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Synthesis and phase behaviour of liquid-crystalline side group polyesters

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Several series of liquid-crystalline side group polymers with a polyester backbone structure have been synthesized using mesogenic diethylmalonate and 1,3-propanediol derivatives. The structures of the polymer backbone and the mesogenic units have been varied systematically. As shown by differential scanning calorimetry, polarizing microscopy and X-ray diffraction, the side group polyesters exhibit nematic and/or smectic mesophases. Polyesters synthesized from mesogenic diethylmalonate derivatives can tolerate long non-mesogenic segments in the polymer main chain without losing their liquid crystal properties. X-ray studies suggest that some of the smectic polymers exhibit interdigitated bilayer S_A phases.

1. Introduction: Liquid-crystalline side group polymers

Thermotropic liquid-crystalline side group polymers generally consist of three basic building elements: a rod-like mesogenic side group, a flexible spacer and a polymer backbone (see Scheme 1). The structure–property relations of this class of materials have been discussed in various review articles [1–4]. The spacer decouples the anisotropically ordered mesogenic side groups from the polymer backbone, which has a tendency to adopt a statistical coil conformation. The polymer backbone determines the typical polymer properties of side group liquid crystal polymers such as mechanical orientability and especially the often desired ability to form stable, ordered glasses below T_g. The most widely used backbone structures are polyacrylates and methacrylates prepared by radical polymerization and polysiloxanes prepared by the polymer analogue reaction [1–4] (Scheme I). Only within the past few years have various other polymerization reactions and backbone structures been described [4]. Also, the wider use of the polymer analogue reactions opened an easy access to many old and new backbone structures [4].

Besides the polymerization and the polymer analogue reaction, polycondensation offers an additional versatile synthetic route to side group liquid crystal polymers (see Scheme 1). Although this method has been widely explored in the synthesis of liquid crystal main chain polymers, it has not been described in much detail for the molecular engineering of side group liquid crystal polymers [5, 6]. One synthetic approach, first described in connection with the combined main chain side group liquid crystal polyesters [5], is the condensation of a mesogenic monomer with a non-mesogenic monomer (see Scheme I). This pathway opens many possibilities for tailoring the backbone properties of side group liquid crystal polymers (e.g. stiffness,

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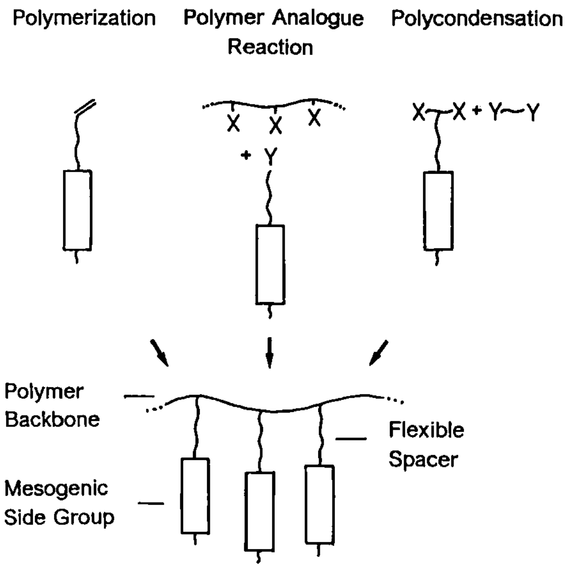


Scheme 1

hydrophilicity, etc.) simply by using the appropriate non-mesogenic condensation monomers.

This paper describes the synthesis and phase behaviour of several series of side group liquid crystal polyesters based on diethylmalonates and 1,3-propanediols substituted with mesogenic side groups. The structure of the backbone and the mesogenic side group have been varied systematically in order to understand the influence of these building elements on the phase behaviour of the side group polyesters.

