Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Influence of molecular weight and polydispersity on phase behaviour of polyesters with laterally fixed or cross-shaped mesogens

Volker Krone[a]; Helmut Ringsdorf[a]
[a] Institut für Organische Chemie, Universität Mainz, Mainz, F. R. Germany

To cite this Article Krone, Volker and Ringsdorf, Helmut(1991) 'Influence of molecular weight and polydispersity on phase behaviour of polyesters with laterally fixed or cross-shaped mesogens', Liquid Crystals, 9: 2, 207 — 220

To link to this Article: DOI: 10.1080/02678299108035498

URL: http://dx.doi.org/10.1080/02678299108035498

LIQUID CRYSTALS, 1991, VOL. 9, NO. 2, 207–220

Influence of molecular weight and polydispersity on phase behaviour of polyesters with laterally fixed or cross-shaped mesogens

by VOLKER KRONE and HELMUT RINGSDORF
Institut für Organische Chemie, Universität Mainz,
J.-J.-Becher-Weg 18-20, D-6500 Mainz, F.R. Germany

(*Received 12 March 1990; accepted 18 August 1990*)

To supplement previous studies of polyesters with laterally attached and cross-shaped mesogens the influence of molecular weight and molecular weight distribution on the phase behaviour has been investigated. For that purpose two polyesters have been fractionated by preparative gel permeation chromatography under high pressure and observed by polarizing microscopy and DSC measurements. A monotropic nematic polyester with laterally attached mesogens shows changing phase transitions up to a molecular weight of 10 000 (M_W); at higher molecular weight only the clearing transition is still slightly influenced. The molecular weight distribution at an average molecular weight of 15 000 (M_W) has no influence on the melting and clearing temperatures, but does effect recrystallization. The tendency to recrystallize decreases with increasing polydispersity, with increasing aberration from a monomodal molecular weight distribution. The recrystallization and the melting enthalpy are most distinguished at molecular weights around 12 000 (M_W) and crystallization disappears at molecular weights under about 5000 (M_W). In this way, fractions with stable nematic phases are obtained. Additionally, the broadness of the biphasic region shows a distinct dependence on molecular weight. Clearing temperatures show the most significant dependence on the molecular weight of an enantiotropic polyester with cross-shaped mesogens dropping significantly below a molecular weight of about 20 000 (M_W). Oligomers with molecular weights below 10 000 (M_W) do not exhibit a mesophase. Polyesters with laterally attached mesogens as well as with cross-shaped mesogens show no new liquid-crystalline phases by varying the molecular weight or the molecular weight distribution.

1. Polymer properties dependent on experimental conditions

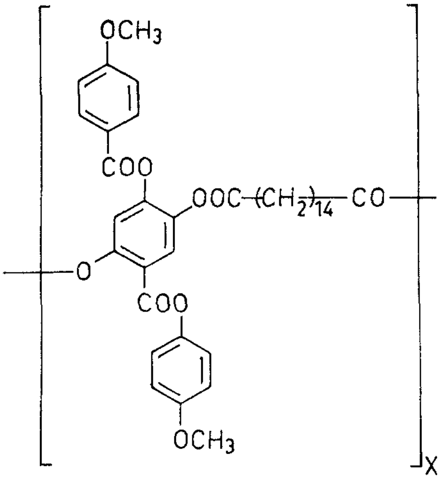
When discussing the phase behaviour of liquid-crystalline polyesters, the significance of the influence of molecular weight or polydispersity remains unaddressed. Normally, such variables depend on the conditions of the synthesis: the purity of the components and the solvents, the reactivity of the components, or the process of separating products from crude materials. Often, the molecular weight and polydispersity of polyesters vary so much that a comparison of the properties of such samples to learn about the relations between structure and properties is difficult. This problem arises especially with oligomeric products. Only with a knowledge of the influence of these variables on the physical properties effects based on the chemical structure of the repeating unit may be separated and the general relationships between molecular architecture and phase behaviour elaborated. With this intent, our study attempts to examine the dependence of phase behaviour of polyesters with laterally attached [1] and cross-shaped [2] mesogens on polymer molecular weight and polydispersity.

0267-8292/91 $3·00

2. Suitability of gel permeation chromatography and of polystyrene standards for molecular weight determination

With the help of oligomeric fractions of polyesters it is often possible to use internal standards for a calibration. For instance for polyester **P1** [1] the distribution curve gained from a GPC chromatogram contains a sequence of relative maxima as listed in table 1. On the assumption that the distances between these relative maxima, which nearly follow a logarithmic function, represent the growth of one repeating unit, a calibration plot may be obtained (see figure 1). Comparing this calibration with the retention volumes of polystyrene standards (see table 1 and figure 1) considerable differences exist only for the lower oligomers ($P = 1, 2, 3$). Oligomers of increasing molecular weight ($P = 4$–8) seem to approach the calibration curve with polystyrene standards asymptotically. Whether the curves intersect each other at higher molecular weight cannot be seen. By extrapolating the calibration curve for the oligomers, however, quite a good conformity with the polystyrene standards is observed. For

Table 1. Comparison of the molecular weights of oligomers of polyester **P1** with polystyrene standards (see also figure 1).



