) that the transition temperatures do not change very much, as long as the crosslinking density is low. Although the peaks become broader with increasing crosslinking density, the transition enthalpy remains the same. For the more highly crosslinked

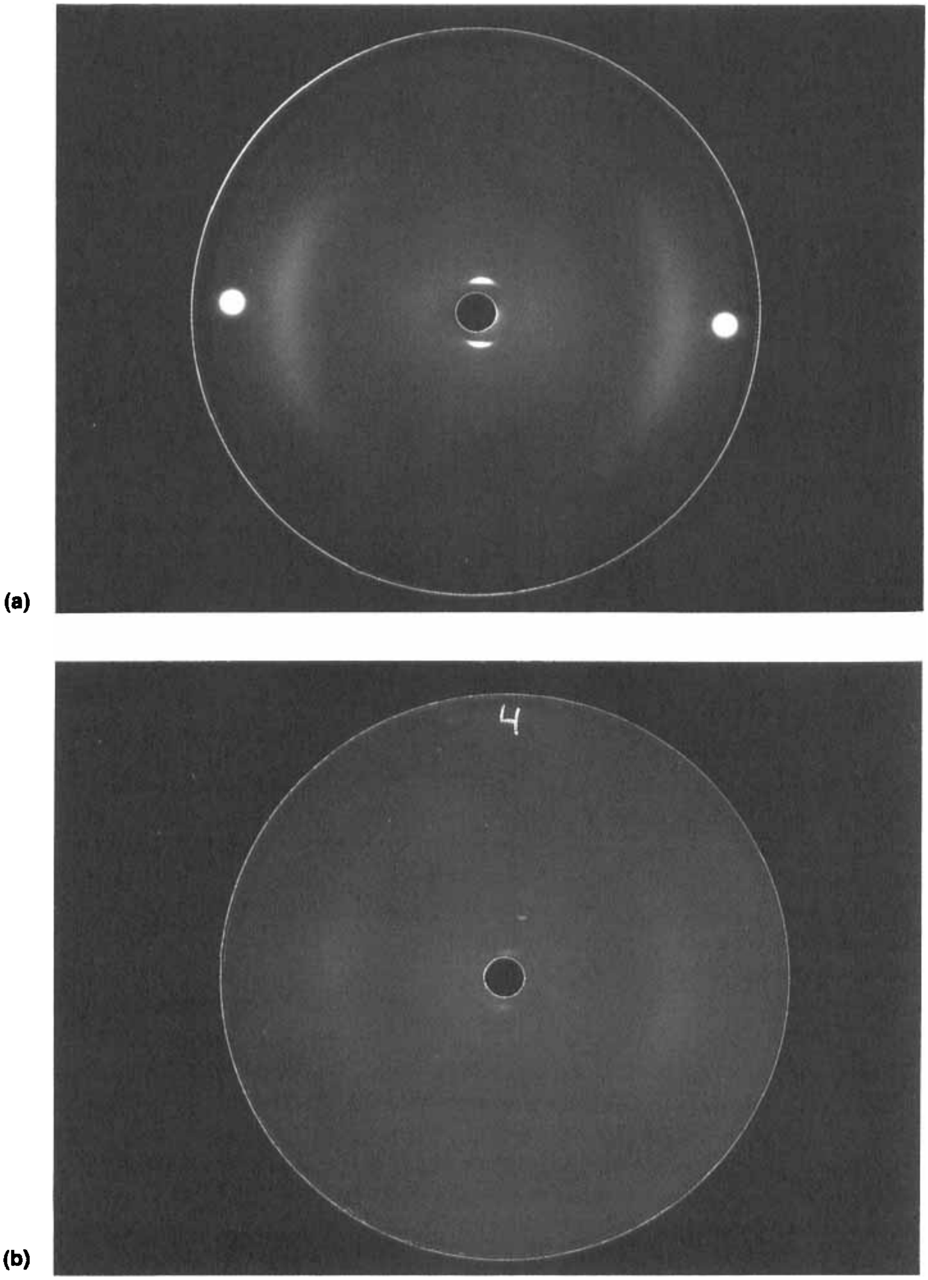
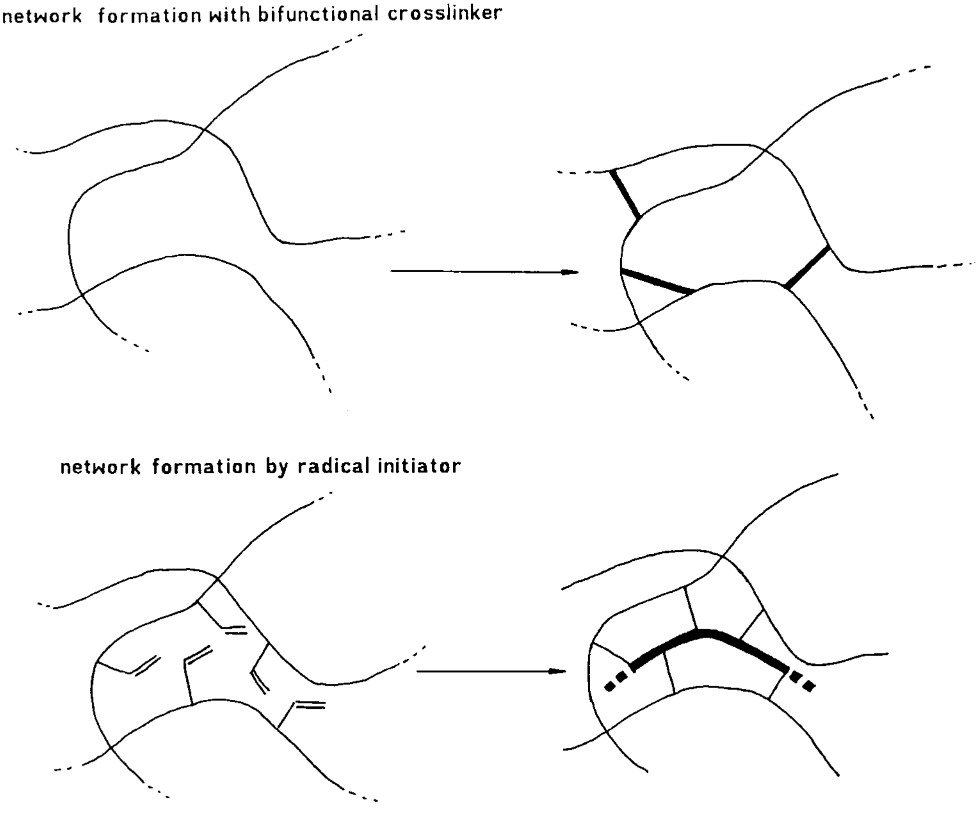