2. Results and discussion

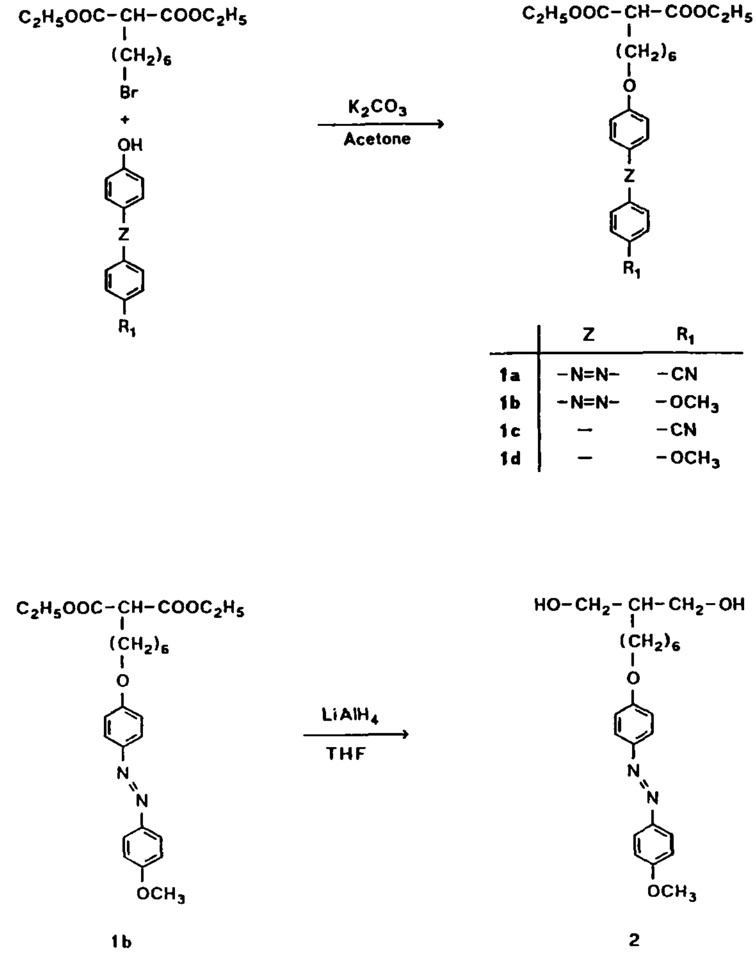
2.1. *Monomer synthesis*

The key compounds for the synthesis of the side group liquid crystal polyesters described here are the mesogenic diethylmalonates **1a–1d**. They were synthesized by etherification of the phenolic groups of various mesogenic precursors with diethyl 6-bromohexylmalonate (see Scheme 2). The condensation monomers **1a** and **1b** have already been employed in the synthesis of the combined main chain side group polymalonates [5]. Reduction of the mesogenic diethylmalonate **1b** with $LiAlH_4$ leads to the mesogenic 1,3-propananediol derivative **2** (see Scheme 2).

2.2. *Polymer synthesis*

The mesogenic diethylmalonates **1a–1d** were reacted with various non-mesogenic diols in a melt polycondensation reaction, which was catalysed by tetraisopropyl orthotitanate, to give the polyesters **3a–3j** (see tables 1 and 2).

The mesogenic 1,3-propanediol derivative **2** was reacted in a solution polycondensation reaction (*o*-dichlorobenzene/pyridine) with different non-mesogenic dicarboxylic acid dichlorides to yield the polyesters **4a–4d** (see table 3). Melt polycondensation of **2** and 4,4′-azobenzene dicarboxylic acid diethylester yielded the combined polyester **4e**.



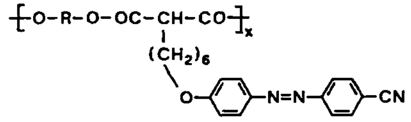
	Z	R_1
1a	$-N{=}N-$	$-CN$
1b	$-N{=}N-$	$-OCH_3$
1c	—	$-CN$
1d	—	$-OCH_3$

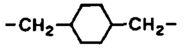
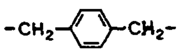
Scheme 2

The condensation monomer **2** was also reacted with the mesogenic diethylmalonates **1a** and **1b** in a melt polycondensation reaction to give the polyesters **5a–5b** (see table 4).

All of the polyesters were purified by preparative gel permeation chromatography (GPC). Their molecular weights were characterized by analytical GPC relative to polystyrene standards. All polymers give the correct elemental analyses. According to the GPC measurements, the polymalonates **3a–3j** (see tables 1 and 2) have molecular weights ranging from 12 000 to 56 000. For liquid-crystalline polysiloxanes it has been claimed that the phase transition temperatures become independent of the molecular weight above a degree of polymerization of ten [7]. Assuming that this relation can also be applied to the side group polyesters, the transition temperatures of polymers **3a–3j** should be unaffected by their molecular weights. In contrast, polymers **4a–4d** and **5a–5b** (see tables 3 and 4), with the exception of **4c**, have lower GPC molecular weights, ranging from 4000 to 8000. Therefore, we have to take into account the fact that the phase transitions of the latter polymers might be slightly affected by differences in their molecular weights.

Table 1. Structures, GPC molecular weights, transition temperatures and transition enthalpies of polymers **3a**–**3g**. Phase assignments: g = glassy, N = nematic, S = smectic, C = crystalline and I = isotropic.



Polymer	*R*	$\bar{M}_{GPC}$(*a*)	Phase transitions (*b*)	ΔH(*b*)/J g^{-1}
3a	$-(CH_2)_6-$	22000	g 9°C S_A 71°C N 77°C I	5·5 (S_A–N–I)
3b	$-(CH_2)_9-$	21000	g 10°C N 64°C I	2·4 (N–I)
3c	$-(CH_2)_6-/-(CH_2)_{12}-$ (*c*)	56000	g 12°C N 65°C I	3·2 (N–I)
3d	$-(CH_2)_{12}$	12000	g 8°C C 39°C N 57°C I	31·0 (C–N) 2·0 (N–I) (*d*)
3e	$-(CH_2CH_2O)_3-CH_2CH_2-$	19000	C 40°C (N 29°C) I (*e*)	29·3 (C–I) 2·6 (I–N)
3f	 cis/trans (f)	14000	g 36°C S 56°C N 78°C I	0·2 (S–N) 2·3 (N–I)
3g		14000	g 38°C S_A 91°C N 100°C I	4·7 (S_A–N–I)

(*a*) Molecular weights from analytical GPC-measurements, relative to polystyrene standards.

(*b*) Transition temperatures (peak maxima) and enthalpies from two DSC heating curves.

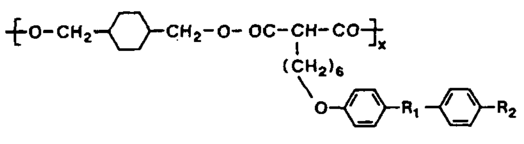
(*c*) Copolyester, monomer feed contained 50 mol % of each diol.