Degree of polymerization (P)	Retention volume of the oligomer signals/ml	$M_{standard}$	$M_{calculated}$†
1	37·4	—	675
2	36·0	600	1335
3	34·6	1100	1995
4	33·6	2000	2655
5	32·9	2500	3315
6	32·3	3200	3975
7	31·8	4200	4635
8	31·4	5100	5295
‡	37·7	—	410
1·5§	36·7	—	942 or 1068

† Molecular weight of oligomers calculated with the molecular weight of the repeating unit.
‡ Educt **11** [9].
§ Additional signal which agrees with the molecular weight of a substance composed of three molecules (2 + 1) of the condensation components.

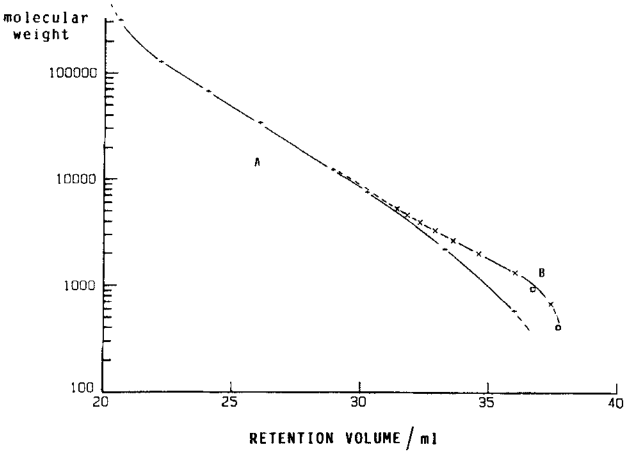


Figure 1. Calibration curves with (A) the polystyrene standards (+) and (B) the oligomers of **P1** (×), to (□) (cf. footnotes ‡ and § of table 1).

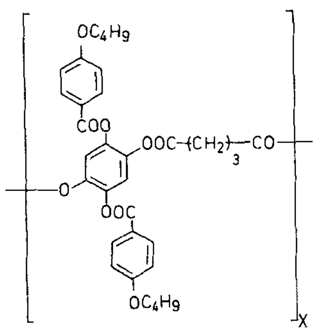
several polyesters [1–3] such agreement has already been seen. If the polyesters had an average of more than 30 repeating units it was useful to make a GPC chromatogram of the raw, unfractionated polyester. The signals of the oligomers still present could then be used for calibration as we have described.

3. Fractionation of a polyester with laterally attached mesogens via high pressure preparative gel permeation chromatography

With preparative gel permeation chromatography it was possible to obtain higher resolutions than via fractionated precipitation [1]. Polyester **P8** [1] with laterally attached 2,5-di(*p*-butoxy)benzoyloxybenzene groups as mesogens was separated into 25 fractions (see figure 2 and table 2). The polydispersity of all but one fraction is low (1·1) and the shapes of the distribution curves are comparable to each other. The differential distribution curves of every third fraction, starting with the combined fractions 6 + 7 are given in figure 2 and compared with the original distribution curve of polyester **P8** before fractionating. The molecular weights determined by analytical GPC and the phase behaviour of the fractions are given in table 2. The dependence of the transition temperature on the molecular weight of all the fractions with comparable polydispersity is summarized in figure 3.

As for classical liquid-crystalline main chain polymers with longitudinally attached mesogens [4, 5], all of the transition temperatures increase with increasing molecular weight. The clearing temperatures show the strongest variation: fraction 25 with the lowest molecular weight has no mesophase. Starting from the combined fraction 23 + 24 with a molecular weight of about 2700, the clearing point increases from 85°C to about 137°C. Above a molecular weight of about 10 000 (M_W) the clearing temperature varies very little and is practically constant above a molecular weight of about 20 000 (M_W). The dependence of the glass transition is less marked and nearly constant above a molecular weight of about 10 000 (M_W). The influence on the melting temperatures is even less pronounced.

