Laterally linked mesogens in main chain polymers

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Laterally linked mesogens in main chain polymers

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The syntheses of liquid-crystalline main chain polyesters with laterally linked mesogens are presented. The terminal groups of the mesogens and the spacers fixation of mesogens, the polyesters with 1,4-di(p-alkoxybenzoyloxy)benzenes 1,4-di(p-alkoxybenzolyloxy)benzenes, 2,5-di(p-alkoxyphenyl)pyrimidines or a 4,4'-bis(p-ethoxyphenylazo)biphenyl derivative. Despite the unusual bilateral fixation of mesogens, the polyesters with 1,4-di(p-alkoxybenzoyloxy)benzenes show mainly monotropic phases which were found to be nematic in investigations with the polarizing microscope, in DSC measurements, temperature-dependent measurements of the Kerr constant and X-ray diffraction experiments. The monotropic nematic character remains when varying the terminal groups of the mesogen as well as the length of the n-alkanedioic acid spacer. However, when the spacer is branched, crystallization can be disturbed effectively and a stable nematic phase can be obtained. All of the polyesters with only 2,5-di(p-alkoxyphenyl)-pyrimidines as mesogens are amorphous. The reason probably lies in the unsymmetric 4,6-substitution of the pyrimidine ring. In contrast to this, oligomers with a 4,4'-bis(p-ethoxyphenylazo)biphenyl derivative show broad, predominantly enantiotropic nematic phases with relatively high clearing temperatures. With the knowledge gained about relations between structure and properties, especially of polyesters with 1,4-(p-alkoxybenzoyloxy)benzenes as mesogens, polyesters with this mesogenic group but with various architectures have been compared. Speculations about possible arrangements of the structural elements have been included to explain the phase behaviour of the polyesters with laterally fixed mesogens.

1. Aspects of lateral substituents in liquid crystals

In comparison with laterally unsubstituted liquid crystals, a lateral substituent normally disturbs the crystallization as well as the formation of the liquid-crystalline state [1, 2]. Crystallization is disturbed because of the lower symmetry of the molecules, and the clearing point decreases usually because the shape of the mesogens becomes less favourable. Packing of mesogens in smectic layers becomes more difficult. Only mesogens with small [3, 4] or aromatic [5, 6] lateral groups show smectic phases in addition to the nematic phase. Nevertheless, there exist some special cases [7, 8] where only smectic phases occur.

Even long lateral substituents do not disturb the formation of liquid-crystalline phases, especially these which are nematic. In accord with other investigations [9–13] this phenomenon indicates that lateral substituents fit closely to the mesogen in the direction of the long molecular axis. This adaptation to the shape of the mesogen seems to become particularly important for lateral substituents longer than five carbon

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atoms: every additional carbon atom affects the length-to-width ratio only insignificantly. Phase transition temperatures reflect trends in shape as a function of the lateral substituent length and remain nearly undisturbed.

A second lateral substituent at the centre of the mesogen decreases drastically the clearing temperature once more. With substituents that are large relative to the length of the mesogen, either absolutely no liquid-crystalline phases are observed or they are only monotropic [2, 9, 14]. Lateral substituents have also been used in classical main chain polymers [15–18]: (I) to lower the high melting and clearing temperatures of the unsubstituted derivatives. Analogous to low molecular weight liquid crystals, the tendency to form smectic layers is decreased and nematic phases predominate over a more opportune temperature range. Several unconventional structural variations of liquid-crystalline polymers use lateral substituents as linkage between mesogens and the polymeric chain: polymers with laterally attached mesogens in the side groups [19–23] (II); some combined polyesters [24] (III) which contain mesogens in the main chain as well as in the side groups; or main chain polyesters which have mesogens fixed not longitudinally but laterally [25–27] (IV) and main chain polyesters which have either laterally and longitudinally fixed [26–28] (V) or even cross-shaped mesogens [25, 29] (VI).
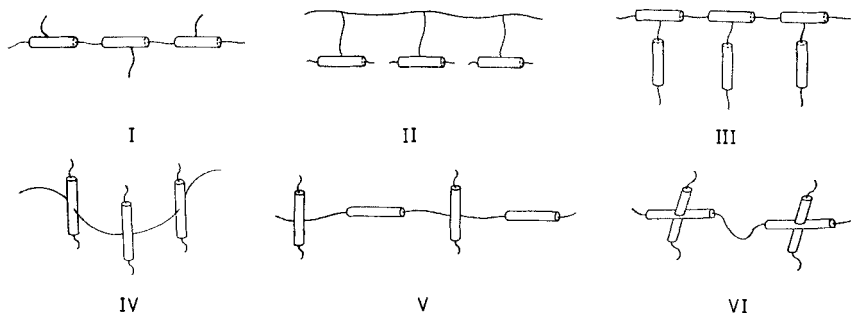

Such a combination of mesogens shown in structures (I)–(VI) suggests that either the mesogens are forced to orient all in the same direction as in case (IV) with the mesogens all oriented perpendicular to the main chain in contrast to conventional main chain polymers (I), or the mesogens themselves stand more or less perpendicular to each other (III), (V) and (VI). Only polymers of structure (II) should behave more or less indifferently in this respect and similarly to low molecular weight liquid crystals: the polymeric chain does not influence the orientation of the long axis of the mesogens, but instead, the short one. In this respect, the biaxial nematic behaviour observed for such polymers [19, 21] is explained. Also from the other structures (III)–(VI), we should expect outstanding properties, at least some interesting structure-property relationships. The synthesis and phase behaviour of polymers of type (IV) with various terminal groups, mesogens and spacer groups will be described and the results discussed in respect of the lateral attachment of the mesogens.

2. Synthesis
2.1. *Polyesters with hydroquinone dibenzoates as mesogens*
Hydroquinone dibenzoates are often used as mesogenic groups in low molecular weight liquid crystals [2, 5, 13, 30–34], side group [35, 36] and main chain polymers [37–40]. Use of them in polyesters with laterally fixed mesogens also allows a comparison of structure-property relationships. A synthetic route is given in scheme 1.
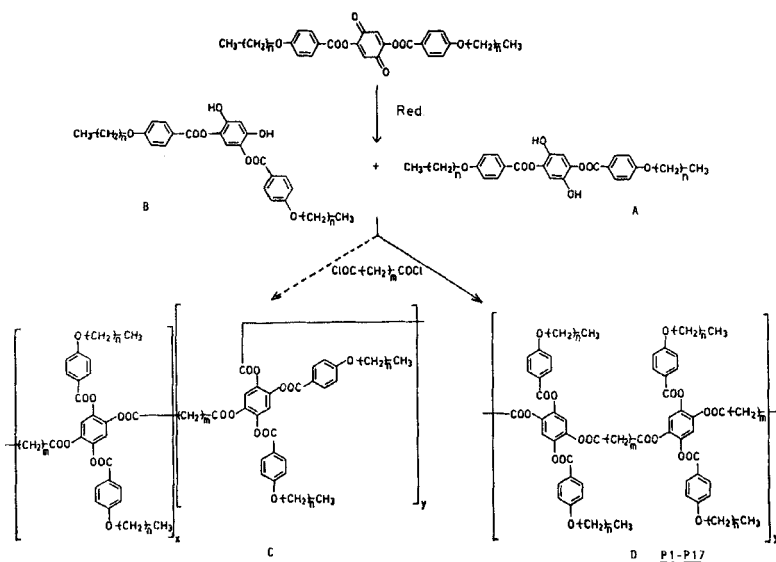
Scheme 1. Synthetic route to polyesters with laterally fixed hydroquinone dibenzoates as mesogens.
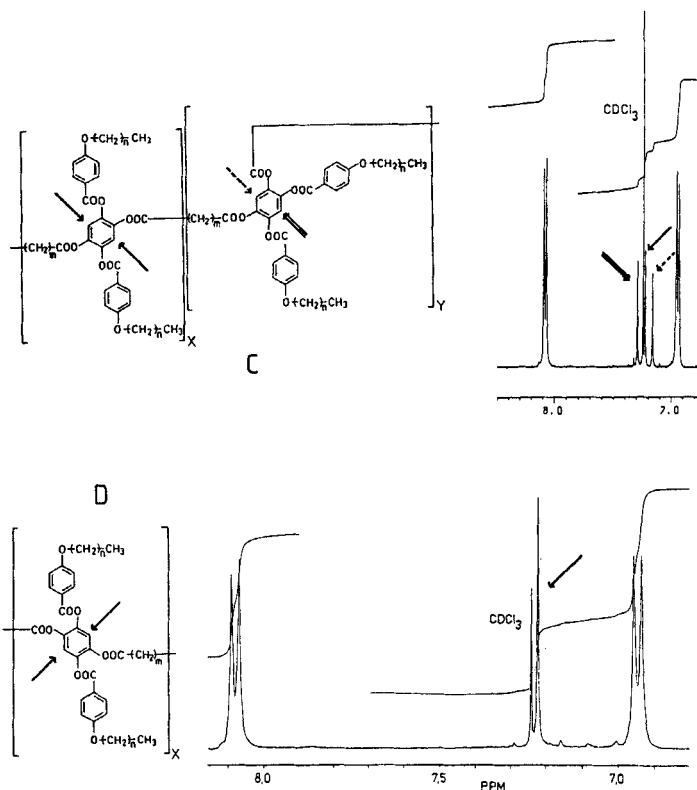

Figure 1. Low field region of the ^{1}H NMR spectra from polyesters with tetrahydroxybenzene ester groups.

2,5-Dibenzoyloxy-*p*-benzoquinone derivatives [14] have been reduced to mixtures of the appropriate 2,5-dibenzoyloxy-*p*-hydroquinone and 4,6-dibenzoyloxyresorcinol derivatives (**A** and **B**) [14]. Similar to the reaction with acid chlorides, these mixtures behave like the pure hydroquinone derivatives **A** as described previously [14]. Thus, the condensation of these mixtures with different diacid dichlorides results in the pure polyesters **D** (**P1–P17**) in most cases, which can be verified by NMR spectroscopy (see figure 1). Only those polymers which can show a 400 MHz ^{1}H NMR spectrum similar to **D** in figure 1 and possess less than 5 per cent of 1,3-dialkoyloxy-4,6-dibenzoyloxybenzene derivatives as repeating units are described further.

Thermal stability was proved by heating a sample of polyester **P8** at 170°C and maintaining the sample at this temperature for 1 hour. The ^{1}H NMR spectrum, the phase transitions and the molecular weight distribution changed only insignificantly. In contrast, a sample kept for 1 hour at 220°C showed drastic changes resulting primarily from transesterification reactions.