FIGURE 8 X-ray pattern of sample 3 (Table III); stretching 100%; distance sample/film: 10 cm; a: room-temperature, frozen smectic A phase; b: 95°C, nematic phase.



SCHEME III

samples (samples 4 and 5) however, no more phase transitions can be determined. Polarizing microscopy shows in these cases only a weak stress birefringence. Therefore the LC phases are destroyed in the more highly crosslinked samples. This is different from the behaviour of LC elastomers prepared by a crosslinking with difunctional crosslinking agents in solution,[10] for which the LC phases are unaffected for even higher crosslinking densities. This difference may be explained by the different topologies of the different types of networks (see Scheme III). In the networks prepared by radical polymerization a new polymer chain is formed, which is directly attached to the mesogenic groups. It is well known from earlier investigations[29,30] that such an arrangement is highly unfavorable for LC phases.

X-ray measurements on the slightly crosslinked polymers show that the networks still exhibit smectic and nematic phases. Due to the crosslinking, the phases can be oriented by elongation of the sample (Figure 8). Thereby the orientation of the mesogens is in all cases parallel to the direction of the main-chain, which is oriented preferably parallel to the stretching direction.[9] The mechanical orientability eases the identification of the different phases by temperature dependent x-ray measurements, as shown for polymer **6** (sample 3) in Figure 8. The diffuse layer lines in the small angle region of Figure 8b are typical for cybotactic nematic phases.[31]

The smectic layer spacings for differently crosslinked samples of polymers **6–8**

TABLE III

Swelling-measurements on different crosslinked samples of polymer **6** (see Table I)

sample	crosslinking conditions			solvent in gel[b)] (weight %)	% sol fraction (weight %)
	initiator[a)]	temp/°C	time/h		
1	-	160	4	96	59
2	-	160	6	94	23
3	-	160	8	92	26
4	BPO 5%	120	0.25	86	2
5	BPO 5%	120	0.5	90	8
6	DCP 5%	140	4	98	60
7	DCP 5%	140	6	97	43
8	DCP 5%	140	8	93	28
9	BDT	80	8	90	75

a) weight % of Benzoylperoxide (BPO), Dicumylperoxide (DCP), are radical initiators; 50 mol % Biphenyldithiol (BDT, bifunctional crosslinker) are added referring to the amount of acrylic ester groups

b) solvent: CH_2Cl_2

are compiled in Table IV. It follows from this comparison that the crosslinking by radical polymerization does not affect the smectic layer spacing. Crosslinking with biphenyldithiol leads however in all cases to an increase of the layer spacing. For the polymers **6** and **8** this increase is slight (0.1 to 0.2 nm) and comparable to the increase observed for combined polymers crosslinked with a bifunctional oligosiloxane.[9] For polymer **7** the increase is high (1.1 nm). It is interesting that this large increase is observed for the polymer with the long tail of the mesogen, for which this tail has to be highly coiled in order to fit into the smectic layer structure of the uncrosslinked polymer (see Tables I and II and Section 2.1.2). As a result of this, networks with a large difference in the structure of the smectic phase can be prepared starting from the same polymer (see polymer **7**, sample 1 and 2 in Table IV).