It is not possible to change from a monotropic to an enantiotropic nematic phase by increasing the clearing temperature via increasing molecular weight as reported for



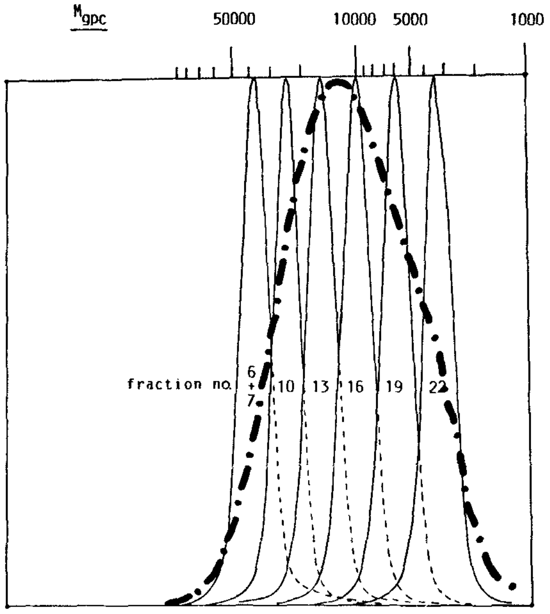


Figure 2. Molecular weight distributions of the polyester **P8** (—·) and some fractions obtained from preparative GPC.

classical main chain polyesters with dibenzoyloxybenzene as the mexogenic unit [5]. In contrast, we can observe from DSC heating curves (see figure 4) and a plot of the melting enthalpy (indium calibration) versus molecular weight (see figure 5) that the intensity of crystallization also decreases drastically with decreasing molecular weight. Fraction 20 with a molecular weight of 5400 (M_W) does not crystallize at all, even after annealing. In contrast to the results for classical main chain polyesters [5], therefore, a stable mesophase can be obtained at a low molecular weight.

The heating curves (see figure 4) also give an insight into the recrystallization behaviour. With increasing molecular weight we observe crystallization in the heating curve of fraction 19 for the first time. For fractions with higher molecular weight the endothermic transitions at the clearing temperature are more and more hidden by the exothermic recrystallization. The position of the recrystallization is about 120 to 130°C with a heating rate of 20°C/min in these cases. The nematic–isotropic transition

Table 2. Molecular weights and phase behaviour of the fractions of polyester **P8** [1] (see formula, figure 2).

Fraction	M_{GPC}	P_{GPC}	M_W	M_N	U	t_g†/°C	t_{NI}†/°C	ΔH_{NI}†/J g^{-1}	B‡/°C	t_{CI}†/°C	ΔH_{CI}†/J g^{-1}
§	13000	22	16200	8100	2·0	56	130	4	15	169	18
1–5	40000	68	50000	24000	2·1	51	(135)	4	23	166	5
6+7	37000	63	38000	34000	1·1	54	137	4	/	168	14
8	32000	54	33000	30000	1·1	55	138	4	8	169	9
9	28000	47	29000	27000	1·1	‖					
10	24000	41	26000	23000	1·1	53	(136)	4	/	168	15
11	21000	36	21500	19000	1·1	‖					
12	18000	30	19000	17000	1·1	54	(133)	4	10	169	16
13	15500	26	16000	14500	1·1	‖					
14	13000	22	14300	12700	1·1	49	(131)	3	/	169	23
15	11500	19	12000	10800	1·1	53	(128)	4	/	168	26
16	9500	16	10500	9500	1·1	49	125	4	14	165	24
17	8000	14	8800	8000	1·1	48	123	4	/	166	17
18	6900	12	7700	6800	1·1	43	119	4	/	163	13
19	5700	10	6200	5700	1·1	42	117	4	16	157	3
20	4700	8	5400	4800	1·1	43	113	4	15	—	—
21	3900	7	4500	4000	1·1	37	107	3	20	—	—
22	3500	6	3800	3400	1·1	38	103	3	25	—	—
23+24	2700	5	2800	2500	1·1	35	85	2	35	—	—
25+	1900	3	¶	¶		28	—	—	—	—	—

† t_g, glass transition; t_{CI}, melting temperatures; t_{NI}, clearing temperature; ΔH_{NI} and ΔH_{CI}, phase transition enthalpies at the clearing and melting points, respectively, determined by DSC with a heating rate of 20°C/min. The values in brackets were calculated [10] from the curves obtained with rates of 40 and 80°C/min.

‡ B, the broadness of the nematic–isotropic transitions measured with a heating rate of 40°C/min was calculated in the following way: the tangents of the two turning points of the transition signal were constructed. The value for the broadness was defined as the distance between the intersections of the tangents with the base line. Only those values which could be obtained without problems were used.

§ Original polyester **P8** before fractionating.

‖ No measurements were carried out with these fractions.

¶ Because of the shape of the GPC curve, the calculation of the number and weight average had no meaning.