2.2. *Polyesters with phenylpyrimidines as mesogens*

The synthetic route is given in scheme 2 and follows a procedure in the literature [41] up to the 4,6-dihydroxy-2,5-diphenylpyrimidine derivatives **1–3**. Unfortunately, it
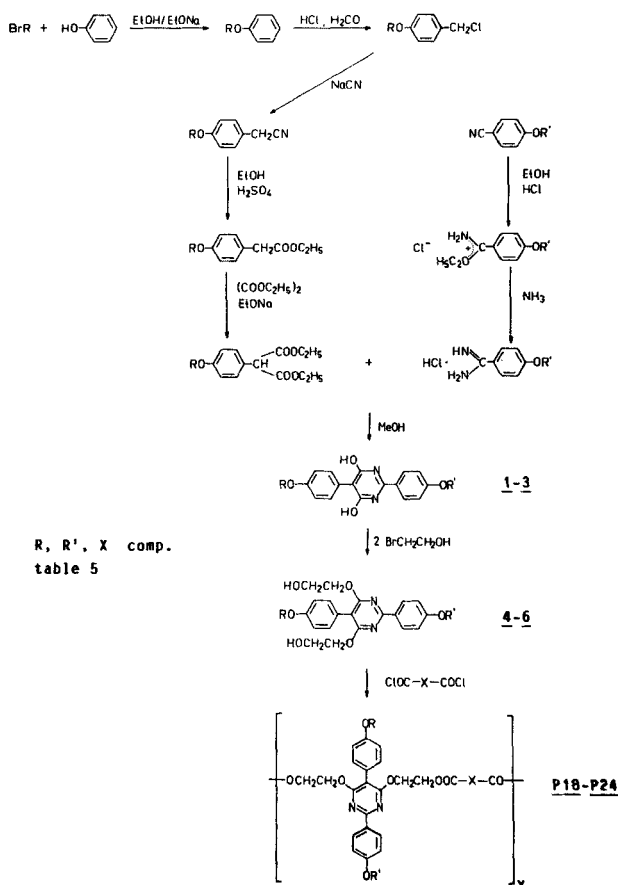
Scheme 2.   Synthetic route to polyesters with phenylpyrimidines as mesogens.

was not possible to condense the phenylpyrimidine derivatives **1–3** by solution or melt condensation, probably because of their poor solubility and the acidic character of the two hydroxy groups. Therefore, the hydroxy groups have been etherified with bromethanol to the 4,6-bis(2,2'-dihydroxyethoxy)pyrimidine derivatives **4–6**, which could be condensed with diacid dichlorides in solution to give polyesters **P18–P24** without further problems.

2.3. *Oligomers with a 4,4'-bis(phenylazo)biphenyl derivative as mesogen*

Oligomers with a 4,4'-bis(*p*-ethoxyphenylazo)-2,2'-biphenyl unit as the mesogen were synthesized starting from 4,4'-bis(*p*-ethoxyphenylazo)-2,2'-biphenyldicarbonic acid diethylester [42] (see scheme 3). The diester was hydrolysed to the diacid **7** and afterwards chlorinated with thionylchloride to the appropriate diacid dichloride **8** which could be converted into oligomers (**P25–P30**) with different diols. These oligomers were fractionated via preparative GPC at high pressure and only the fractions with the highest molecular weight were used for further investigations. Yields, elemental analyses, molecular weights of all polymers are given in the experimental part (see table 7).
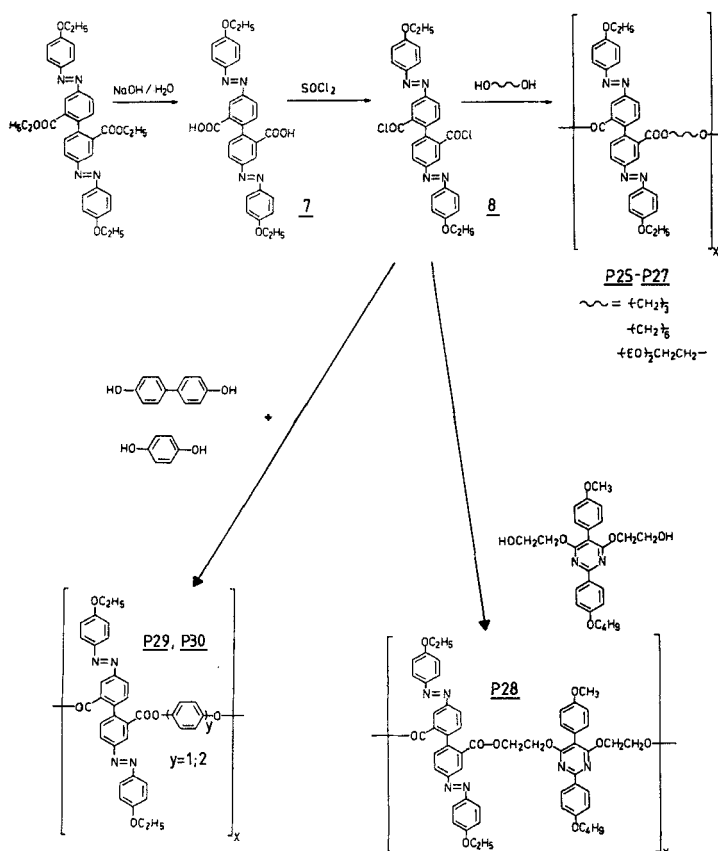
Scheme 3. Synthetic route to oligomers with a 4,4'-bis(phenylazo)-biphenyl derivative as mesogen.

3. Phase behaviour of polyesters with laterally fixed 2,5-dibenzoyloxy-*p*-benzoquinone derivatives

To explain the complicated phase behaviour of the first derivatives a more detailed description of **P1** follows. This polymer has already been described [25] but the 60 MHz ^{1}H NMR spectra for characterization was not sensitive enough to detect some amount of incorporated resorcinol derivative (see **B** and **C**, scheme 1) as has been been seen later. So, the present glass transition and the clearing point differ by a few degrees from the earlier data. Nevertheless, the tendency towards crystallization as well as the melting temperature are both much higher for the purer polyester **P1** mentioned here, as can be seen in figure 2.

For the heating run, the first DSC curve was recorded after quenching the sample from the isotropic state on a cooled metal block. Heating at 20°C/min, the sample passes the glass transition at about 30°C and changes to a liquid-crystalline state as can be seen with the polarizing microscope. A careful observation of the double refraction obtained showed that tension or shearing forces are not the cause. However, the liquid-crystalline state is not stable and an exothermic crystallization soon follows. The polymer **P1** melts to the isotropic state at approximately 150°C. By cooling the sample (M_W: 10 800), even at 80°C/min, the sample crystallizes before the clearing temperature

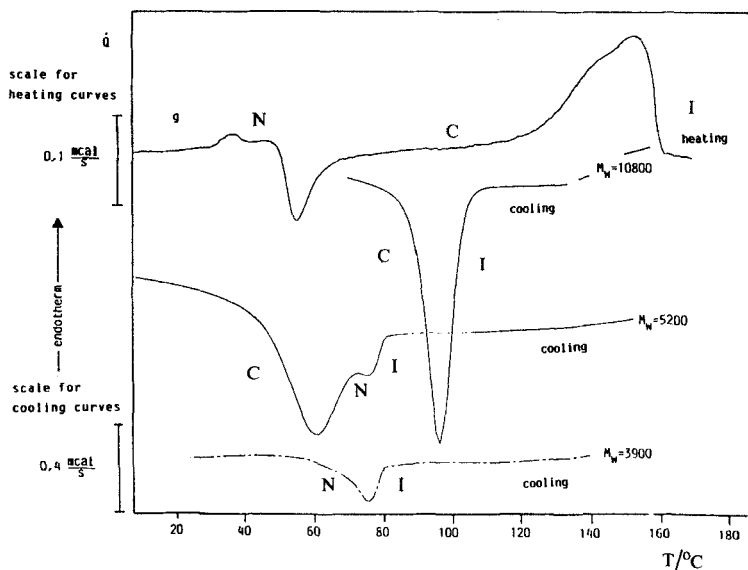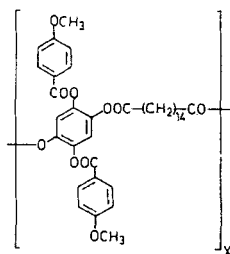Figure 2.   Thermal behaviour of polyester **P1** with a long spacer and terminal methoxy groups. Heating rate 20°C min^{-1}; cooling rate 80°C min^{-1}.

can be reached. This picture changes when analysing the cooling runs of samples with lower molecular weights obtained from fractionated precipitation of the primary polyester **P1** (M_W: 10 800): the second cooling run, with a sample of molecular weight 5200 (M_W) shows two transitions which turned out to be an isotropic to liquid-crystalline and a liquid-crystalline to crystalline transition. The growing influence of the end groups of the polymeric chains on the crystallization, which constantly decreases with molecular weight, can be seen in the last cooling run for a sample of molecular weight 3900 (M_W). The clean transition to the liquid-crystalline state without crystallization can be seen. The transition enthalpy of *c.* 4 J/g points to a nematic phase, which was verified by X-ray experiments. The easily movable texture itself, observed by polarizing microscopy gives no clear statement concerning the type of liquid-crystalline phase because this sample could not be annealed long enough before crystallization takes place.

A more detailed analysis of the influence of the molecular weight on the phase behaviour of liquid-crystalline main chain polyesters with laterally fixed mesogens is provided in a further communication [43].

3.1. *Influence of the length of the terminal groups and the length of the spacers*

The mesophase of **P1** is difficult to observe because of its monotropic character. To see if it is possible to obtain stable liquid-crystalline phases with dibenzoyloxyhydroquinones as laterally fixed mesogens in the main chain, structure-property relationships were studied in detail. First, the terminal groups at the mesogens were varied, retaining the long tetradecane diacid spacer of **P1**. The methoxy groups were changed to methyl (**P15**) and longer alkoxy substituents (see **P2–P5**, table 1). A view of the DSC measurements (see figure 3) shows that the crystallization of the polymers **P2–P5** becomes even faster as the terminal groups become longer. The exothermic recrystallization shifts to lower temperatures as do the glass transitions. For polyesters **P4** and **P5**, recrystallization is so fast that, even during the pre-treatment of the samples (see heating run **P1**) crystallization occurs. Going from methoxy terminal groups to methyl groups (**P15**) does not result in any significant change.