2.2.3. Mechanical properties. The measurement of mechanical properties is an important method to characterize crosslinked polymers. For these measurements[32] larger samples had to be crosslinked, which were measured in the plate and plate geometry with a Rheometric Mechanical Spectrometer. Swelling experiments per-

TABLE IV

Phase-characterisation of thermally and chemically crosslinked networks

sample	crosslinking conditions			phase-transitions/°C[b)]	d/nm[c)]
	reagent[a)]	temp/°C	time/h		
6.3	-	160	8	g 29 s_A 110 n 147 i	2.51
6.9	BDT	80	8	g 20 s_A 67 n 133 i	2.61
7.1	-	160	8	g 23 s_A 67 n 123 i	2.52
7.2	BDT	80	8	g 25 s_A 68 n 122 i	3.67
8.1	-	160	8	g 24 s n^* 126 i	2.61
8.2	BDT	80	8	g 13 s 48 n^* 108 i	2.69

a) 50 mol % of Biphenyldithiol (BDT, as bifunctional crosslinker) are added referring to the acryate ester groups

b) see table 1 footnote c

c) see table 1 footnote d

TABLE V

Swelling-measurements of the big samples of crosslinked **6** used for mechanical measurements

sample	crosslinking conditions			solvent in gel weight %	sol fraction weight %
	initiator[a)]	temp/°C	time/h		
11	BPO 1%	120	8	96	75
12	-	160	8	93	74
13	DCP 5%	140	6	92	47
14	BPO 5%	120	8	81	8

a),b) see footnotes in table 3

formed with these samples (see Table V) were used as an independent measure of the crosslinking density.

Figure 9 shows the storage modulus G', the loss modulus G'' and the tangential loss G'/G'' for uncrosslinked polymer **6**. There is a good coincidence between changes in mechanical behaviour and phase-transitions. The glass transition smectic-nematic leads to a strong decrease of G', the minimum of which is reached in the nematic phase due to shear thinning effects. G' increases again at the transition to the isotropic phase (see Reference 32 for a detailed discussion). Such effects are typical for nematic polymers.[33,34] The increase of G' at high temperatures in the isotropic phase is due to a thermally activated crosslinking.

For the different crosslinked samples (Figure 10a,b) the increase in the crosslinking density shows up in larger values of G' especially in the nematic phase. Since the increase of G'' (proportional to the dissipated energy) is much smaller than the increase of G' (proportional to the elastically stored energy), the ability of the network to store energy reversibly grows with crosslinking density. Both, the swelling experiments

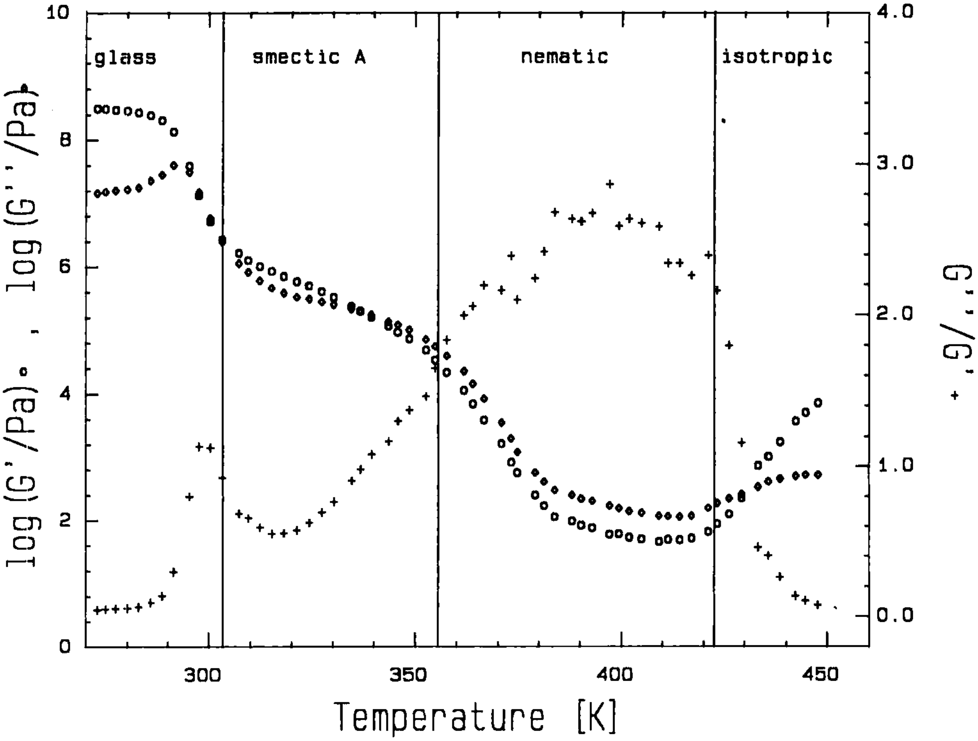


FIGURE 9 Shear-storage-modulus *G'* ○, loss-modulus *G''* ◇, and tangential loss *G''*/*G'* + against temperature for uncrosslinked polymer **6**, the vertical lines indicate the phase transition temperatures determined by DSC.

and the mechanical measurements give the same sequence of increasing crosslinking density (increasing from sample 11 to 14). The strong increase of *G'* in the high-temperature region can be explained by a continuation of the crosslinking reaction. In accordance with the DSC-measurements, the most highly crosslinked network (sample 14 in Table V) shows no transitions that are due to LC phases.