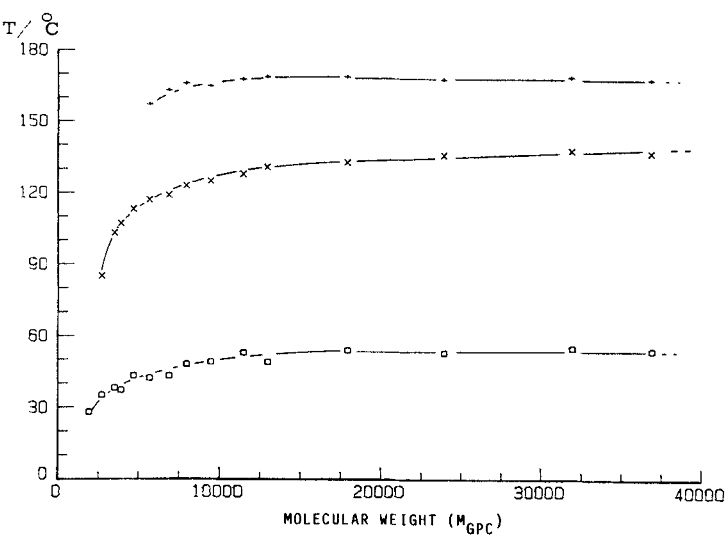


Figure 3. Dependence of the transition temperatures for the fractions of polyester **P8** (for the formula, see figure 2) on molecular weight; +, melting temperature; ×, clearing temperature; □, glass transition.

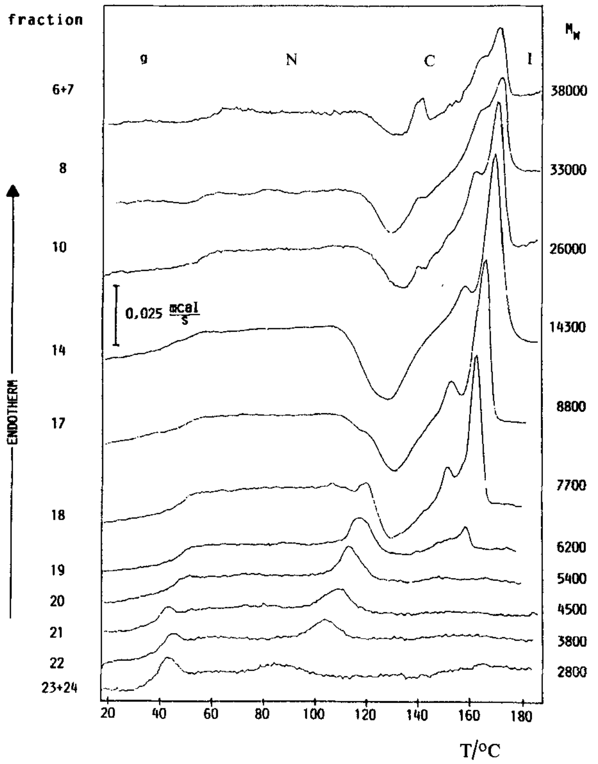


Figure 4. DSC heating curves for the fractions of polyester **P8** (for the formula, see figure 2) with respect to the molecular weight.

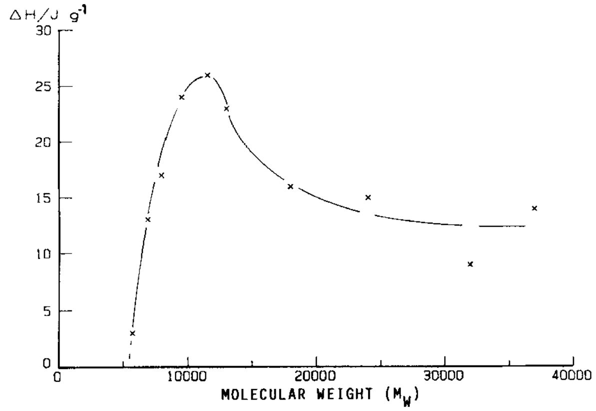


Figure 5. Melting enthalpy of polyester **P8** (for the formula, see figure 2) with respect to the molecular weight (values determined by DSC; all samples pretreated in the same way; heating rate: 20°C/min).

increases until 137°C with increasing molecular weight; the endothermic clearing transition of the high molecular weight fractions (6–10) becomes positioned on the right-hand side of the minimum of the exothermic recrystallization signal therefore, instead of the left-hand side. Additionally, with increasing molecular weight, the melting enthalpies become smaller again (see figure 5): the polymer fractions crystallize more slowly because of increasing viscosity. The crystallization tendency is strongest at medium molecular weights; for polyester **P8**, at about 12 000 (M_W). At lower molecular weights, the crystallization tendency is weaker and disappears for the oligomeric case, probably because of the influence of the chain end groups.