It appears that long terminal groups in polyesters with long spacer groups act as plasticizers. The flexibility of the mesogens is higher and the thermodynamically stable crystalline phase is attained more quickly. Short spacer groups should counteract this tendency, especially when they have an odd number of carbon atoms which leads to a lower symmetry and so to further hindrance of the crystallization. Polyesters **P4**, **P6–P8** (see table 2; figure 4) clearly demonstrate this effect, although the heating rate for the DSC measurements (see figure 4) is extremely high again. The differences in the molecular weights of **P4**, **P6–P8** have no real influence on the phase behaviour in this case [43]. Shortening the spacer from fourteen (**P4**) to seven carbon atoms (**P6**) clearly separates the recrystallization from the glass transition. Diminishing the spacer to five carbon atoms (**P7**) shifts the recrystallization to higher temperatures and by shortening again by two to three carbon atoms (**P8**), the clearing temperature can be reached without further crystallization ($\Delta H_{NI} = 4$–5 J/g). This behaviour changes again when using slower heating rates (cf. figure 6). Further comments on the effects of using slower heating rates on the transition temperatures, especially the crystallization as well as the thermal history is not needed. Great attention was paid to the pre-treatment of all samples so that the comparisons made are justified.

An example of the influence of the thermal history is given in figure 5 where the annealing of a sample of **P3** shifts the melting temperature by about 30°C. An example

Table 1. Influence of the terminal groups on the phase behaviour of the polyesters **P1**–**P5** and **P15** with tetradecane diacid spacers.
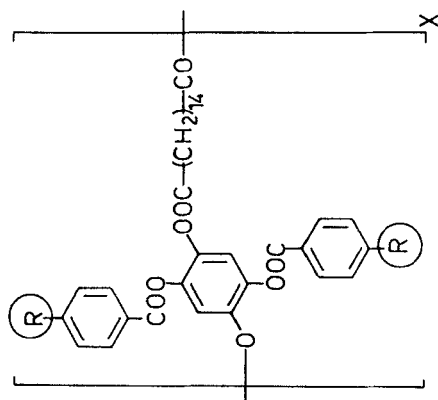
Polyester	Terminal groups R	M_{GPC}	M_w‡	P_w	U	Phase behaviour†/°C heating rate/20°C min⁻¹	ΔH_{Cl}/J g⁻¹	Clearing temperature†/°C
P15	$-CH_3$	9200	11400	18	1·7	g 27 r 47 C 162 I	41	<100
P1	$-OCH_3$	7200	10800	16	1·9	g 33 r 56 C 152 I	42	<105
P2	$-OC_2H_5$	10000	12200	18	1·8	g 31 r 46 C 154 I	41	<105
P3	$-OC_3H_7$	8000	8600	12	1·7	g 18 r 38 C 132 I	36	<80
P4	$-OC_4H_9$	8900	11100	15	1·9	g § § C 129 I	26	~85
P5	$-OC_5H_{11}$	10500	11600	15	1·9	g § § C 130 I	22	<70

†Values determined by DSC. g, glass; r, recrystallization (exothermic); C, crystalline phase; I, isotropic phase; ΔH_{Cl}, melting enthalpy.

‡The number average values can be calculated with the help of the polydispersity. The deviation of the molecular weight distribution from the normal distribution is the reason for differences between M_{GPC} and M_w values.

§The glass transitions (see also figure 3) are not comparable because these polyesters partially crystallize, during quenching of the samples. The transitions shift to higher temperatures.
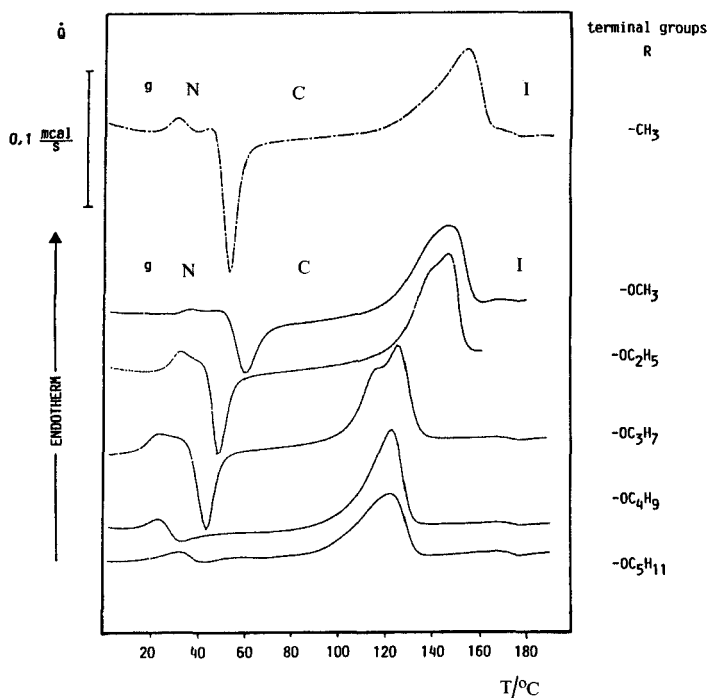
Figure 3. Comparison of the crystallization behaviour of polyesters **P1–P5**, **P15** (for the formula see table 1). Heating rate 40°C min.

of the influence of the heating rate on polyester **P8** is shown in figure 6. With a fast heating rate, the DSC curve contains only the glass and the nematic–isotropic transition. With decreasing heating rate, recrystallization occurs shifting towards the glass transition. The melting temperature increases, because the crystals become more perfect. Remarkably, the shift of the recrystallization towards the glass transition is rather slow and, under the polarizing microscope, a movable texture could be seen for more than half-an-hour before crystallizing with heating rate of 1·25°C/min.

To determine whether the influence of the thermal groups for polyesters with short spacers is the same as for polyesters with long spacers (**P1–P5**) the phase behaviour of polyesters **P8–P14** (see table 3) was investigated. As can be seen in figure 7 the behaviour is indeed different: the most favourable length for the terminal group is, in this case, about five carbon atoms. The tendency to crystallize increases as well with longer terminal groups (**P13**; $n = 12$), probably because they can act as a plasticizer as for polyesters **P1–P5**, and as with shorter terminal groups (**P8–P11**). The pentyloxy groups seem to behave as the best disturbance to crystallization. Thus, polyester **P8** shows only a small recrystallization and melting above the clearing point ($n = 4$) at a heating rate of 40°C/min. In a sample of **P11** with $n = 3$, the clearing transition can just be seen and a sample of **P10** no longer shows the nematic to isotropic transition because of the early start of the recrystallization.

3.2. *Substituted spacer groups*

The installation of a branched terminal group, an optically active (-)2-methylbutyl ether, resulted in the amorphous polyester **P14** which crystallizes like **P12** with

Table 2. Molecular weights, transition temperatures and enthalpies of the polyesters **P4**, **P6–P8** with butyloxy terminal groups and spacers of different lengths.
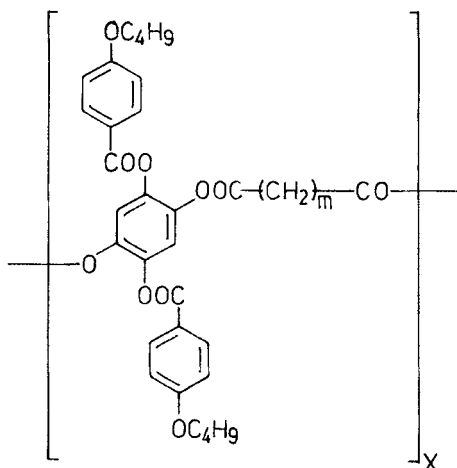
Polyester	Spacer length m	M_{GPC}‡	M_W	P_w	U	Phase behaviour†/°C heating rate/80°C min^{-1}	ΔH_{Cl}/J g^{-1}
P4	14	8900	11100	15	1·9	g § C 130 I (N ∼ 85)	26
P6	7	38000	40000	62	1·9	g 38 C 181 I (N ‖)	32
P7	5	13200	15800	26	1·9	g 45 C 183 I (N 140)	33
P8	3	13000	16200	27	2·0	g 59 N 136 I ¶	—

†,‡,§ See footnotes to table 1.

N, nematic phase; (N...), monotropic nematic phase; heating rate was choosen to be exceptionally high to demonstrate better the thermal behaviour (see also figure 4).

‖ Under the polarizing microscope the clearing point could not be determined because of the very rapid crystallization.

¶ If slower heating rates were used, polyester **P8** crystallizes as well (see also figure 6).

pentyloxy groups during annealing. A stable mesophase could be obtained by substituting the spacer with a methyl group using non-branched terminal groups again. This results in more disorder of the polymeric chain (see figure 8). For instance, in polyester **P16** (see table 4), different repeat units exist in proportion to the 2-methyl group of the 2-methylglutaric acid spacer. However, annealing over 20 hours in the remaining liquid-crystalline phase did not produce any crystallization. In contrast, with polyester **P8** with an unsubstituted glutaric acid spacer, the clearing temperature dropped by about 60°C to 73°C. The installation of a second 2-methyl group leads also to a non-crystallizating polyester (**P17**), which remains only amorphous. Pre-transitional phenomena to the nematic phase of this polymer and the extrapolated clearing temperature below the glass transition are discussed in a later section.