Mechanical measurements on a network crosslinked with biphenyldithiol give similar results (see Figure 11). In this case, however, no strong increase of *G'* can be observed in the isotropic phase. Since thiols are inhibitors for radical polymerizations, they inhibit a continuation of the crosslinking process.

As a result of these investigations it can be seen that the crosslinking density of the networks can be varied in a systematic way e.g. by increasing the reaction time or by adding additional radical initiators. Problems may however arise, if polymers prepared in different batches are compared. These polymers may contain differing amounts of radical initiators (peroxides) or impurities acting as radical inhibitors, depending on the purity of the solvents used.

2.3. Photocrosslinking

It is the advantage of photocrosslinking that it can be started at a given time at variable temperatures. In this case, it is desirable to crosslink in the LC phase, if

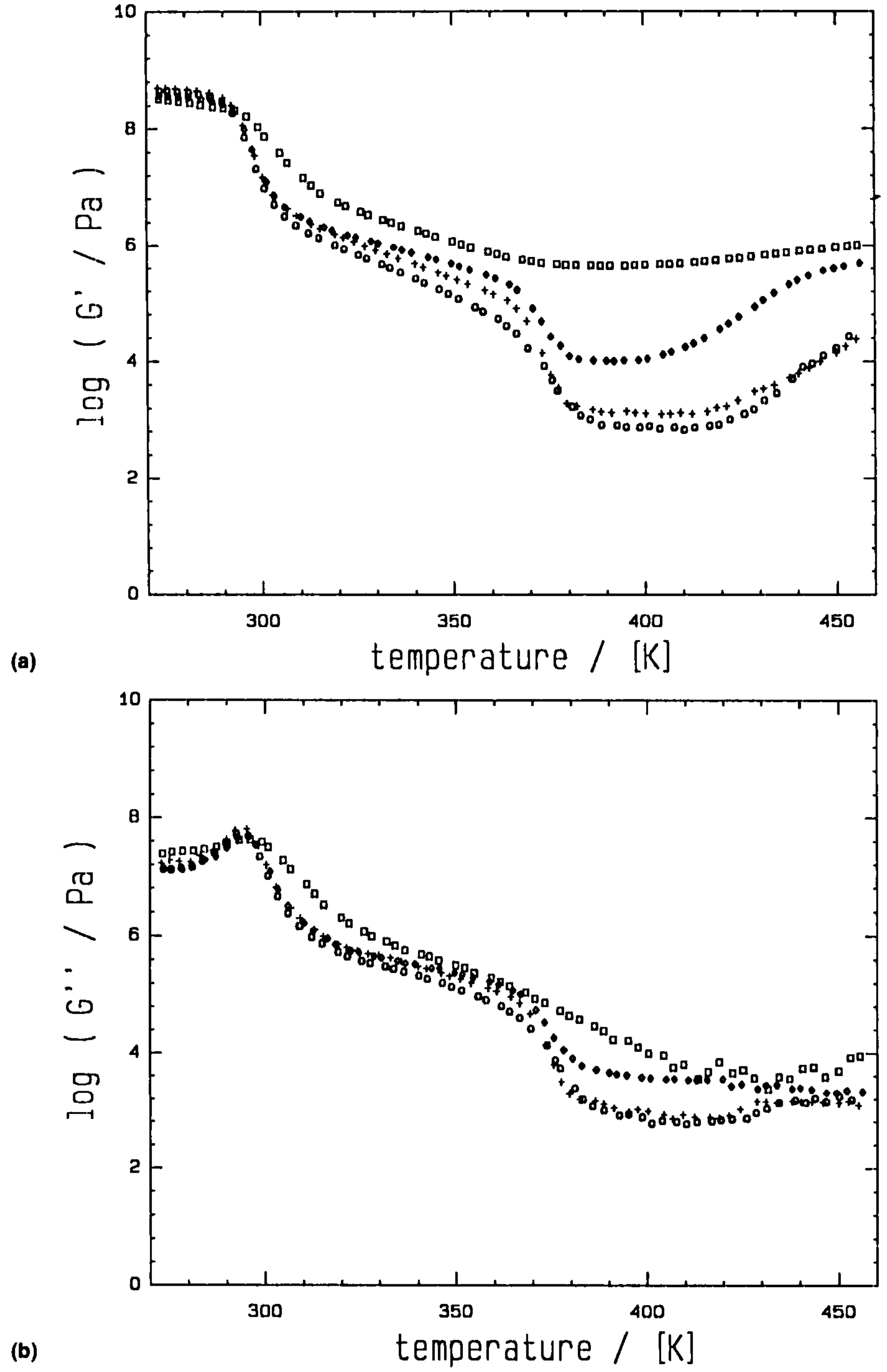


FIGURE 10 a: Shear-storage modulus G' for polymer **6** samples 11○, 12+, 13◇, 14□ (see Table V); b: shear-loss G'' modulus for the same samples.