(*d*) Enthalpies from heating curve taken after annealing for 5 hours at 27°C.

(*e*) Temperature and elthalpy of the monotropic transition I–N taken from DSC cooling curve; values for the transition C–I taken from heating curve after annealing for 2 hours at 27°C.

(*f*) 400 MHz ^1H NMR shows 75+/−2 per cent trans and 25+/−2 per cent cis units.

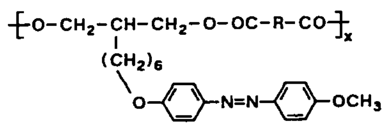
Table 2. Structures, GPC molecular weights, transition temperatures and transition enthalpies of polymers **3f** and **3h–3j**.

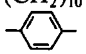
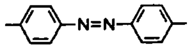


Polymer	R_1	R_2	$\bar{M}_{GPC}$(*a*)	Phase transitions (*b*)	ΔH(*b*)/J g^{-1}
3f (*c*)	-N=N-	-CN	14000	g 36°C S 56°C N 78°C I	2·3 (N–I)
3h	-N=N-	$-OCH_3$	24000	g 33°C S 60°C I	1·9 (S–I)
3i (*d*)	–	-CN	24000	g 38°C N 47°C I	0·3 (N–I)
3j	–	$-OCH_3$	35000	g 31°C C 53°C (S_1 39°C S_2 45°C) I (*e*)	18·7 (C–S) 4·7 (I–S_2–S_1)

(*a*) Molecular weights from analytical GPC-measurements, relative to polystyrene standards.
(*b*) Transition temperatures (peak maxima) and enthalpies from two DSC heating curves.
(*c*) 400 MHz ^{1}H NMR shows 75 +/− 2 per cent trans and 25 +/− 2 per cent cis units.
(*d*) 400 MHz ^{1}H NMR shows 77 +/− 2 per cent trans and 23 +/− 2 per cent cis units.
(*e*) Temperatures and enthalpies of the transitions I–S_2–S_1 taken from DSC cooling curve.

Table 3. Structures, GPC molecular weights, transition temperatures and transition enthalpies of polymers **4a**–**4e**.

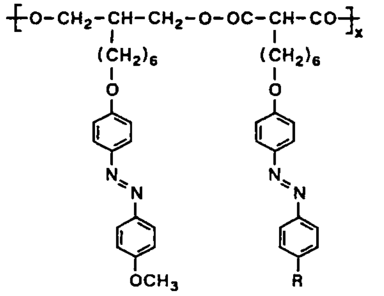


Polymer	*R*	$\bar{M}_{GPC}$(*a*)	Phase transitions (*b*)	ΔH(*b*)/J g^{-1}
4a	$-(CH_2)_4-$	5000	C 65/74°C (N 48°C) I	43·1 (C–I) 2·1 (I–N)
4b	$-(CH_2)_8-$	6000	g 2°C C 53/61°C (N 36°C) I	38·4 (C–I) 2·1 (I–N)
4c	$-(CH_2)_{10}-$	19000	g 11°C C 58/66°C (N 36°C) I	42·3 (C–I) 2·5 (I–N)
4d		8000	g 50°C N 63°C I	0·3 (N–I)
4e		5000	g 48°C C 101°C S 180°C I	8·4 (C–S) 13·8 (S–I)

(*a*) Molecular weights from analytical GPC-measurements, relative to polystyrene standards.

(*b*) Transition temperatures (peak maxima) and enthalpies from two DSC heating curves; the values for the monotropic transitions were obtained from cooling curves.

Table 4. Structures, GPC molecular weights, transition temperatures and transition enthalpies of polymers **5a**–**5b**.



Polymer	*R*	$\bar{M}_{GPC}$ (*a*)	Phase transitions (*b*)	Δ*H* (*b*)/J g^{-1}
5a	-CN	5000	g 40°C S 174°C I	9·3 (S–I)
5b	-OCH$_3$	4000	g 50°C C 100°C (S 91°C) N 136°C I	8·4 (N–S) 4·4 (N–I)

(*a*) Molecular weights from analytical GPC-measurements, relative to polystyrene standards.

(*b*) Transition temperatures (peak maxima) and enthalpies from two DSC heating curves; the value for the monotropic transition was obtained from cooling curves.

2.3. *Mesomorphic properties of the side group polyesters*

The mesomorphic properties of the side group polyesters were examined by means of differential scanning calorimetry (DSC) and polarizing microscopy. In some cases, additional X-ray diffraction and miscibility studies were performed.

