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Liquid-crystalline monomers, dimers and side group polymers containing phenylpyrimidine mesogens

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Liquid-crystalline monomers, dimers and side group polymers containing phenylpyrimidine mesogens

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Phenylpyrimidine derivatives were used to synthesize monomers, dimers and side group polymers. Only a few monomers and dimers show liquid-crystalline behaviour whereas almost all of the polysiloxanes, polyacrylates and polymethacrylates prepared possess enantiotropic liquid-crystalline phases. The structure of the main chain and of the mesogenic unit as well as the length of the spacer and of the terminal groups were modified. The relation between structure and phase behaviour is discussed.

1. Introduction

Heterocyclic rings in liquid crystals

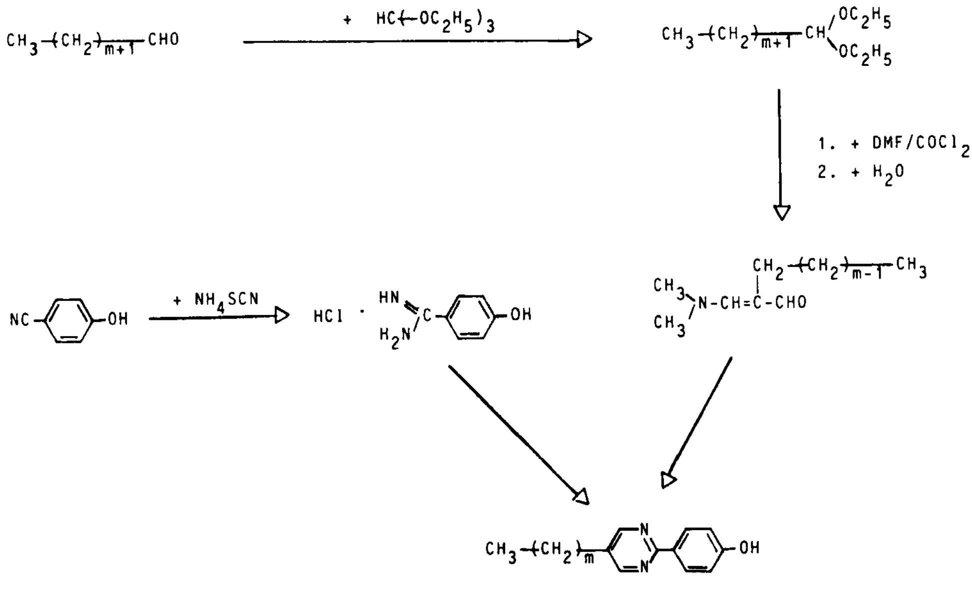
Structural variations of liquid-crystalline polymers [1] can be accomplished by two methods; either by modifying the classical structures of main chain and side group polymers [2, 3] or by changing single elements of the polymers such as the spacer group, the polymeric backbone or the mesogenic group. This paper is concerned with the second approach, namely the introduction of phenylpyrimidines as mesogenic side groups in polyacrylates, polymethacrylates and polysiloxanes.

The replacement of aromatic rings in phenyl benzoate or biphenyl containing mesogens by aromatic and non-aromatic heterocyclic units has been of particular interest for low molar mass liquid crystals. Dithianes [4-7], different dioxane derivatives [7-13], saturated or unsaturated rings with one to four nitrogen atoms [13-21], heterocyclic rings with two different types of heteroatoms such as oxathianes [22], mesogens with two different heterocyclic rings [23] or even boron containing rings [24] have been described. Low molar mass mesogens containing 1,3-dioxane and 2,5-disubstituted phenylpyrimidine units [25-33] are of particular interest because of their wide nematic ranges and their favourable properties for liquid crystal displays. Mixtures with phenylpyrimidines as mesogenic units possess an especially favourable high degree of orientational order, suitable elastic constants and a high polarizibility for such applications. Contributing to the highly mesogenic character of phenyl substituted pyrimidine derivatives is the planar alignment of their aromatic rings and subsequently the uninterrupted resonance interaction of the aromatic rings. In addition, the nitrogen atoms in the heterocyclic rings contribute towards a high positive anisotropy [31].