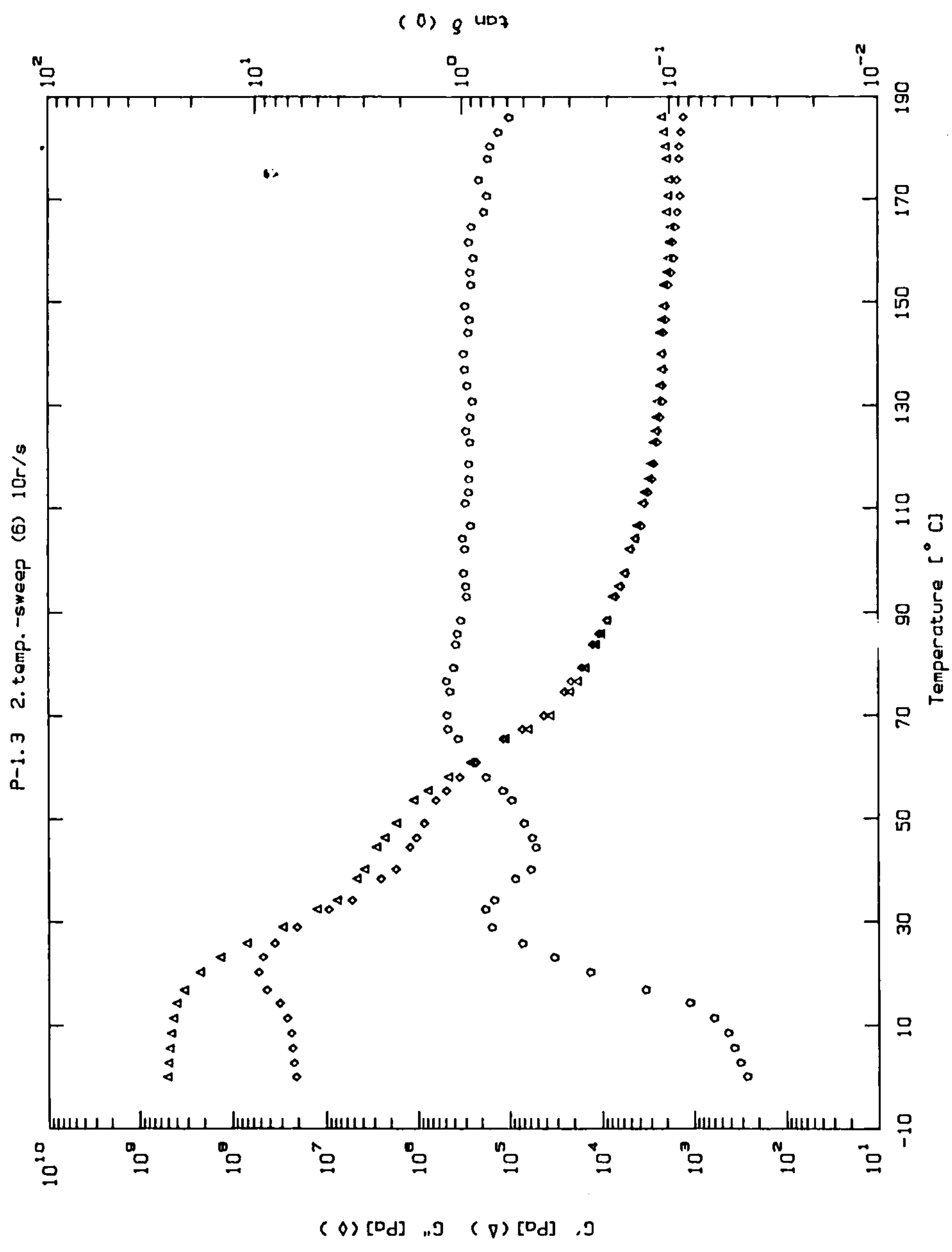


FIGURE 11 Shear-storage-modulus G', loss-modulus G'', and tangential loss G''/G' against temperature for polymer 6 sample 9.