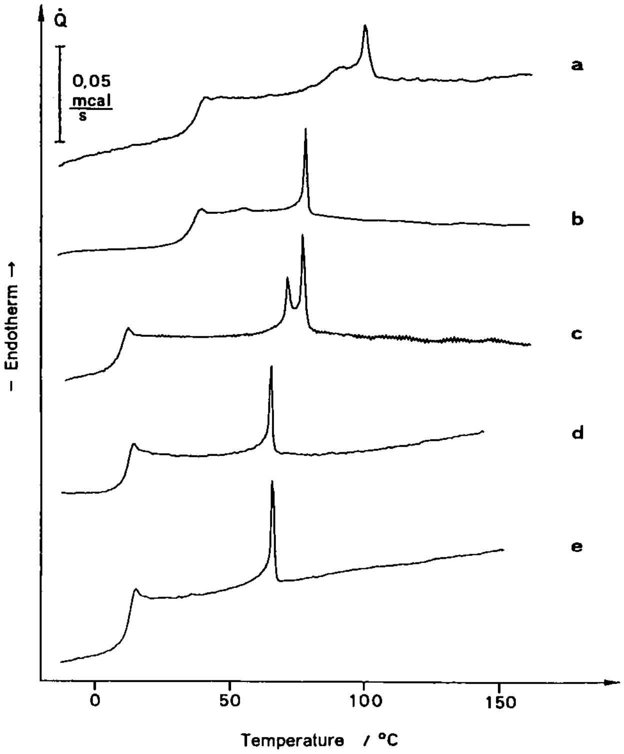


Figure 1. DSC heating curves for side group polyesters taken with a heating rate of 10 K/min immediately after cooling the polymers from 150°C at 10 K/min (= second heating curve). (*a*) Polymer **3g**, (*b*) polymer **3f**, (*c*) polymer **3a**, (*d*) polymer **3c**, (*e*) polymer **3b**.

Table 1 summarizes the chemical structure, molecular weight data and transition temperatures of the side group polyesters **3a**–**3g** synthesized from the mesogenic diethylmalonate **1a** and various non-mesogenic diols. All polymers of this series show liquid-crystalline behaviour. Their DSC heating curves (see figure 1) exhibit distinct glass transitions. In addition, one or more endothermic peaks are observed, which correspond to the transitions nematic–isotropic, smectic–nematic and crystalline–nematic. In their nematic phase, the polyesters exhibit homogeneous birefringent textures with very few disclinations. Upon transition into the smectic phase, the homogeneous textures remain almost unchanged. Only in the case of polymer **3a** have areas with a distinct smectic fan-texture been observed. Therefore, in some cases X-ray experiments were carried out in order to determine the type of the low temperature mesophase. Manually drawn fibres of polymers **3a** and **3g** gave diffraction patterns typical for a smectic A phase: a diffuse wide angle halo centred at the equator and sharp meridional reflections due to the smectic layers. Polyesters **3d** and **3e** have a crystalline low temperature phase as judged from the texture and the large enthalpy of the corresponding transition. For polymer **3e** the nematic phase is monotropic, which means that it can only be observed if the sample is supercooled. A second series of side group polymalonates having identical backbone structures but different mesogenic side groups was synthesized from 1,4-(bis-hydroxymethyl)-cyclohexane and the mesogenic diethylmalonates **1a–1d**. The structures, molecular weight data and transition temperatures of these polymers are summarized in table 2. The polymers with methoxy tail groups (**3h** and **3j**) exhibit only smectic mesophases as concluded from DSC, texture and X-ray studies. The polyesters with cyano tail groups show nematic (**3i**) or nematic and smectic (**3j**) behaviour.

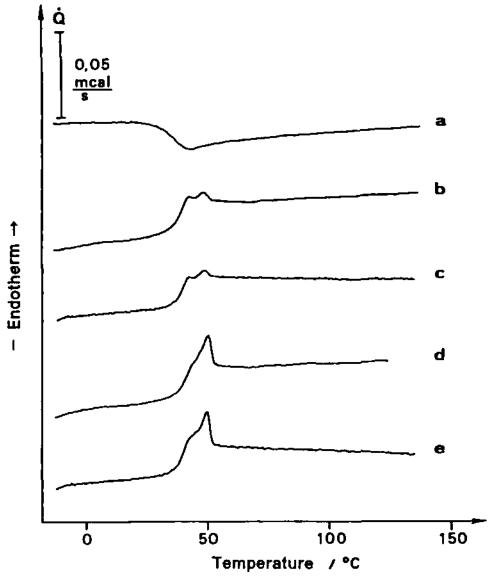


Figure 2. DSC curves for polymer **3i** taken with a rate of 10 K/min. (*a*) Cooling curve, (*b*) subsequent heating curve, (*c*) heating curve after rapid quenching from 150°C, (*d*) heating curve after annealing for 15 min at 40°C, (*e*) heating curve after annealing for 12 hours at 40°C.

The nematic phase of **3i** was also identified by its complete miscibility with a low molar mass nematic mixture (S1114 PCH, Fa. Merck). This polymer shows a very interesting peculiarity: upon fast cooling from the isotropic phase; we can obtain completely non-birefringent samples. In such isotropic samples birefringence develops only slowly on annealing above T_g. Correspondingly, the enthalpy of the nematic–isotropic transition depends strongly on the thermal history of the sample (see figure 2). The DSC cooling curve of polymer **3i** recorded with a rate of 10 K/min (see figure 2 (*a*)) shows no nematic–isotropic transition. The subsequent heating curve (see figure 2 (*b*)) is identical with the heating curve taken from a rapidly quenched sample (see figure 2 (*c*)), showing a weak endothermic peak at 47°C. On annealing at 40°C, the enthalpy ΔH_{NI} increases, showing identical DSC curves for both short time (15 min, see figure 2 (*d*)) and long time (12 hours, see figure 2 (*e*)) annealing. Thus, on cooling with rates of 10 K/min or faster, we can obtain an isotropic glass of polymer **3i**. During the recording of the heating curves, a small fraction of the polymer undergoes the isotropic–nematic transition and gives rise to the weak endotherm observed in figures 2 (*b*) and (*c*). On annealing slightly above the glass transition temperature, the isotropic–nematic transition seems to be completed in less than 15 min as shown by the fact that longer annealing causes no further increase of the enthalpy. This supercooling behaviour of the nematic phase of **3i** is probably due to a strong coupling between the glass transition and the nematic–isotropic transition. The slowing down of the dynamics of the isotropic–nematic transition can be clearly seen in Kerr effect measurements on polymer **3i**, which have been reported elsewhere [8].