Plotting the broadness of the clearing transition, which may be obtained from the DSC measurements as well as from the biphasic region (isotropic and nematic) observed in the polarizing microscope versus molecular weight, a hyperbolic relation can be seen (see figure 6). The broadness of the biphasic region is approximately

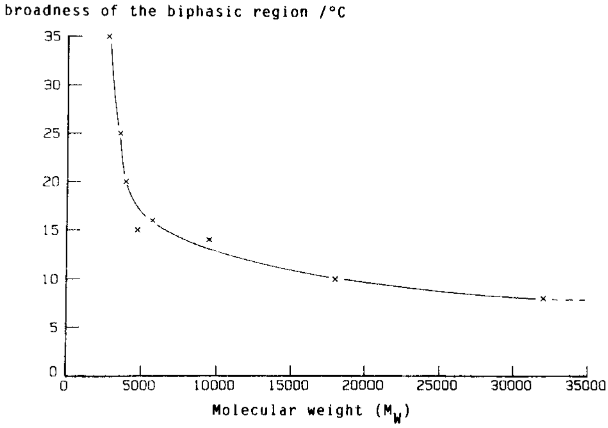


Figure 6. Broadness of the nematic–isotropic transition for polyester **P8** (for the formula, see figure 2) versus molecular weight.

proportional to the reciprocal of the molecular weight. At high molecular weight the polymer chains of different length and a polydispersity of 1·1 have practically the same properties. The polydispersity of a sample has an influence, therefore, only on the broadness of the nematic–isotropic transition when either the polydispersity is high (compare fraction 1–5 with fraction 8 in table 2) or at low molecular weight. In this respect, the differences in the phase behaviour of the oligomeric chain content are apparent. For nematic main chain polymers of the classical structure, the existence of the biphasic region is explained by an enrichment of the longer polymer chains in the nematic part of the biphasic region and an additional separation based on molecular weight in the nematic domains [6]. The areas of polymer chains with a high molecular weight are distinguished by a higher transition entropy [7], a higher order parameter [4, 8] and a higher clearing point, as mentioned already. These considerations could probably explain the existence of the biphasic region also for polyester **P8** with laterally attached mesogens in the main chain. However, these properties are based on a molecular weight dependent correlation between the mesogenic repeating units and may differ for polyesters with laterally attached mesogens.

By combining different fractions as given in tables 2 and 3, we can obtain samples of polyester **P8** with nearly the same average molecular weight but with different molecular distribution curves. Samples U1–U3 possess a monomodal distribution of different polydispersities. Samples U4 and U5 have a bimodal distribution. The distribution curves and comparable DSC curves obtained from them are shown in figure 7. The position of the melting and clearing transitions are nearly independent of polydispersity and the shape of the distribution. However, an influence on the speed and intensity of the recrystallization can be noted. Although the melting enthalpy of samples U1–U3 (see table 3) is nearly identical, sample U1 with the highest polydispersity crystallizes more slowly than U2, which is even more slowly than U3. The higher the intensity of recrystallization, the smaller is the endothermic nematic-isotropic transition (see figure 7). The samples with a bimodal distribution of molecular weight behave in a way that could be expected from samples with a monomodal distribution but with a higher polydispersity. In this regard, U5 recrystallizes more slowly then U1, although the calculated polydispersity of U5 is smaller.

It is remarkable that no new or additional liquid-crystalline phases could be observed, either by varying the molecular weight or by varying the molecular distribution.

4. Influence of the molecular weight on the phase transitions of a polyester with cross-shaped mesogens

A polyester with cross-shaped mesogens (**P43** [2]) was fractionated in the same way as sample **P8** containing laterally attached mesogens (see figure 8). Because of the higher molecular weight of the original polyester **P43**, the separation was more difficult and the fractions obtained had a higher polydispersity which decreased with decreasing molecular weight (see table 4). Because of the relatively small influence of the polydispersity on the transition temperatures, a detailed comparison of the different fractions was also undertaken in this case to compare the influence of varying molecular architecture.

Phase behaviour dependence on molecular weight can be discussed using the DSC heating curves (see figure 9) and the plot shown in figure 10 in the following way: the *glass transition* changes only little with increasing molecular weight and is constant above 20 000 (M_W). As for polyester **P8**, the fractions with 20–30 repeating units

Table 3. Influence of the molecular weight distribution on the phase behaviour of polyester **P8** [1] (for the formula, see figure 2).

Sample No.	M_{GPC}	P_{GPC}	M_W	M_N	U	t_{CI}†/°C	ΔH_{CI}†/J g^{-1}	t_{NI}†/°C	ΔH_{NI}†/J g^{-1}
U1§	13000	22	16200	8100	2·0	169	18	130	4
U2	13000	22	14700	11300	1·3	169	20	(133)	3
U3	13000	22	14300	12700	1·1	169	23	(131)	3
U4	18000 + 9000	30 + 15	14700	10600	1·4	169	19	(132)	3
U5	24000 + 6800	41 + 12	16500	9100	1·8	166	6	130	3

†, § See footnotes to table 2.