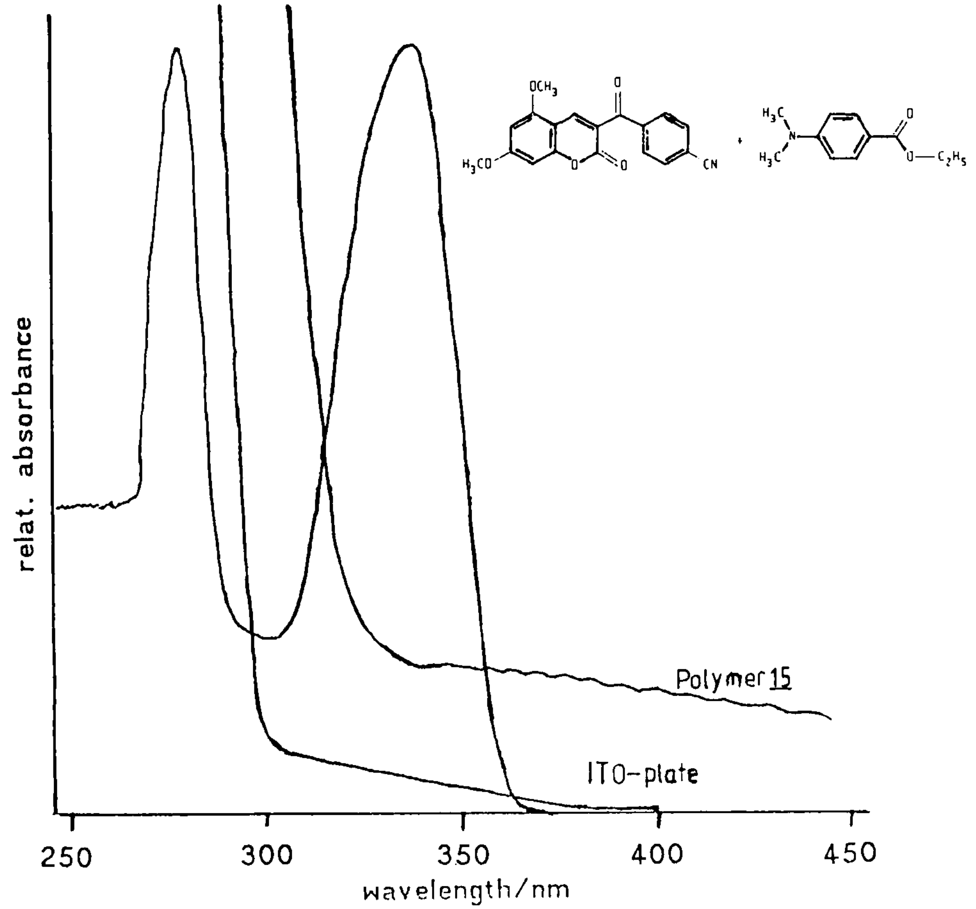


FIGURE 12 UV-spectra of polymer **15** the photoinitiator system and ITO-coated glass.

a desirable orientation (preferably a monodomain) has been obtained. Since the aromatic mesogens absorb in the UV-region, a radical photoinitiator is necessary, which absorbs in the near UV. With the photoinitiator system[35] presented in Figure 12, it is possible to crosslink the polymers **13–15** (see Table II) between two indium-tin oxide coated glass plates.

IR-measurements allow it to follow the crosslinking reaction by measuring the decay of the =C—H deformation band of the acrylate groups[36] at 735 cm^{-1} (see Figure 13). Since the band overlaps, however, strongly with the =C—H deformation bands of the aromatic ring, a quantitative evaluation of the conversion is not possible. A comparison with a thermally crosslinked elastomer (sample 3, Table III), shows that the conversions are comparable in both cases.

First examples of the photo crosslinking show, that it is possible to freeze the LC textures by the crosslinking reaction. A sample of **15** with photoinitiator is oriented on a glass-plate by shearing. One part of the preparation is covered with a foil. Now the sample is exposed to UV-light of 365 nm at 75°C. If the film is heated afterwards above the clearing-point, both sites become isotropic. After