A third series of side group polyesters (**4a–4d**) was prepared from the mesogenic 1,3-propanediol **2** and different dicarboxylic acid dichlorides. The structures, molecular weight data and transition temperatures of these polymers are summarized in table 3. Included in this table for comparison are the data for polymer **4e**, which was synthesized from **2** and 4,4′-azobenzene dicarboxylic diethylester via melt condensation. This polymer belongs to the combined type of liquid crystal polyesters which are described elsewhere [5, 9]. The polyesters synthesized from aliphatic diacids (polymers **4a–4c**) are crystalline materials exhibiting only monotropic nematic phases. Their crystallization can be supercooled easily so that identification of the nematic phases is possible by polarizing microscopy and miscibility studies. Polymer **4d** containing terephthalic acid in the main chain, is non-crystalline and has a small enantiotropic nematic phase, which can be supercooled similarly to the nematic phase of polymer **3i**. If the terephthalic acid is replaced by 4,4′-azobenzene dicarboxylic acid, the resulting combined polymer **4e** shows a broad smectic phase, which was identified by its fan-texture. At low temperatures this polymer crystallizes.

Polyesters **5a** and **5b** were synthesized from the mesogenic 1,3-propandiol **2** and the mesogenic diethylmalonates **1a** and **1b**. Polymer **5a** represents a copolyester with a strictly alternating sequence of cyano- and methoxyazobenzene side group mesogens. Above its glass transition at 40°C, it exhibits a very broad smectic phase with a clearing temperature at 174°C (see figure 3). Replacement of the cyanoazobenzene by another methoxyazobenzene side group leads to polymer **5b** which has a nematic phase and a considerably lower clearing temperature of 136°C. In addition, polymer **5b** has a crystalline and a monotropic smectic phase (see the DSC curves in figure 3).

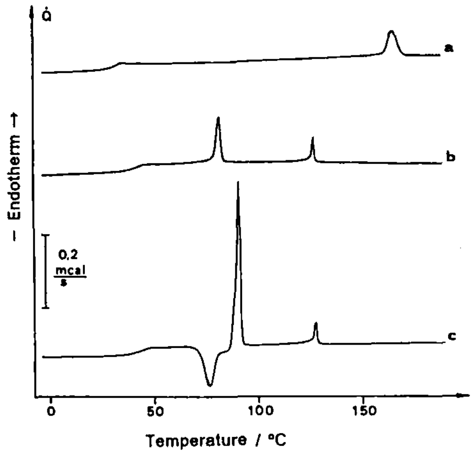


Figure 3. DSC heating curves for polymers **5a** and **5b**. (*a*) Second heating curve for polymer **5a**, (*b*) second heating curve for polymer **5b**, (*c*) heating curve for polymer **5b** after annealing for 12 hours at 55°C.

2.4. *Structure-property relations of the side group liquid crystal polyesters*

The side group liquid crystal polymalonates **3a–3g** all have the same 4-cyanoazobenzene side group but different non-mesogenic diols incorporated into the polymer chain (see table 1). The backbone structure strongly influences the clearing temperature and mesophase type of these polymers. With respect to the observed phase sequences, the polyesters **3a–3g** can be subdivided into two groups: the polymers with shorter diol components (**3a, f, g**) which show nematic and smectic behaviour and the polymers containing longer diols (**3b–3e**) which exhibit only nematic mesophases (see figure 4).

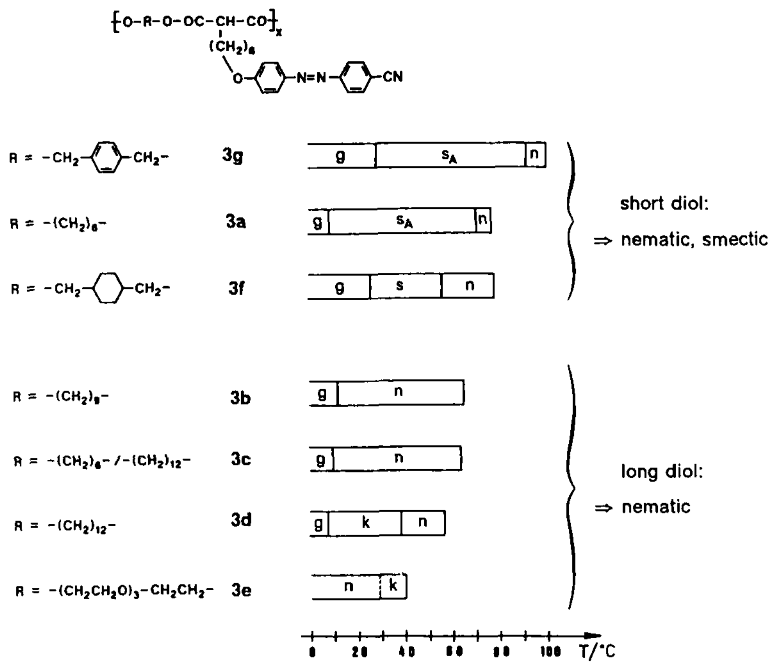


Figure 4. Schematic illustration of the relationship between the structure of the diol unit and the phase behaviour of polymers **3a–3g**. Broken lines represent monotropic phase transitions.