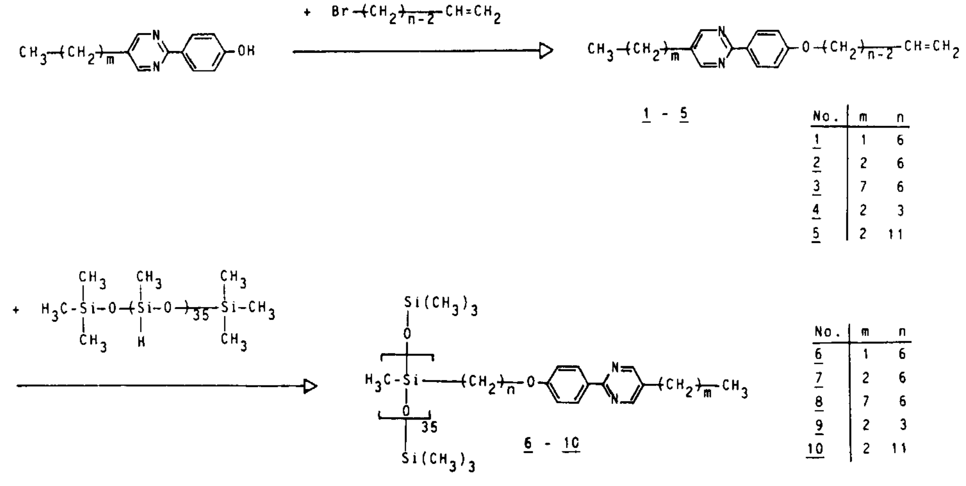
Surprisingly polymeric liquid crystals containing heteroaromatic rings as mesogens have received little attention. The first reports were those concerning the synthesis and characterization of side-chain liquid-crystalline polymers containing mesogens with 1,3-dioxane units [34, 35]. To our knowledge there are neither reports of liquid-crystalline polymers nor of dimeric mesogens [40–47] with the phenylpyrimidine group. In this contribution we describe the synthesis and characterization of liquid-crystalline precursors, low molar mass liquid crystals having two mesogenic units, polyacrylates, polymethacrylates and polysiloxanes containing the phenylpyrimidine group.

2. Synthetic routes to dimers and side group polymers with the phenylpyrimidine group

There are several routes to synthesize 2,5-disubstituted pyrimidines [25, 30, 31, 36]. A convenient method [27] is the condensation of α-alkyl-β-dimethylamino-acroleins [37, 38] with *p*-substituted phenylamidines [39]. The resulting 2-(4-hydroxyphenyl)-5-alkylpyrimidines used in this work were synthesized according to this procedure



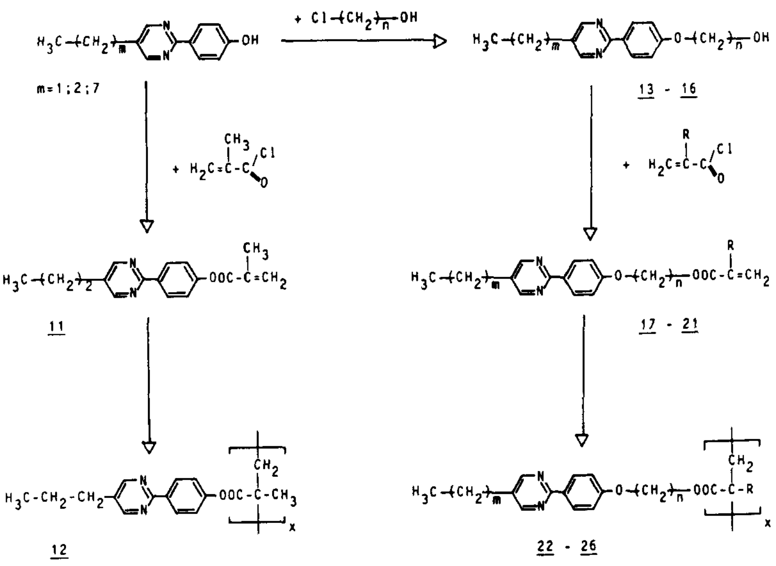
Scheme 1.