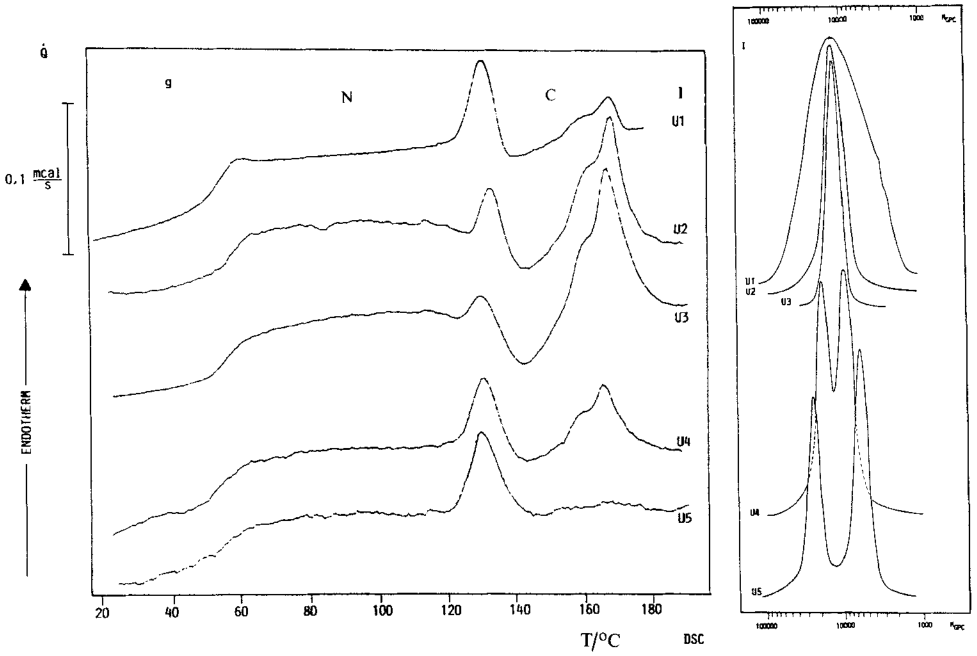
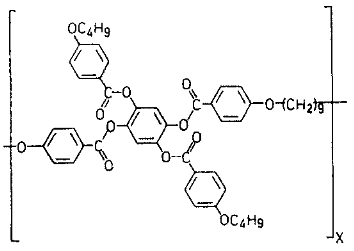


Figure 7. Molecular weight distributions and DSC heating curves for different samples of polyester **P8** (for the formula, see figure 2).



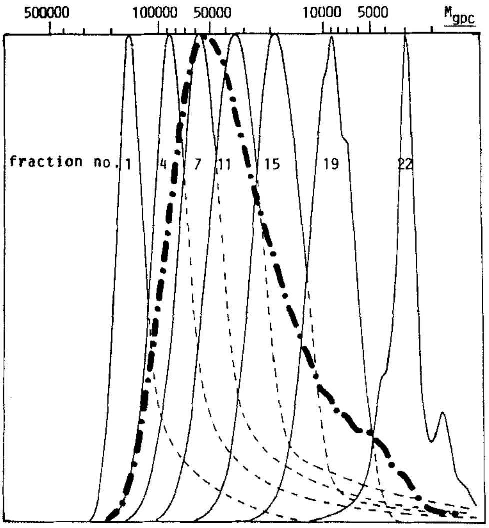


Figure 8. The molecular weight distribution of polyester **P43** (—·) with some fractions obtained from preparative GPC.

Table 4. Molecular weights and phase behaviour of the fractions of polyester **P43** [2] with cross-shaped mesogens (for the formula, see figure 8).

Fraction	M_{GPC}	P_{GPC}	M_W	M_N	U	t_g†/°C	t_{CN}†/°C	ΔH_{CN}†/J g^{-1}	t_{NI}†/°C	ΔH_{NI}†/J g^{-1}
‡	53000	62	50000	21000	2·4	44	168	9	191	4
1	145000	169	117000	65000	1·8	§				
2	120000	140	96000	49000	2·0	42	163	6	193	4
3	105000	122	88000	47000	1·9	44	163	7	192	4
4	90000	105	79000	41000	1·9	43	163	7	192	4
5	80000	93	70000	35000	2·0	39	165	7	192	4
6	64000	75	57000	30000	1·9	44	167	9	191	4
7	58000	68	52000	26000	2·0	§				
8	50000	58	47000	24000	2·0	39	166	9	190	4
9	44000	51	42000	22000	1·9	41	165	9	190	4
10	39000	45	38000	19000	2·0	40	166	10	190	4
11	35000	41	34000	18000	1·9	42	165	10	188	4
12	30000	35	29000	16000	1·8	39	164	10	188	4
13	26000	30	26000	15500	1·7	40	163	12	187	4
14	23000	27	22000	14500	1·5	39	160	13	186	4
15	19500	23	19300	13700	1·4	36	157	13	—	—
16	17000	20	16300	12500	1·3	35	153	13	—	—
17	14000	16	14000	11600	1·2	35	143	14	—	—
18	11000	13	12300	9900	1·2	35	139	12	—	—
19	9000	10	9800	8700	1·1	34	127	10	—	—
20	7000	8	7200	6600	1·1	34	133	10	—	—
21	4800	5–6	4800	4400	1·1	33	—	—	—	—