According to space filling molecular models, the repeating units of polymers **3a**, **3f** and **3g** all have approximately the same length of 13 Å. Nevertheless, the clearing temperatures of **3a** and **3f** are more than 20 K lower than that of **3g**. This decrease is probably due to the higher flexibility of the 1,6-hexane diol and 1,4-cyclohexyldimethanol used in **3a** and **3f** compared to the 1,4-benzenedimethanol used in polymer **3g**. The increase in the length of the non-mesogenic main chain segment causes a further decrease of the clearing temperature. The doubling of the number of methylene groups from six in **3a** to twelve in **3d** leads to a drop in the clearing temperature of 20 K. Furthermore, the extension of the non-mesogenic segments seems to disturb the smectic layer packing considerably, since all polymers containing more than six methylene groups (**3b–3e**) exhibit only nematic phases. Interestingly, polymer **3b** made from 1,9-nonane diol shows almost identical phase behaviour to polymer **3c**, which was synthesized using a 1/1 mixture of 1,6-hexane diol and 1,12-dodecane diol. Thus, at the same level of flexibility, the clearing temperature seems to be determined mainly by the total number of methylene groups in the backbone and not by their distribution along the chain. The replacement of the dodecane diol unit of polymer **3d** by the only slightly shorter tetraethyleneglycol unit in **3e** leads to a decrease of the clearing temperature of about 30 K. Apparently, the presence of the polar tetraethyleneglycol segments disturbs the interaction between the mesogenic side groups and causes a destabilization of the nematic phase. In order to understand the influence of the main chain structure on the phase behaviour it is helpful to consider the results of X-ray studies of polymer **3a** and **3g**. Diffraction patterns taken at room temperature from manually drawn fibres give smectic layer spacings which are considerably larger than the length of the mesogenic side group (including the side group spacer) as determined from molecular models: length of the mesogenic side groups: 22·5 Å; smectic layer spacing polymer **3a**: 37·0 Å; smectic layer spacing polymer **3g**: 38·5 Å. Therefore, we can assume that the smectic A phases of these polymers belong to the interdigitated bilayer type. Such structures have often been reported for polymeric [1, 11–14] and low molar mass liquid crystals [10] with cyano-substituted mesogenic groups. The interdigitation is explained by an anti-parallel correlation of the cyano-dipoles. A structural model which accounts for the experimental layer spacings found for the smectic A phases of polymers **3a** and **3g** is shown in figure 5. According to this model, the non-mesogenic units in the main chain seem to act as an extension of the side group spacer. Hence, they contribute considerably to the smectic layer spacing. For liquid-crystalline copolysiloxanes, Ringsdorf and Schneller [15] and Diele *et al.* [16, 17] have already discussed the function of non-mesogenic monomer units as that of a main chain spacer (spacer 2. Art). A similar concept has also been discussed for mono and multilayer forming amphiphilic polymers [18]. Similarly to the liquid crystal polyesters described in this work, the side group liquid crystal polysiloxanes can tolerate a large fraction of non-mesogenic main chain segments (i.e. main chain spacer) without losing their mesomorphic properties. Even though the structural model for the latter polymers derived by Diele *et al.* from X-ray data is somewhat similar to the structure proposed in figure 5, there are distinct differences between side group liquid crystal polyesters and polysiloxanes. In the polysiloxanes the layer thickness increases linearly with the fraction of non-mesogenic chain segments. Furthermore, smectic phases are observed even at very high degrees of dilution with non-mesogenic siloxane segments. This led to the conclusion that there is microphase separation between the mesogenic side groups and the incompatible siloxane backbone [19]. According to this model the siloxane main chain segments

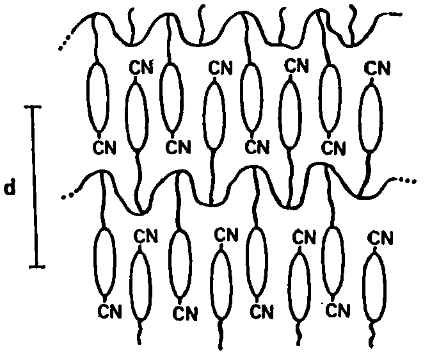


Figure 5. Structural model of the smectic A phase of the side group liquid crystal polymalonates; *d* represents the smectic layer spacing.

form a sublayer and therefore do not disturb the interaction of the mesogenic side groups in the smectic phase. On the other hand, in the side group liquid crystal polyesters there is probably no incompatibility between main chain and side groups. Therefore, we observe a destabilization of the smectic layer packing and a decrease of the clearing temperature with increasing length of the main chain spacer.