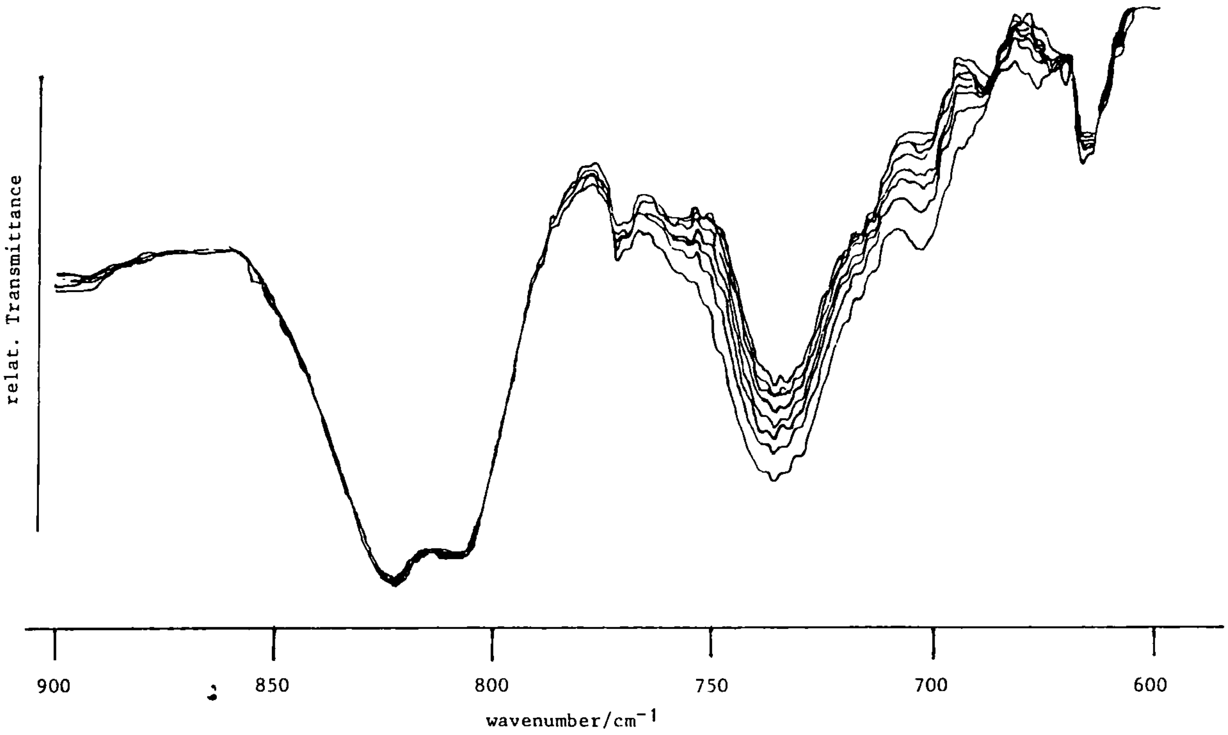


FIGURE 13 Infrared-spectra of **15**; exposing time to UV-light between the scans: 15s; temperature: 70°C, λ = 365 nm.

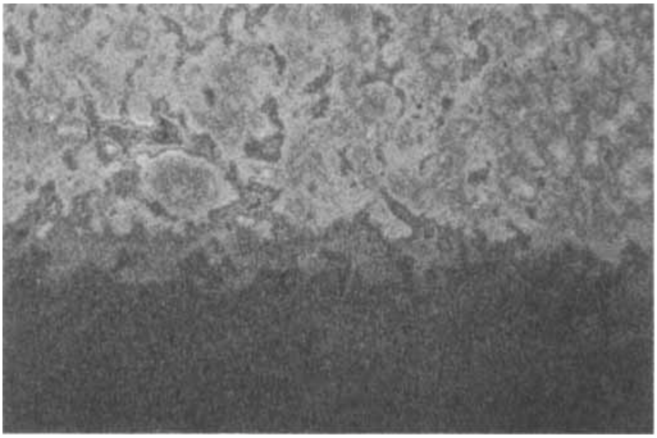


FIGURE 14 Optical texture of photocrosslinked (upper side) and uncrosslinked **15** after heating into the isotropic phase and cooling to room temperature; magnification 100×. See Color Plate XI.

cooling, the crosslinked area restores the orientation that it had before crosslinking, whilst the uncrosslinked area shows an unoriented texture (Figure 14).

EXPERIMENTAL

The OH-functionalized precursor polymers have been prepared in accordance to Reference 28. The polymer analogous DCC-esterification is described ibid. The crosslinkable polymers (**6–8, 13–15**) were prepared in two esterification steps. The first was carried out with a 1.2 molar excess of saturated acid (referred to all phenolic groups) and DCC according to the method mentioned above. This leads to a conversion of 50 to 60% of all phenolic OH-groups. The second reaction is carried out with a 1.5 fold excess of acrylic acid (referred to the initial amount of phenolic groups) and DCC.

The phase transitions were determined by a Mettler DSC 30 at a heating-rate of 10 K/min. The peak-maxima and midpoints of the glass-steps are taken as transition temperatures. For polarizing microscopy an Olympus BS-H2 with an Olympus OS-2 camera was used together with a Mettler FP 82 hotstage connected on an FP 80 controller. The x-ray films were exposed in a flat-camera with nickel-filtered CU-K_α radiation from a Siemens K8/OA generator. Drawn fibres of the uncrosslinked polymers were investigated at room temperature. The crosslinked polymers were stretched in a self-made stretching device[9] and investigated at variable temperatures. For the crosslinking of the big samples of teflon-crucible with a diameter of 16 mm and a flat bottom was used. The swelling measurements were carried out with CH_2Cl_2 as solvent. During one week the solvent was changed several times. The unsoluble part of the polymer (gel fraction) was weighed after 48 hours drying at room temperature.

The mechanical measurements were carried out with a Rheometrics Mechanical Spectrometer Model 800 in the plate-plate geometry. The shear storage modulus

G', loss modulus G'' and loss tangent (tan δ) were obtained as a function of temperature at constant frequency of 1 Hz and heating rate of 1 K/min as described in Reference 32.

The photocrosslinking reaction was carried out with 0.5 wt% ketocumarine as sensibilisator and 1.5 wt% aniline-derivative as activator. The crosslinking is carried out at 75°C for 3 min irradiation with a 4 W low-pressure lamp in 5 cm distance.