† t_g, glass transition; t_{CN}, melting temperature; t_{NI}, clearing temperature; ΔH_{CN} and ΔH_{NI}, phase transition enthalpies at the melting point and clearing point, respectively. Values determined by DSC with a heating rate of 20°C/min.

‡ Original polyester **P43** before fractionation.

§ No measurements were carried out with these fractions.

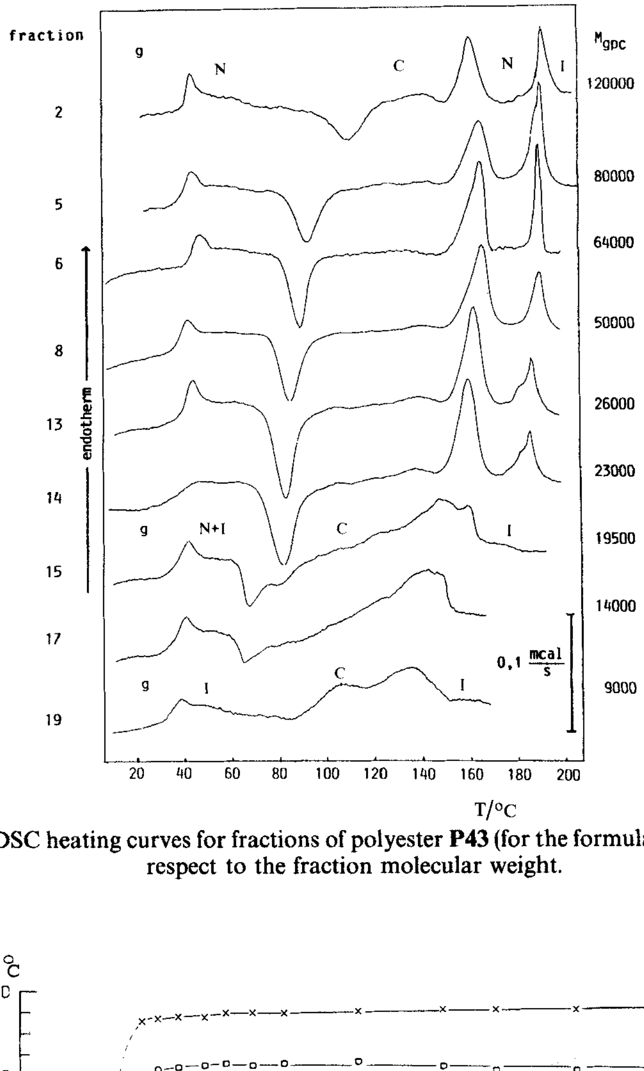


Figure 9. DSC heating curves for fractions of polyester **P43** (for the formula, see figure 8) with respect to the fraction molecular weight.

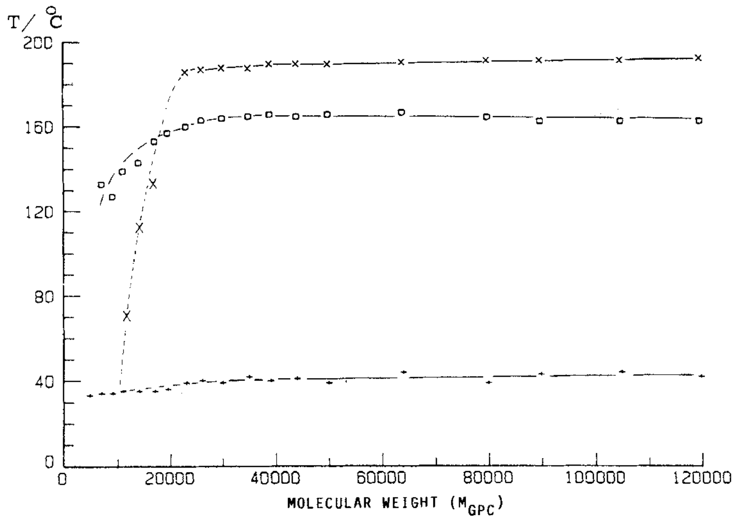


Figure 10. Dependence of phase transition temperatures for the fractions of polyester **P43** (for the formula, see figure 8) on the fraction molecular weight; +, glass transition; □, melting point; ×, clearing point.