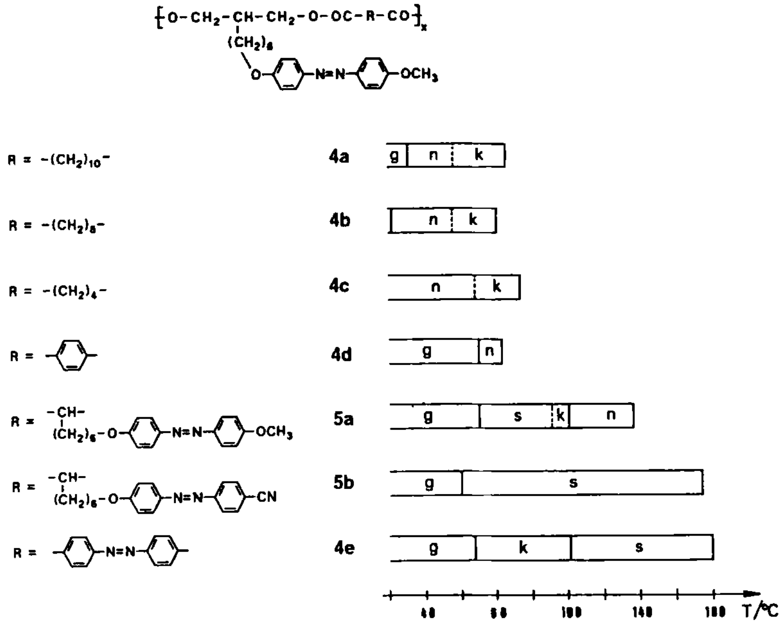


Figure 6. Schematic illustration of the relationship between the structure of the acid unit and the phase behaviour of polymers **4a–4e** and **5a–5b**.

Figure 6 illustrates the correlation between molecular structure and mesomorphic properties for the side group polyesters derived from the mesogenic 1,3-propane diol compound **2**. The polymers **4a–4c** containing aliphatic dicarboxylic acids with 4, 8 and 10 methylene groups, represent crystalline materials and show only monotropic nematic phases. Only if the aliphatic diacids are replaced by terephthalic acid, does the clearing temperature increase to 63°C, resulting in a small enantiotropic nematic phase in **4d**. Replacement of the terephthalic acid by the mesogenic 4,4′-azobenzene dicarboxylic acid gives a smectic polymer (**4e**) with a clearing temperature of 180°C. This polymer represents a combined main chain side group polymer. As in other polymers of this type [5, 9], the high clearing temperature can be explained by a constructive interaction between mesogens in the main chain and the side groups.

The liquid crystal polyesters **5a** and **5b** contain mesogenic side groups both in the diol and in the diacid unit. These two polymers have a much higher concentration of mesogenic side groups along the backbone and consequently exhibit considerably broader mesophases than the other side group liquid crystal polyesters described here. Polymers **5a** and **5b** differ only in the structure of the tail group in the mesogenic malonate moiety, which consists of a cyano group in **5a** and a methoxy group in **5b**. Despite their relatively similar chemical structures, **5a** and **5b** exhibit a very different phase behaviour. Polymer **5a** shows a single smectic phase and its clearing temperature is almost 40 K higher than that of polymer **5b**, which has a nematic and a monotropic smectic phase. It is known from low molar mass liquid crystals and side group liquid crystal polymers that cyano terminated mesogens give higher clearing temperatures than methoxy terminated mesogens. Also cyano groups favour smectic phases whereas methoxy groups favour nematic phases. For polymer **5a** we can also consider interactions between the donor substituted methoxyazobenzene mesogens and the acceptor substituted cyanoazobenzene mesogens as a cause for the high clearing smectic phase of **5a**.

Summarizing the results of this work, we can conclude that the polycondensation of mesogenic side group containing diols and diesters represents a versatile synthetic route to new liquid-crystalline polymers. By varying the chemical structure of the backbone and the mesogenic groups, polyesters with either nematic or smectic behaviour or a combination of both have been obtained. Polyesters derived from mesogenic diethylmalonates have been shown to accommodate non-mesogenic diols with up to 12 methylene groups without losing their mesomorphic properties. Thus, the synthetic concept described here opens straightforward routes to functionalized liquid-crystalline polymers by incorporation of various non-mesogenic condensation monomers. The practicability of this approach has already been demonstrated by the synthesis of mono and multilayer forming liquid crystalline polyesters [20] and of chiral liquid crystalline polyesters containing non-linear optical moieties [6].

2.5. *Experimental part*

The mesogenic diethylmalonates **1a–1d** were synthesized from diethyl 6-bromohexylmalonate and the corresponding mesogenic precursors as described previously [5].

2.5.1. *2-[6-{4-(4′-Methoxyphenylazo)phenoxy}hexyl] 1,3-propanediol 2*

A solution of 43 mmol of diethyl 6-{4-(4′-methoxyphenylazo)phenoxy}hexylmalonate **1b** in 200 ml of dry THF was added dropwise at room temperature to a suspension of 78 mmol lithium aluminum hydride in 450 ml of dry THF. Upon completion of the addition the mixture was refluxed for 2 hours. After cooling, the excess $LiAlH_4$ was destroyed by careful addition of ice. The THF was evaporated and the residue was dissolved in 200 ml of H_2O and 50 ml of 2N HCl. The aqueous phase was extracted several times with a total of 1000 ml of methylene dichloride. The organic phase was washed with H_2O and dried with Na_2SO_4. The residue obtained after evaporation of the solvent was recrystallized three times from ethyl acetate, dissolved in acetone and filtered through 100 g of silica gel using ethyl acetate as eluent. Yield: 3·6 g (22 per cent) m.p. 119–120°C.