3.3. *Investigations of the nematic phase*

With polyester **P16** it was possible to obtain textures, by polarizing microscopy, which can be annealed for several hours and are comparable to textures known for low molecular weight liquid crystals (see figure 9). They are similar to those of normal nematics. No zig-zag-lines [44] or other anomalies which have been described for biaxial nematics [19] could be observed. Conoscopic observations have not been
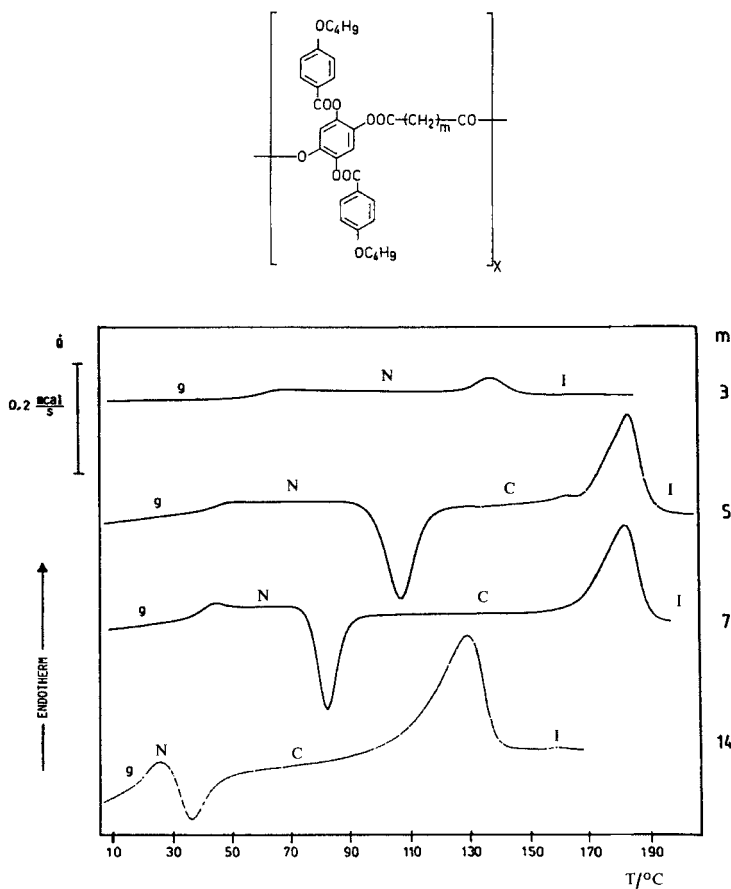
Figure 4. DSC curves of polyesters with butyloxy terminal groups and spacers of different lengths.
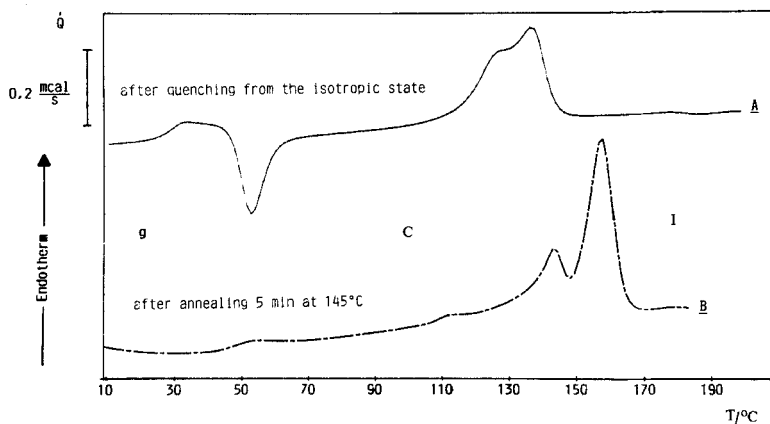
Figure 5. Influence of the thermal history on the phase behaviour of polyester **P3** (for the formula see table 1). Heating rate 80°C min^{-1}.
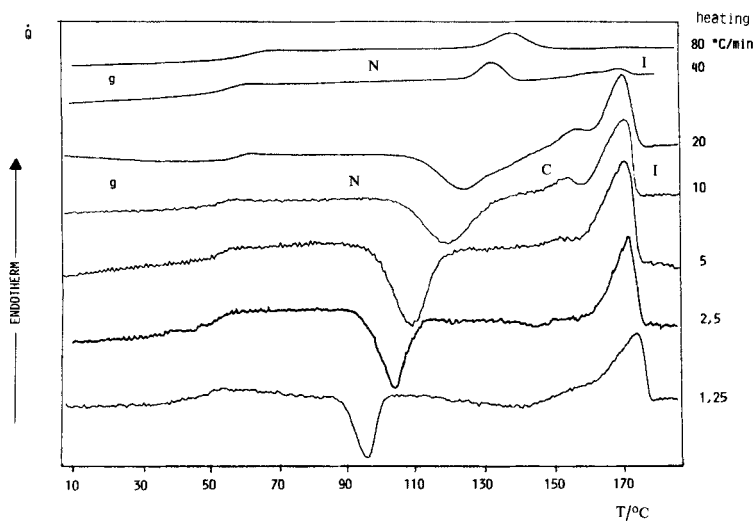
Figure 6.   Influence of the heating rate on the phase behaviour of polyester **P8** (for the formula see table 2).
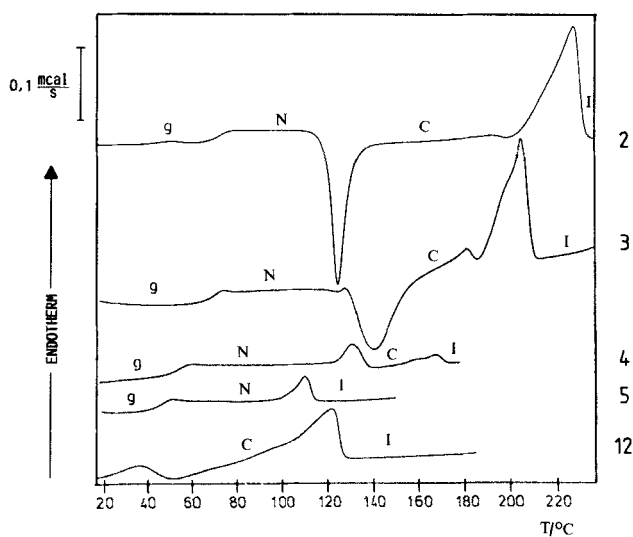
Figure 7.   DSC heating curves of polyester **P8, P10–P13** with a short spacer and alkyloxy terminal groups of different length (for the formula see table 3). Heating rate 40°C min^{-1}.
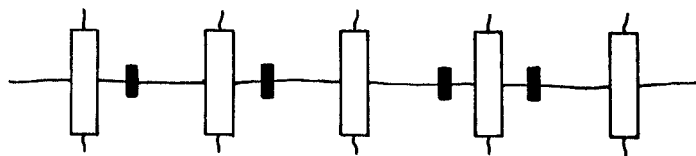
Figure 8.   Possible positions of the methyl groups in the spacer of polyester **P16, P17** (for the formula see table 4).

Table 3. Molecular weights, transitions temperatures and enthalpies of the polyesters **P8–P14** with glutaric acid spacers and different terminal groups.
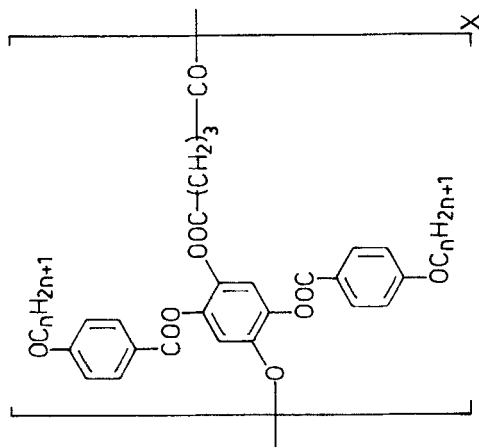
Polyester	Terminal groups	M_{GPC}‡	M_w	P_w	U	Phase behaviour†/°C		Heating rate†	ΔH_{NI}/J g^{-1}
P9	n=1	8100	8900	18	1·6	g 88 N 169 I r	C 220 I	40	4·5
P10	2	7800	10000	19	1·4	g 71 ‖	r 125 C 227 I	40	—
P11	3	10200	13500	24	1·9	g 72 N 130 I r 156	C 211 I	40	4
P8	4	13000	16200	27	2·0	g 56 N 131 I r	C 169 I	40	4
P12	5	10200	12700	21	1·5	g 44 N 108 I r §	C 141 I	40	4
P13	12	9500	11700	14	1·4	g 23	C 122 I	40	—
P14	n=5 (optically active)	12600	20500	33	1·9	g 60	r § C 161 I	20	—

† See table 1. N, nematic phase; ΔH_{NI}: clearing enthalpy; a heating rate of 40°C/min is necessary in most cases to reach the clearing transition before recrystallization starts (cf. figure 7).
‡ See table 1.
§ Only after annealing can the sample crystallize.
‖ The clearing temperature observed in the polarizing microscope is 126°C.

Table 4. Polyester with different glutaric acid spacers.
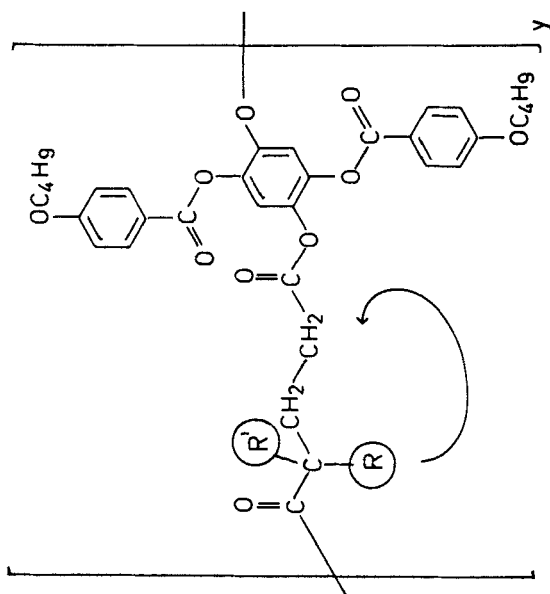
| Polyester | Terminal groups | | M_{GPC}‡ | M_w | P_w | U | Phase behaviour†/°C heating rate/20°C min^{-1} | $\Delta H_{NI}/J\,g^{-1}$ |
	R	R'						
P8	–H	–H	13000	16200	27	2·0	g 56 C 169 I (*N* 130)	4
P16	–CH$_3$	–H	13000	18000	30	2·0	g 55 N 73 I	2
P17	–CH$_3$	–CH$_3$	26000	40000	65	2·7	g 61 I	—

†,‡ See footnotes to tables 1–3.