recrystallize the earliest above the glass transition and have the highest exothermic transition enthalpy. In contrast to polyester **P8**, the low molecular weight fractions of polyester **P43** also recrystallize. The *melting point* increases by about 40°C in this case with increasing molecular weight and is constant above 30 000 (M_W). In addition, the melting transition becomes sharper. The most significant changes occur at the *clearing temperatures*. With decreasing molecular weight from about 120 000 to 25 000 (M_W) the clearing point is constant at about 190°C and the transition becomes broader below about 50 000 (M_W). In fraction 15 the transition is broad, more than 20°C, and has, in part, a monotropic character as observed with the polarizing microscope. At lower molecular weight the liquid-crystalline phase could be seen only with the polarizing microscope because of the very broad nematic–isotropic transition. At a molecular weight of 16 000 (M_W) the clearing region is about 130°C, at 14 000 (M_W) about 110°C and the fraction of about 12 000 (M_W) is partially isotropic already above the glass transition. Below a molecular weight of about 10 000 (M_W) there exists no mesomorphic behaviour, in contrast to some monodisperse low molecular weight model compounds [9]. Why the liquid-crystalline phase changes so dramatically above a relatively high molecular weight is not yet understood.

5. Experimental

5.1. *Analytical gel permeation chromatography*

Molecular weights of the polymer fractions were measured using an analytical GPC (Waters) equipped with 10^3 Å and 10^4 Å PL-gel columns (Polymer Laboratories; $l = 2 \times 600$ mm; $d = 7$ mm). Chloroform was used as eluent with a flow rate of 1 ml/min. Polystyrene standards (see figure 1) were supplied by Merck. Calibration, as well as single measurements, were reproducible with aberrations of about 1 s during a running time of about 35 min. The longitudinal diffusion of the instrument configuration used could be neglected; a monodisperse model compound **25** [9] ($M = 902$) showed a GPC chromatogram with a calculated polydispersity smaller than 1·01. The peak maxima of the elution curves were taken as M_{GPC} values; the M_N and M_W values were calculated by progressive integration of the elution curves. The polydispersity was calculated from the quotient of M_W and M_N ($U = M_W/M_N$).

5.2. *Preparative gel permeation chromatography*

Preparative fractionation of the polyesters was carried out under similar conditions as those used for analytical GPC. A preparative HPLC pump equipped with a RI, UV detector and a fraction collector (Knauer) were used in addition to 10^3 Å and 10^4 Å PL-gel columns (Polymer Laboratories; $l = 2 \times 600$ mm; $d = 25$ mm). The eluent was chloroform with a flow rate of 10 ml/min. Each sample was fractionated three separate times (30 mg each), the fractions with identical elution time combined, and all fractions subsequently analysed by analytical GPC.

Differential scanning calorimetry was carried out as described previously [1]. Textures were observed with a POL-BK II polarizing microscope (Leitz) equipped with a FP 5 hot stage (Mettler).

References

[1] KRONE, V., RINGSDORF, H., EBERT, M., HIRSCHMANN, H., and WENDORFF, J. H., 1991, *Liq. Crystals*, **9**, 165.

[2] KRONE, V., RINGSDORF, H., EBERT, M., HIRSCHMANN, H., and WENDORFF, J. H., 1991, *Liq. Crystals*, **9**, 195.

[3] BERG, S., KRONE, V., and RINGSDORF, H., 1986, *Makromolek. Chem. rap. Commun.*, **7**, 381.

[4] Blumstein, R. B., Stickles, E. M., Gauthier, M. M., and Blumstein, A., 1984, *Macromolecules*, **17,** 177.

[5] Zhou, Q.-F., Duan, X.-Q., and Liu, Y.-L., 1986, *Macromolecules*, **19,** 247.

[6] Volino, F., Allonneau, J. M., Giroud-Godquin, A. M., Blumstein, R. B., Stickles, E. M., and Blumstein, A., 1984, *Molec. Crystals liq. Crystals*, **102,** 21.

[7] Blumstein, R. B., Stickles, E. M., and Blumstein, A., 1982, *Molec. Crystals liq. Crystals Lett.*, **82,** 205.

[8] Blumstein, R. B., Blumstein, A., Stickles, E. M., Poliks, M. D., Giroud, A. M., and Volino, F., 1983, *Polymer Preprints*, **24,** 275.

[9] Berg, S., Krone, V., Ringsdorf, H., Quotschalla, U., and Paulus, H., 1991, *Liq. Crystals*, **9,** 151.

[10] Illers, K.-H., 1974, *Polym. J.*, **10,** 911.