2.5.2. *4,4′-Azobenzene dicarboxylic acid*

A suspension of 0·7 mol of 4-nitrobenzoic acid, 3·8 mol of KOH and 1·5 mol of zinc-dust was refluxed in 500 ml of a $MeOH/H_2O$ mixture (3/1 v/v) for 20 hours. The mixture was diluted with 10 l of water and filtered. The filtrate was acidified with 6N HCl. The precipitate was filtered off, washed with water and acetone and dried. This crude diacid was converted into the diacid chloride by means of $SOCl_2$. To a solution of the diacid dichloride in 150 ml of CH_2Cl_2 a mixture of 70 ml ethanol and 100 ml pyridine was added dropwise. The mixture was refluxed for 7 hours. Upon cooling to room temperature, orange crystals separated from the solution. This precipitate was filtered off and recrystallized three times from toluene; yield 16·4 g (14 per cent), m.p. 145°C, (lit. m.p.) [21]: 143°C.

2.5.3. *Diols*

Commercially available diols were used for the synthesis of polyesters **3a–3j**. 1,6-Hexane diol, 1,9-nonane diol, 1,12-dodecane diol (Aldrich) and 1,4-bishydroxymethylbenzene (Janssen) was purified by recrystallization. Tetraethylene glycol (Fluka) was vacuum distilled prior to use. 1,4-Bishydroxymethylcyclohexane (Janssen, 99 per cent) was used without further purification. According to its 400 MHz ^{1}H NMR spectrum, this monomer consists of 23 per cent of the cis and 77 per cent of the trans isomer.

2.5.4. *Melt polycondensation*

The melt polycondensations were carried out in Schlenk tubes equipped with magnetic stirring bars using between 1 and 3 mmol of diol and diester. Depending on the volatility of the diol, this component was used in 5 to 15 mol % excess of the equimolar amount in order to compensate for evaporation losses during the reaction. Tetra (isopropyl) orthotitanate (Merck) was used as a transesterification catalyst (0·2–0·5 wt % with respect to the total monomer weight). The polycondensations were performed in three stages. First, the monomers were melted under argon at atmospheric pressure. Two thirds of the designated amount of catalyst was added to the melt in form of a 10 vol % solution in dry diethylene glycol dimethyl ether using a syringe. After a short induction period, ethanol started to condense in the upper part of the polymerization tube. It was removed by passing a slow stream of argon through the reaction vessel. After the ethanol evolution slowed down (typically after 1–4 hours), the second stage of the reaction was started by slowly applying reduced pressure using a water pump, and in some cases by raising the temperature by 10 K. The reduced pressure was applied for about 1–5 hours. The third reaction stage started with the addition of the remaining amount of catalyst solution. The temperature was raised by another 10 K and high vacuum ($<$ 0·01 m bar) was applied for 1–8 hours in order to complete the polycondensation. The individual time/temperature/pressure profile was chosen according to the volatility of the diol component. After cooling the polymers were dissolved in THF and filtered through a filter paper in order to remove insoluble catalyst residues. An aliquot corresponding to 500 mg polymer dissolved in 20 ml of THF was chromatographed using a 54 × 6·4 cm preparative GPC column containing Sephadex LH-60 gel (Pharmacia) and THF as eluent. Using a refractive index detector (Waters), the polymer peak was isolated. After evaporation of the solvent, the polymers were dried at 60–70°C under high vacuum for 2 days. All polymers give correct elemental analyses.

2.5.5. *Solution polycondensation*

The acid dichlorides used for the synthesis of polyesters **4a–4d** were prepared from the commercially available diacids by standard procedures using $SOCl_2$. The aliphatic acid chlorides were purified by vacuum distillation. Terephthalic acid chloride was recrystallized from dry hexane. The solution polycondensation leading to polymers **4a–4d** were carried out similarly to a procedure described for combined liquid-crystalline polyesters [9]. The mesogenic propanediol derivative **2** was dissolved in a mixture of dry pyridine and *o*-dichlorobenzene and a stoichiometric amount of the corresponding diacid dichloride was added as a solution in *o*-dichlorobenzene. After stirring the reaction mixtures for one week at room temperature, the polymers were precipitated for methanol. Further purification was achieved by preparative GPC following the procedure described by polymers **3a–3j**.

2.5.6. *Characterization methods*

The structures of the low molar mass compounds were confirmed by elemental analysis, IR and NMR spectroscopy. The polymers were characterized by elemental analysis and analytical GPC. The latter was carried out using a HPLC set-up equipped with a UV detector (Waters) and a $10^4/10^5$ Å column combination (Polymer Laboratories). Chloroform was used as eluent and the system was calibrated (peak maxima) with narrow polystyrene standards. The phase transitions of the polymers were determined by differential scanning calorimetry (DSC-2C, Perkin–Elmer). The scan speed was 10 K/min and the peak maxima were taken as the transition temperatures. The birefringent textures were observed with a POL-BK II microscope (Leitz) equipped with a FP52 hot stage (Mettler). The samples were mounted between untreated glass slides.

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