(I)

(II)

(III)

(IV)
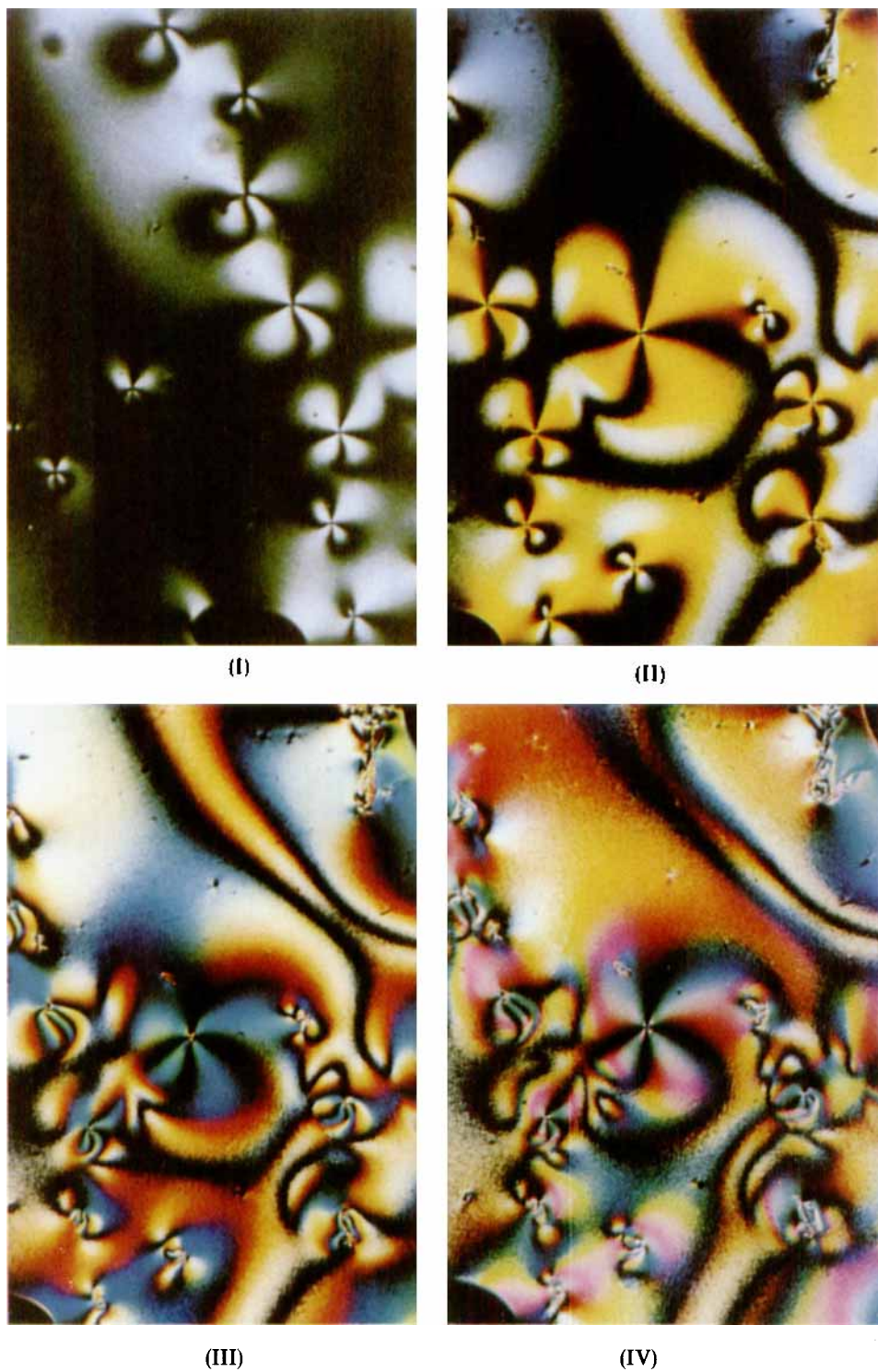
Figure 9. Development of a schlieren texture for **P16** (for the formula see table 4) cooling slowly from the isotropic to the liquid crystalline state.
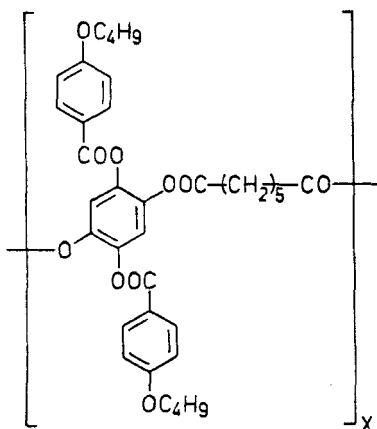
Figure 10. Flat chamber exposure of a crystallized fibre of polyester **P6** produced from the liquid-crystalline state.

(a)   (b)
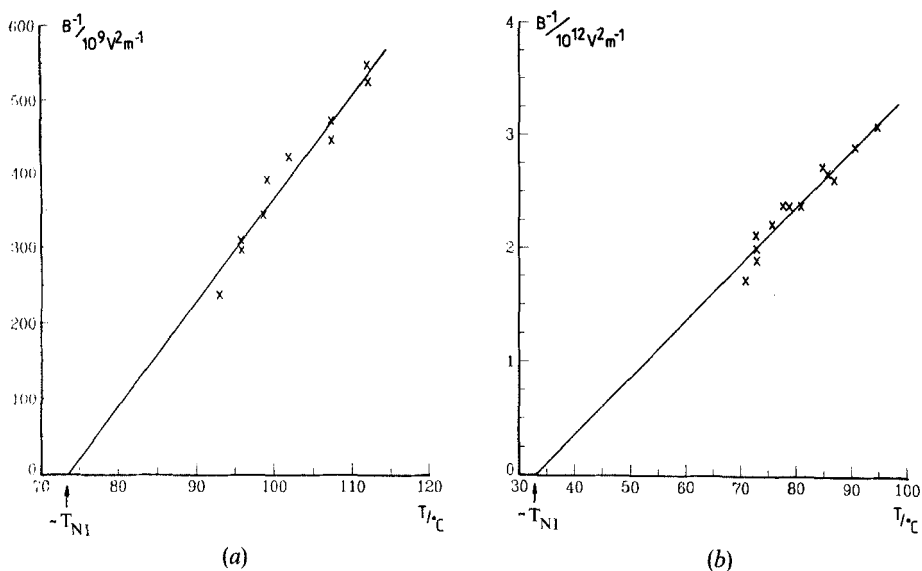
Figure 11. Plots of the reciprocal value of the Kerr constant, B, as a function of temperature, (a) polyester **P16** and (b) polyester **P17** (for the formula see table 4).

realized because it was not possible to obtain a good homeotropic orientation, either with the aid of coated glass slides or with a magnetic field of 7 T.

X-ray measurements of polyesters **P1**, **P6–P8**, **P11**, **P12** and **P16** on fibres drawn from the nematic state, on crystallized fibres and on powders gave the following results. All of the polyesters are nematic; the lateral distance between the mesogens is about 4·2 Å; fibres are usually well oriented and when crystallized, the orientation remains in the fibre (see figure 10). Also, the Kerr constant (which indicates pretransitional effects at the nematic–isotropic transition in both polymeric [45,46] and low molecular weight liquid crystals) shows no anomalous behaviour when followed as a function of temperature (see figure 11). The extrapolated clearing temperature of the nematic phase of **P16** is 73°C, in agreement with DSC measurements and observations using the

polarizing microscope. In addition, for the amorphous polyester **P17**, it was possible to predict a nematic–isotropic transition at about 33°C if there was no glass transition at 61°C (see figure 11 (*b*)).

In summary, there is no evidence for the existence of an anomalous nematic phase such as a biaxial nematic. A detailed model examination (see later) leads to the conclusion that the biaxiality of the nematic phase must not be necessarily expected, even though the bilateral attachment of the mesogens suggests this.

3.4. *Comparison of liquid-crystalline polymers with different architectures*

In figure 12 several polymers with different architecture are contrasted, all possessing 1,4-di(*p*-alkoxybenzoyloxy)benzenes as mesogens. Dividing the spacers of the polyester **A** arbitrarily, two butyloxy groups can be assigned as terminal groups to each mesogen, just as in polymers **B** and **C**. The lateral alkyl-substituted main chain polyester **D** is taken up in the following comparison too, although it has an ester linkage between the mesogens and spacers instead of an ether linkage.

Main chain polyesters of type **A** [38] show crystalline and nematic phases for all spacer lengths (2 to 11 methylene groups). With increasing length of the spacer, which is consistent with an increasing length of the terminal groups of the mesogen, smectic phases also appear. Clearing temperatures show a strong odd–even effect and decrease from 390°C for a polyester with two methylene groups to 250°C for eleven methylene groups.

Polymethacrylates of type **B** with laterally linked mesogens in the side groups [20] have only nematic, non-crystalline phases, independent of the length of the spacer and terminal groups. In comparison to analogous polyacrylates or polychloracrylates [19],
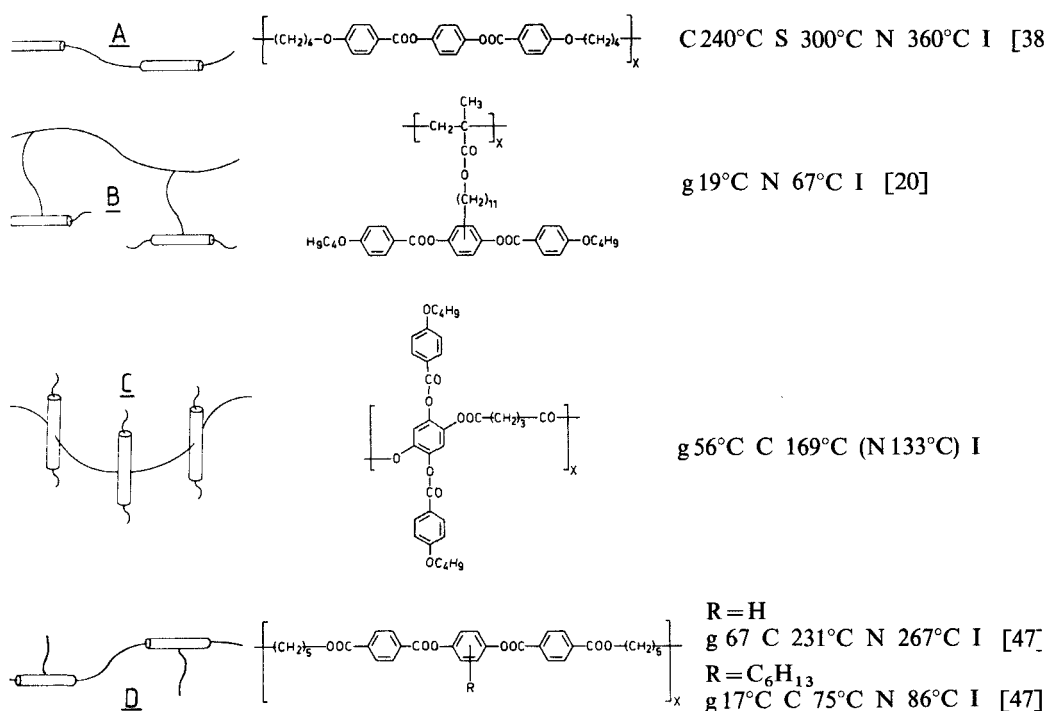

Figure 12. Comparison of liquid-crystalline polymers with different architectures.

no influence of the main chain on the clearing temperature can be claimed; the mesogens seem to be totally decoupled from the main chain. Of course, the glass transition increases with increasing stiffness from polyacrylates to polychloracrylates to polymethacrylates. In contrast to the polymethacrylates, several of the more flexible polyacrylates and polychloracrylates crystallize and have monotropic nematic phases. The length of the spacer [19] only has an influence on the glass transition, but not on the clearing temperature. Now, the polyesters with laterally fixed mesogens in the polymer main chain C, exhibit a distinctive dependence of the thermal behaviour on the type and length of the terminal groups as well as from the spacer. All polyesters with non-branched spacers crystallize and display monotropic nematic phases with clearing temperatures between those from polyesters **A** and the polymers **B**. Long terminal groups act as a plasticizer and lead to rapidly crystallizing polyesters. Short spacers especially decrease the flexibility of the polymeric chain and inhibit crystallization. No smectic phases have been obtained and installation of branched, short spacer groups (**P16,P17**) results in strongly decreased clearing and the absence of crystallization.