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References

1. H. J. Cantow and N. A. Platé (eds.), Polymer Liquid Crystals II/III, Adv. Polym. Sci. 60/61, Springer-Verlag, Berlin (1984).
2. S. L. Kowlek, P. W. Morgan and J. R. Schaefgen, in Encyclopedia of Polymer Science and Engineering, Vol. 9, pp. 1–61 (1987).
3. C. B. McArdle (ed.), Side Chain Liquid Crystal Polymers, Blackie, Glasgow (1989).
4. R. Zentel, H. Poths, F. Kremer, A. Schönfeld, D. Jungbauer, R. Twieg, C. G. Willson, and D. Yoon, Polym. Adv. Tech. 3, 211 (1992).
5. C. B. McArdle, in [3], p. 357.
6. J. Strzelecki and L. Liebert, *Bull. Soc. Chim. Fr.* (1973) 597; S. N. Bhadani and D. G. Gray, *Mol. Cryst. Liq. Cryst. Lett.*, **129**, 255 (1984); D. J. Broer, R. J. Gossink and R. A. M. Hikmet, *Angew. Makromol. Chem.*, **183**, 45 (1990); R. A. M. Hikmet, *Mol. Cryst. Liq. Cryst.*, **198**, 357 (1991).
7. R. Zentel, *Angew. Chem., Adv. Mat.*, **101**, 1437 (1989); *Angew. Chem. Int. Edn. Engl., Adv. Mat.*, **28**, 1407 (1989).
8. W. Gleim and H. Finkelmann, in [3], p. 387.
9. R. Zentel, G. F. Schmidt, J. Meyer and M. Benalia, *Liq. Cryst.*, **2**, 651 (1987).
10. R. Zentel and M. Benalia, *Makromol. Chem.*, **188**, 655 (1987).
11. G. R. Mitchell, F. J. Davis and A. Ashman, *Polymer*, **28**, 639 (1987).
12. R. Zentel and G. Reckert, *Makromol. Chem.*, **187**, 1915 (1986).
13. W. Gleim and H. Finkelmann, *Makromol. Chem.*, **188**, 1489 (1987).
14. J. Schätzle, W. Kaufhold and H. Finkelmann, *Makromol. Chem.*, **190**, 3269 (1989).
15. G. R. Mitchel, F. J. Davis, W. Guo and R. Cywinski, *Polymer*, **32**, 1347 (1991).
16. M. Bräuchler, C. Boeffel and H. W. Spiess, *Makromol. Chem.*, **192**, 1153 (1991).
17. R. G. Kirste and H. G. Ohm, *Makromol. Chem. Rapid Commun.*, **6**, 179 (1985); F. Moussa, J. P. Cotton, F. Hardouin, P. Keller, M. Lambert, G. Pepy, M. Mouzak and H. Richard, *J. Phys. (Les Ulis, Fr.)*, **48**, 1079 (1987).
18. H. Brand, *Makromol. Chem. Rapid Commun.*, **10**, 57 (1989).
19. M. Warner, K. P. Gelling and T. A. Vilgis, *J. Chem. Phys.*, **88**, 4008 (1988).
20. J. Kupfer and H. Finkelmann, *Makromol. Chem. Rapid Commun.*, **12**, 717 (1991).
21. R. Zentel, *Liq. Cryst.*, **1**, 589 (1986).
22. N. R. Barnes, F. J. Davis and G. R. Mitchell, *Mol. Cryst. Liq. Cryst.*, **168**, 13 (1989).
23. R. Zentel, *Liq. Cryst.*, **3**, 531 (1988); R. Zentel, G. Reckert, S. Bualek and H. Kapitza, *Makromol. Chem.*, **190**, 2869 (1989).
24. S. U. Vallerien, F. Kremer, E. W. Fischer, H. Kapitza, R. Zentel and H. Poths, *Makromol. Chem., Rapid Commun.*, **11**, 593 (1990).
25. W. Meier and H. Finkelmann, *Makromol. Chem., Rapid Commun.*, **11**, 599 (1990).
26. H. Brand, *Makromol. Chem., Rapid Commun.*, **10**, 441 (1989).
27. H. Brand, *Makromol. Chem., Rapid Commun.*, **11**, 606 (1990).
28. H. Kapitza and R. Zentel, *Makromol. Chem.*, **192**, 1859 (1991).
29. H. Finkelmann and G. Rehage, in Reference 1, p. 100 ff.
30. V. Percec and C. Pugh, in Reference 3, p. 30 ff.

31. A. de Vries, *Mol. Cryst. Liq. Cryst.*, **131**, 125 (1985).
32. T. Pakula and R. Zentel, *Makromol. Chem.*, **192**, 2401 (1991).
33. G. Marrucci, *Mol. Cryst. Liq. Cryst.*, **721**, 153 (1981).
34. K. F. Wissbrun, *Faraday Discuss. Chem. Soc.*, **79**, 161 (1985).
35. D. P. Specht, P. A. Matric and S. Farid, *Tetrahedron*, **38**, 1203 (1982).
36. G. J. Smets, S. N. Hamoudy and T. J. Oh, *Pure & Appl. Chem.*, **563**, 439 (1984).