In comparing polyester **C** with **D** [47], it must be noted that when compared to polyester **A** one lateral substituent on the hydroquinone ring (**D**) decreases the nematic–isotropic transition more than the bilateral, symmetric substitution of polyester **C** does. Larger lateral substituents in **D** like octyl or decyl groups disrupt the structure so much, that mesophases are no longer obtained [47]. For polyesters of type **C**, however, nematic phases could be observed with long tetradecane dicarboxylic acid spacers. In conclusion, lateral substituents on mesogens can be effective in influencing phase behaviour in different ways depending on their function: as a disruptor as for polyester **D** or as spacer groups as for **B** and **C**. In comparison with low molecular weight bilaterally substituted 1,4-di(*p*-alkoxybenzoyloxy)-benzenes [14], where not even a monotropic liquid-crystalline phase could be found, lateral attachment of the mesogens in main chain polyesters of type **D** seem to support the mesophase.

3.5. *Model examination*

In line with initial expectations, packing behaviour should depend strongly on the length of the spacer, as shown in figure 13. Polyesters with long spacers show only nematic phases in accord with the results for low molecular weight liquid crystals having one long lateral substituent [1, 2, 10–13]. The observed adaptation to the shape of the mesogen contributes to the model in figure 13(b). Also, the mesogens orient themselves in the direction of tension which is normally identical to the mean orientation of the polymeric chain, respective to the spacers in this case.

This picture must change when the spacers are shortend. Figure 13(a) shows a model which would just fit for polyesters with glutaric acid spacers (**P8–P13**): the mesogens along the chain were kept distanced from each other so that other mesogens in the vicinity may just find a place in-between that distance. A liquid-crystalline phase of such a type is reminiscent of interdigitated S_A phases. No such phases could be found and consequently this model must be modified. The following idea leads to pictures (see figures 15 and 16) with possible arrangements which fit all of the results.

Experience with the classical semiflexible liquid-crystalline main chain polyesters [48–51] shows that mesogens are also able to co-orient the polymeric chain. Spacers with an even number of methylene groups are forced into an all-trans conformation, but spacers with odd numbers of methylene groups must possess gauche conformations to achieve parallel orientation of the mesogens. That is not necessary for polyesters

(*a*)   (*b*)
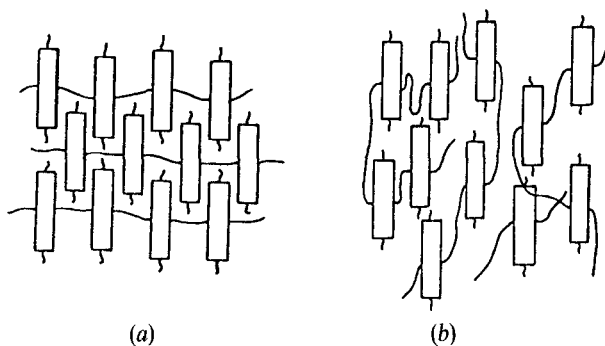
Figure 13.   Possible arrangements of laterally fixed mesogens in the main chain (*a*) with a short spacer and (*b*) with long spacer.
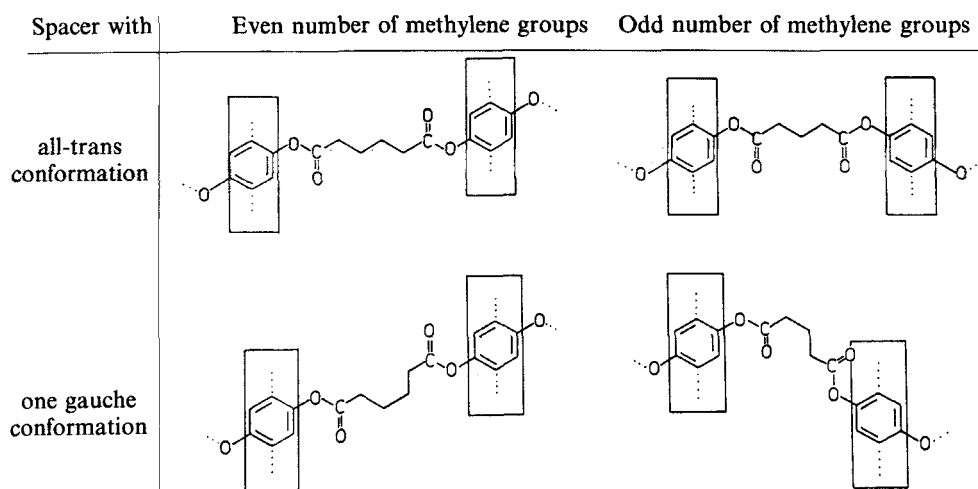
Figure 14.   Polyester segments with different spacer conformations with an odd or even number of atoms.

with laterally fixed mesogens in the main chain. The architecture allows a parallel orientation of the mesogens with an all-trans as well as with one or more gauche conformations in the spacer. This is depicted in figure 14 with polyester segments containing three or four methylene groups in the spacer. We should expect that during quenching from the isotropic state the ratio between gauche and trans conformers of short, relatively inflexible spacers changes only slowly; when the clearing temperature is reached there would subsequently be no need for a particular conformation as for classical main chain polymers. Thus, the model in figure 13 (*a*) may be revised, giving what is depicted in figure 15. Such a model exhibits a nematic arrangement of the mesogens as found for polyesters with short spacers. According to the flexibility of the polymeric chain, an annealing in the mesophase probably leads to a transformation of the spacer gauche conformations to all-trans conformations which are possibly thermodynamically slightly more stable. Instead of changing to a mesophase with a layered structure, however, the polyesters crystallize so they have no branching in the spacers. In other words, we can speculate that sometimes the monotropic metastable nematic mesophase will have produced such a high percentage of all-trans conformers on the way to achieving an equilibrium between trans and gauche conformations that
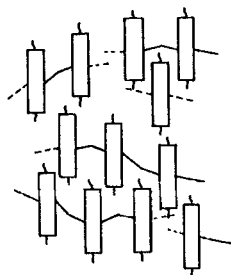
Figure 15.   Possible arrangement of the laterally fixed mesogens in the main chain with short spacers and gauche conformations.

(a)   (b)
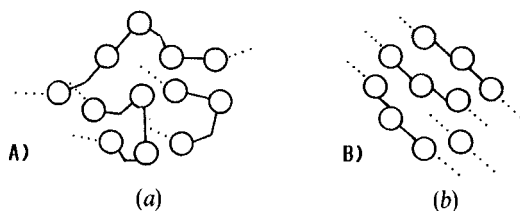
Figure 16.   Arrangement of the spacers, observed from the direction of the mesogenic long axes for (a) uniaxial and (b) biaxial nematic polymers.

the nematic arrangement of the mesogens (see figure 15) changes to an arrangement as given in figure 13 (a). Such an arrangement is probably closely related to the situation in the crystalline state. Of course, all such processes would be kinetically determined by the detailed molecular structure of the polymer. An indication that crystallization in this case would be a process without any extensive rearrangements is the observation that oriented fibres obtained from the liquid-crystalline state crystallize without change under the polarizing microscope. It seems that only a small shift of the structural elements is necessary during this process. This means that, in a way, the mesogens in the liquid-crystalline state oriented by mechanical stretch to form a monodomain are able to crystallize to single-crystalline fibres which have the same orientation as in the liquid-crystalline state (cf. figure 10).

A possible reason to explain why polyesters **P16, P17** fail to crystallize is as follows: unsymmetric substitution of the spacer results in different repeating units (see figure 8) introducing too high an extent of main chain irregularity.

Observing the polymeric chains from the direction of the mesogenic long axis (see figure 16) we can see different arrangements depending on whether the spacers have only trans (b) or trans and gauche conformations (a). In the case of an arrangement with gauche conformations of the spacers (a), no uniformly oriented second axis exists. Such a second axis is only expected with a uniform all-trans oriented spacer (b) which leads to rapid crystallization. Consequently, we must not take into account a biaxial nematic behaviour for the polyesters described here.

4.   Phase behaviour of polyesters with laterally attached phenylpyrimidine derivatives

To investigate the influence of the central stiff component of the mesogen on the phase behaviour, 4,6-dihydroxy-2,5-diphenylpyrimidine derivatives were incorporated. Phenylpyrimidines have proved to be excellent mesogens in low molecular weight [41, 52–55] and polymeric side group liquid crystals [56] because of the

Table 5. Molecular weights and phase behaviour of the polyesters with 2,5-diphenylpyrimidines as laterally fixed mesogens in the main chain.

Polyester	Spacer (X)	Terminal groups		M_{GPC}	M_w	P_w	U	Phase transition temperatures/°C†
		R	R'					
P18	$\{CH_2\}_3$	$-CH_3$	$-CH_3$	17000	18000	35	2·1	g 57 I
P19	$\{CH_2\}_3$	$-CH_3$	$-C_4H_9$	10500	10500	19	1·9	g 46 I
P20	$\{CH_2\}_3$	$-C_4H_9$	$-C_4H_9$	10000	11000	19	2·1	g 37 I
P18	$\{CH_2\}_3$	$-CH_3$	$-CH_3$	17000	18000	35	2·1	g 57 I
P21	$\{CH_2\}_4$	$-CH_3$	$-CH_3$	15000	17000	33	1·7	g 48 I
P19	$\{CH_2\}_3$	$-CH_3$	$-C_4H_9$	10500	10500	19	1·9	g 46 I
P22	$\{CH_2\}_4$	$-CH_3$	$-C_4H_9$	13000	12000	21	2·2	g 34 I
P23	$p\text{-}C_6H_4$	$-CH_3$	$-C_4H_9$	45000	42000	72	2·6	g 94 C>200 decomposes
P24	$m\text{-}C_6H_4$	$-CH_3$	$-C_4H_9$	35000	35000	60	2·1	g 92 C>200 decomposes

† Values determined by DSC with a heating rate of 20°C/min.

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Table 6. Molecular weights and phase behaviour of oligomers with bis(phenylazo)biphenyl derivatives as laterally fixed mesogens.
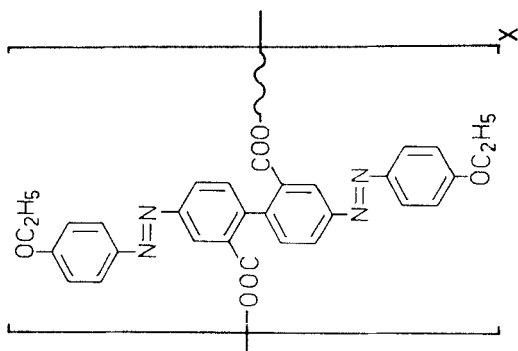
Oligomer	Spacer	M_{GPC}	M_w	P_w	U	Phase transition temperatures/°C†	ΔH_{NI}/J g^{-1}†
P25	$(CH_2)_3$	5000	5500	10	1·3	g 101 LC 202 N 207 I	6§
P26	$(CH_2)_6$	5000	5800	9	1·3	g 83 C‡ 193 N 222 I	6
P27	$(CH_2-CH_2-O)_2CH_2-CH_2-$	6200	6800	10	1·3	g 65 N_b 110 N_a 176 I	1+4§
P28	"	9000	9500	10	1·6	g 126 N 155 I	3·5
P29	"	6300	7400	12	1·3	g ~170 I	
P30	"	6000	6600	10	1·2	g ~165 I	

† Values determined by DSC with a heating rate of 20°C/min. g, glass transition; LC, mesophase; N_a, N_b, nematic phases; ΔH_{Nb} transition enthalpy.
‡ The weak crystallization could be observed only after annealing.
§ **P25**, sum of the transition enthalpies of both mesophases; **P27**, enthalpies at the melting and the clearing transition (cf. figure 17).
|| For the formula see scheme 3.

planarity of the two aromatic rings and the corresponding high anisotropic polarization. Also 2,5-diphenylpyrimidine derivatives have been described as nearly planar high polarizable mesogens because of the aromatic character of the whole system [57]. Instead of the symmetrical linkage of the mesogenic 2,5-dibenzoyloxyhydroquinones, the 4,6-disubstituted phenylpyrimidines are attached asymmetrically in the polymeric chain. Due to this asymmetry, they should be ideal elements for non-crystallizing polymers with laterally attached mesogens in the main chain. As expected, crystallization occurs only for two polyesters with aromatic spacer groups (**P23, P24**, table 5). Nevertheless, although the spacers and the terminal groups at the mesogens were varied none of the polyesters showed liquid-crystalline behaviour. Furthermore, investigations of pretransitional effects by measuring the Kerr constants gave no indication of liquid-crystalline behaviour below the glass transition.

Asymmetric attachment of the mesogens in the polymer chain probably not only prevents crystallization but also any liquid-crystallinity. Nevertheless, it appears that in copolymers of the same phenylpyrimidines with other mesogens (see later and [26]) liquid-crystalline phases can be obtained.

5. Phase behaviour of oligomers with laterally attached 4,4′-bis(phenylazo)-biphenyl derivative

Another type of asymmetry can be found in derivatives of 2,2′-substituted biphenyls. Hindrance of the rotation around the central linkage results in atropisomers. Additionally, the two azo groups in the derivative used in oligoesters **P25–P30** occur as cis/trans isomers (10–20 per cent cis isomers have been found by ^{1}H NMR spectroscopy). Therefore, the oligomers are composed of several slightly different repeating units. At the clearing temperatures (see table 6) all four of the oligomers with flexible spacers (**P25–P28**) show characteristic nematic droplets. Oligomer **P25** exhibits a second liquid-crystalline phase which can be hardly differentiated via DSC from the transition at the clearing temperature. It also exhibits a reversible alternation of the schlieren texture at about 200°C. Exactly which type of liquid-crystalline phase this is, has not yet been determined. Oligomer **P27** shows a special feature: the DSC curves indicate a reversible transition at about 110°C which can be supercooled slightly (see
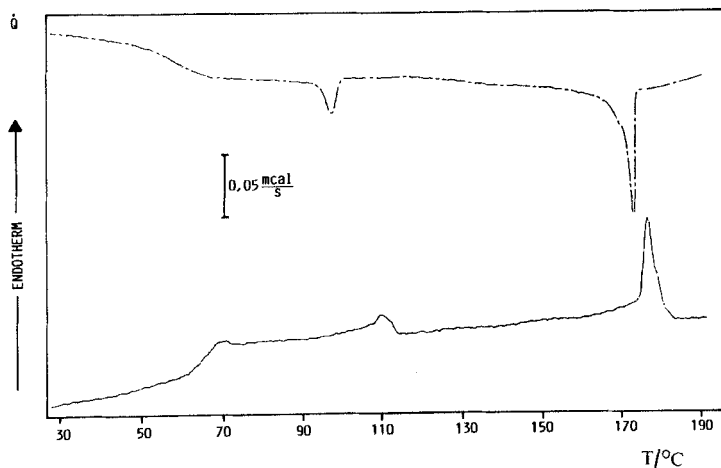

Figure 17.   DSC: heating and cooling curves for oligomer **P27** (for the formula see scheme 3).

figure 17). By polarizing microscopy and X-ray experiments, however, no difference between N_a and N_b could be detected. When the spacer is substituted with a stiff hydroquinone or a 4,4'-biphenyldiol unit, no more mesophases could be observed (**P29, P30**). In summary, the 4,4'-bis(*p*-ethoxyphenylazo)biphenylene containing four aromatic rings is the best mesogen. Although the molecular weight is low, in contrast to polyesters with dibenzoyloxyhydroquinone units, broad enantiotropic mesophases were obtained. The insignificant tendency to crystallize (**P26**) is caused probably by the low molecular weight [43] and the different isomers.

In comparison with unsubstituted low molecular weight liquid crystals, lateral attachment of mesogens in the polymer main chain lowers the clearing temperatures. In comparison with low molecular weight and semi-flexible polymeric liquid crystals which are substituted laterally (except of carboxylic groups— as **7**), we can also speak of a stabilizing effect of the polymeric attachment on the mesophase for laterally linked mesogens in polymer main chains.

6. Experimental

6.1. *4,6-Dihydroxy-2,5-diphenylpyrimidines 1–3*

Following exactly the procedure given in the literature [41], the following pyrimidines 1–3 were produced:
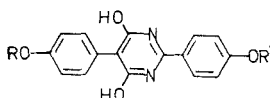
	Terminal groups		Recrystallized from	Yield in %	Elemental analysis			
No	R	R'				%C	%H	%N
1	–OCH$_3$	–OCH$_3$	DMF	51	Calc.	66·66	4·97	8·64
					Found	66·48	4·94	8·57
2	–OCH$_3$	–OC$_4$H$_9$	Pyridine	67	Calc.	68·84	6·05	7·65
					Found	68·89	6·14	7·65
3	–OC$_4$H$_9$	–OC$_4$H$_9$	Pyridine	74	Calc.	70·57	6·91	6·86
					Found	70·66	6·75	6·53

^{1}H NMR of **2** (400 MHz in DMSO-d_7): (in ppm) = 8·09 and 7·05 (dd, 4 H, arom.), 7·49 and 6·87 (dd, 4 H, arom.), 4·05 (t, 2 H, OCH$_2$), 3·75 (s, 3 H, OCH$_3$), 1·71 (m, 2 H, OCH$_2$-CH_2), 1·44 (m, 2 H, CH_2CH$_3$), 0·93 (t, 3 H, CH$_2$CH_3).

6.2. *4,6-Di(hydroxyethyloxy)-2,5-di(p-alkoxyphenyl)pyrimidines 4–6*

To a solution of 13 mmol of the appropriate 4,6-dihydroxy-2,5-diphenyl-pyrimidine (**1–3**) in 120 ml of purified dimethylformamide were added 20 g of dry pulverised potassium and 29 mmol 2-bromoethanol. After stirring and refluxing for 24 and 48 hours 3 mmol of bromoethanol were added again and the reaction was stopped after about 70 hours. The yellowish mixture lost colour with the progressive reaction and could be followed by thin layer chromatography (silica gel 60 F 254, Merck) with chloroform as eluent. The reaction mixture was poured into water and a white oily product precipitated, which was extracted with chloroform. The organic phase was

dried over sodium sulphate and the chloroform was subsequently evaporated. The raw material was purified by repeated flash chromatography (Merck, silica gel 60; 0·040–0·063 mm;).

	Terminal groups					Elemental analysis		
No.	R	R'	Eluent	Yield in %	T_{cl}†/°C		%C	%H	%N
4	–OCH$_3$	–OCH$_3$	CH$_2$Cl$_2$/aceton 8:1	69	156	Calc.	64·07	5·86	6·79
						Found	63·93	6·06	6·78
5	–OCH$_3$	–OC$_4$H$_9$	CH$_2$Cl$_2$/aceton 12:1	72	95	Calc.	66·07	6·65	6·16
						Found	66·07	6·47	6·18
6	–OC$_4$H$_9$	–OC$_4$H$_9$	CH$_2$Cl$_2$/aceton 20:1	62	117	Calc.	67·76	7·31	5·64
						Found	67·15	7·16	5·65

† Melting temperatures were determined by DSC (heating rate: 10°C/min).

^{1}H NMR of **5** (200 MHz in CDCl$_3$): (in ppm) = 8·27 and 6·94 (dd, 4 H, arom.), 7·40 and 6·92 (dd, 4 H, arom.), 4·59 (t, 4 H, pyr-O–CH_2), 4·00 (t, 2 H, bz-O–CH_2), 3·90 (broad signal, 4 H, HO–CH_2), 3·81 (s, 3 H, OCH$_3$), 3·21 (broad signal, 2 H, OH), 1·78 (m, 2 H, OCH$_2$CH_2), 1·49 (m, 2 H, CH_2CH$_3$), 0·98 (t, 3 H, CH$_2$CH_3).

6.3. *4,4' Bis(p-ethoxyphenylazo)biphenyl-2,2'-dicarbonic acid 7*

2·9 g of 4,4'-bis(*p*-ethoxyphenylazo)biphenyl-2,2'-dicarbonic acid ethylester [42] were refluxed with 6 g of potassium hydroxide, 15 ml of water and 30 ml of ethanol for 20 hours. Most of the solids were dissolved. After cooling the reaction mixture was poured into 1 l of water and the ethanol was distilled azeotropically. The remaining aqueous solution was filtered and the diacid precipitated with dilute hydrochloric acid. The diacid was filtered and dissolved in dioxane. The clean product precipitated when petrol was added. The product was dried in vacuum at 100°C.

Yield: 2·55 g ≅ 97 per cent. Melting temperature about 330°C; nematic phase observed. Elemental analysis:

Calculated	66·91% C	4·87% H	10·40% N
Found	66·96% C	4·93% H	10·43% N

6.4. *4,4'-Bis(p-ethoxyphenylazo)biphenyl-2,2'-dicarbonic acid dichloride 8*

For 2 hours 2·5 g of 4,4'-bis(*p*-ethoxyphenylazo)biphenyl-2,2'-dicarbonic acid **7** were refluxed with thionyl chloride which was previously distilled over cottonseed oil. The excess thionyl chloride was evaporated afterwards and the residue recrystallized from dioxane.

Yield: 2·3 g ≅ 93 per cent. Melting and clearing temperature: 178°C. Elemental analysis:

Calculated	62·60% C	4·20% H	9·73% N	12·34% Cl
Found	62·34% C	4·10% H	9·45% N	12·81% Cl

6.5. *Polyesters P1–P30*

All of the alkyl dicarbonic acid dichlorides have either been supplied or synthesized from the appropriate diacids with thionyl chloride or phosphorus pentachloride and have been either fractionated in vacuum or recrystallized. Pyridine was distilled over calcium hydride and 1,1,2,2-tetrachloroethane was fractionated over phosphorus pentoxide. Both solvents were flushed with dry argon.

In a Schlenk tube, about 1 mmol of the appropriate dicarbonic acid dichloride was dissolved in 3 ml of absolute tetrachloroethane. An appropriate amount of the diol in a mixture of 0·5 ml of pyridine and 2 ml of tetrachloroethane was added to the diacid dichloride solution. The tube was closed under a stream of dry argon and stirred for 3 to 5 days. It was not necessary to cool the tubes at the beginning of the reaction. When a persistent precipitate occurs, the reaction temperature was increased until the precipitate redissolved.

Afterwards the reaction mixtures were diluted with chloroform to 10 ml and precipitated dropwise in 100 ml of methanol. The polyesters were separated by centrifugation, dissolved again in 10 ml of chloroform and reprecipitated again either once or twice. In those cases where the polyesters are soluble in benzene, they were subsequently freeze-dried. All other polyesters were dried in vacuum until constant weight. Oligomeric products were either fractionated by precipitation by adding methanol dropwise to a solution of the oligomer in chloroform and separating the precipitate by centrifugation, or were fractionated by preparative GPC [43]. The yields, molecular weights and elemental analyses of the fractionated oligomers and polyesters are summarized in table 7.

Table 7. Yields, molecular weights (M_{GPC}) and elemental analyses of polyesters **P1–P30**.

Polymer	Yield in %	M_{GPC}		Elemental analysis %C	%H	%N
P1	74	7200	Calc.	69·08	6·71	
			Found	68·73	6·83	
P2	72	10000	Calc.	69·75	7·02	
			Found	69·81	7·08	
P3	78	8000	Calc.	70·37	7·31	
			Found	69·91	7·15	
P4	72	8900	Calc.	70·95	7·58	
			Found	71·03	7·49	
P5	76	10500	Calc.	71·48	7·82	
			Found	70·78	7·85	
P6	76	38000	Calc.	68·72	6·55	
			Found	68·84	6·37	
P7	38	13200	Calc.	67·95	6·19	
			Found	67·37	6·18	
P8	76	13000	Calc.	67·11	5·80	
			Found	66·24	5·82	
P9	24†	8100	Calc.	64·09	4·38	
			Found	63·88	4·76	
P10	54†	7800	Calc.	65·17	4·90	
			Found	64·75	5·18	
P11	61	10200	Calc.	66·19	5·37	
			Found	66·13	5·07	

Table 7 (*continued*).

Polymer	Yield in %	M$_{GPC}$	Elemental analysis			
				%C	%H	%N
P12	45	10200	Calc.	68·02	6·02	
			Found	67·60	6·16	
P13	62†	9500	Calc.	72·21	8·16	
			Found	71·72	8·28	
P14	47	12600	Calc.	68·02	6·20	
			Found	67·34	6·64	
P15	74	9200	Calc.	72·59	7·05	
			Found	72·16	7·17	
P16	88	13000	Calc.	67·54	6·00	
			Found	67·20	6·34	
P17	66	26000	Calc.	67·95	6·19	
			Found	67·91	6·28	
P18	66	17000	Calc.	63·77	5·55	5·51
			Found	63·68	5·76	5·66
P19	55	10500	Calc.	65·44	6·22	5·09
			Found	64·99	6·43	5·38
P20	40	10000	Calc.	66·88	6·80	4·72
			Found	66·27	6·81	4·95
P21	35‡	13000	Calc.	64·36	5·79	5·36
			Found	64·79	5·77	4·95
P22	76	15000	Calc.	65·98	6·43	4·96
			Found	65·99	5·89	4·65
P23	96	45000	Calc.	67·80	5·52	4·79
			Found	67·51	5·61	4·77
P24	86	35000	Calc.	67·80	5·52	4·79
			Found	67·53	5·41	4·83
P25	8‡	5000	Calc.	68·50	5·23	9·68
			Found	68·18	5·35	9·02
P26	18‡	5000	Calc.	69·66	5·85	9·02
			Found	69·72	6·38	8·92
P27	15‡	6200	Calc.	64·66	5·43	8·38
			Found	65·83	5·44	8·11
P28	15‡	9000	Calc.	69·03	5·48	8·78
			Found	69·03	5·50	8·30
P29	9‡	6300	Calc.	70·58	4·61	9·14
			Found	70·01	5·09	9·80
P30	5‡	6000	Calc.	73·25	4·68	8·13
			Found	72·29	5·65	9·49

† The original product had been subjected to a fractioned precipitation; only the high molecular weight fractions were used further.

‡ The polyester had been fractionated by preparative GPC under high pressure [43]; only high molecular weight fractions were used further.

6.6. *Characterization methods*

All of the phenylpyrimidines, azo derivatives and polyesters prepared were characterized by ^{1}H NMR spectra. Particular samples were also characterized by IR spectroscopy. Analytical and preparative GPC were carried out as described in a following publication [43]. The thermal behaviour was examined with a POL-BK II polarizing microscope (Leitz) equipped with a FP 5 hot stage (Mettler) and with a

differential scanning calorimeter (DSC-2C; Perkin–Elmer). Because of the importance of the DSC measurements, some further clarification is given. Since the thermal history (see figure 5) as well as the processing of the polyesters (precipitation conditions, purification, drying) are critical in influencing the phase transitions, especially recrystallization and melting temperatures, and the melting enthalpies, all of the compared DSC samples were pretreated identically. The procedure most often used was as follows: a sample (about 5 mg) was closed in a DSC aluminium pan and the first heating curve was measured giving an estimate of the melting temperature. A new sample of the same polyester was heated briefly to the isotropic phase and quenched on a metal block to $-10°C$. A second heating curve was measured which was usually the basis for the judgement of the phase behaviour. With these conditions, the recrystallization temperature and enthalpy were very reproducible. In addition, several cooling and further heating runs with different temperature scanning rates on samples with different thermal history were carried out to determine kinetically dependent crystallization or ageing phenomena. Peak maxima were used to determine the transition temperatures for the polyesters; for the low molecular weight compounds the onset-temperatures were used. Glass transition temperatures were determined from the turning points. All of the DSC curves given were normalized to 1 mg of the sample.

^{1}H NMR of **P10** (400 MHz in $CDCl_3$): in ppm) = 8·01 and 6·90 (dd, 8 H, $O–C_6H_4–COO$), 7·19 (s, 2 H, arom.), 4·02 (q, 4 H, OCH_2), 2·40 (t, 4 H, $OOC–CH_2$), 1·85 (m, 2 H, $OOC–CH_2CH_2$), 1·38 (t, 1·38 (t, 6 H, CH_3).

IR (KBr) of **P10**: 1770 cm^{-1} and 1740 cm^{-1} (C = O, ester), 1605 cm^{-1}, 1580 cm^{-1} and 1510 cm^{-1} (C = C, arom.).

^{1}H NMR of **P19** (200 MHz in $CDCl_3$): (in ppm) = 8·31 and 6·93 (dd, 4 H, arom.), 7·39 and 6·88 (dd, 4 H, arom.), 4·66 (broad signal, 4 H, pyr-O–CH_2), 4·39 (broad signal, 4 H, CH_2–OOC), 4·00 (t, 2 H, bz-O–CH_2), 3·77 (s, 3 H, OCH_3), 2·28 (t, 4 H, $OOC–CH_2$), 1·80 (m, 4 H, $OOCCH_2CH_2$ and $CH_2CH_2CH_3$), 1·49 (m, 2 H CH_2CH_3), 0·98 (t, 3 H, CH_2CH_3).

^{1}H NMR of **P29** (400 MHz in $CDCl_3$): (in ppm) = 8·61 (2 H, ortho to –COO), 8·01 (2 H, para to –COO), 7·36 (2 H, meta to –COO), 7·86 (4 H, meta to OEt), 6·91 and 6·84 (4 H, ortho to OEt and 4 H ortho to –OOC), 4·03 (4 H, CH_2), 1·38 (6 H, CH_3), only stronger signals corresponding to trans-azo repeat units are considered; all of the signals were broad, no splitting could be obtained.

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