No.	m	n
1	1	6
2	2	6
3	7	6
4	2	3
5	2	11

No.	m	n
6	1	6
7	2	6
8	7	6
9	2	3
10	2	11

Scheme 2.

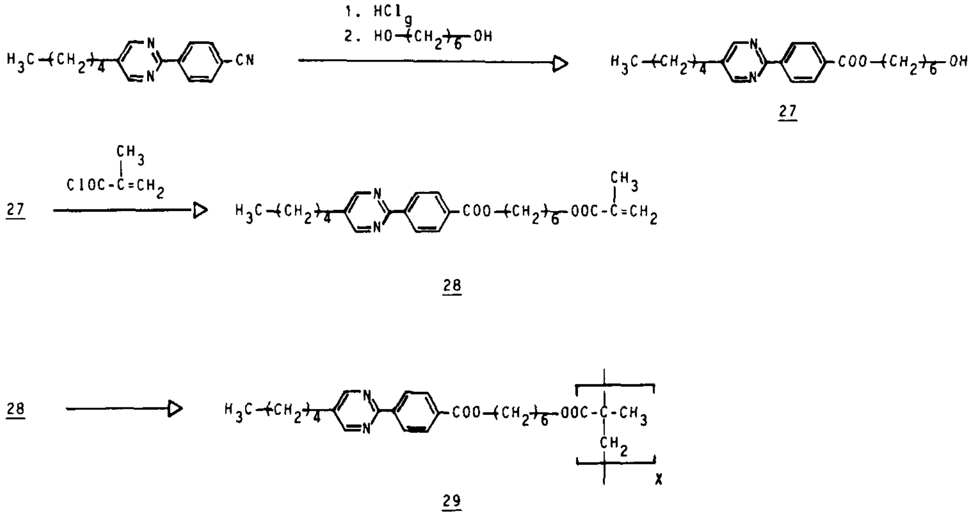


No.	m	n
13	1	6
14	2	6
15	2	2
16	7	6

No.	m	n	R
17	1	6	CH_3
18	2	6	CH_3
19	2	2	CH_3
20	7	6	CH_3
21	7	6	H

No.	m	n	R
22	1	6	CH_3
23	2	6	CH_3
24	2	2	CH_3
25	7	6	CH_3
26	7	6	H

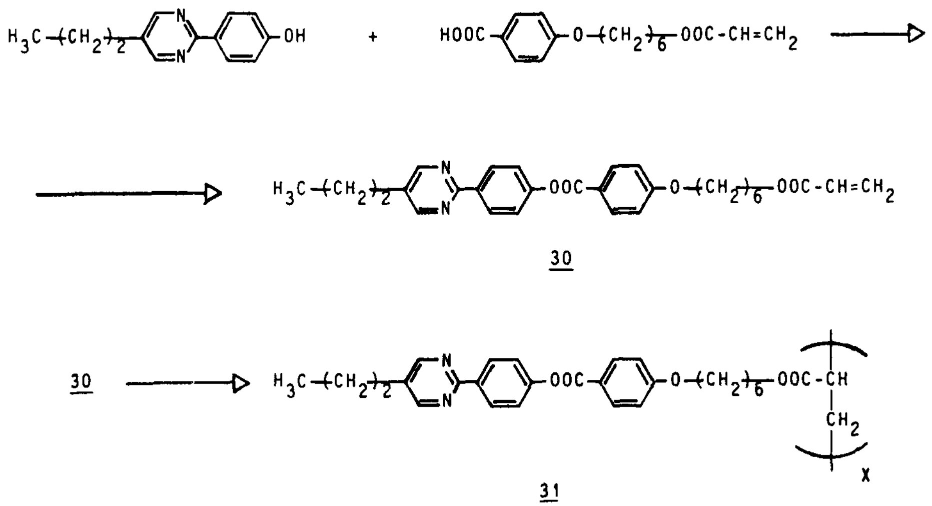
Scheme 3.



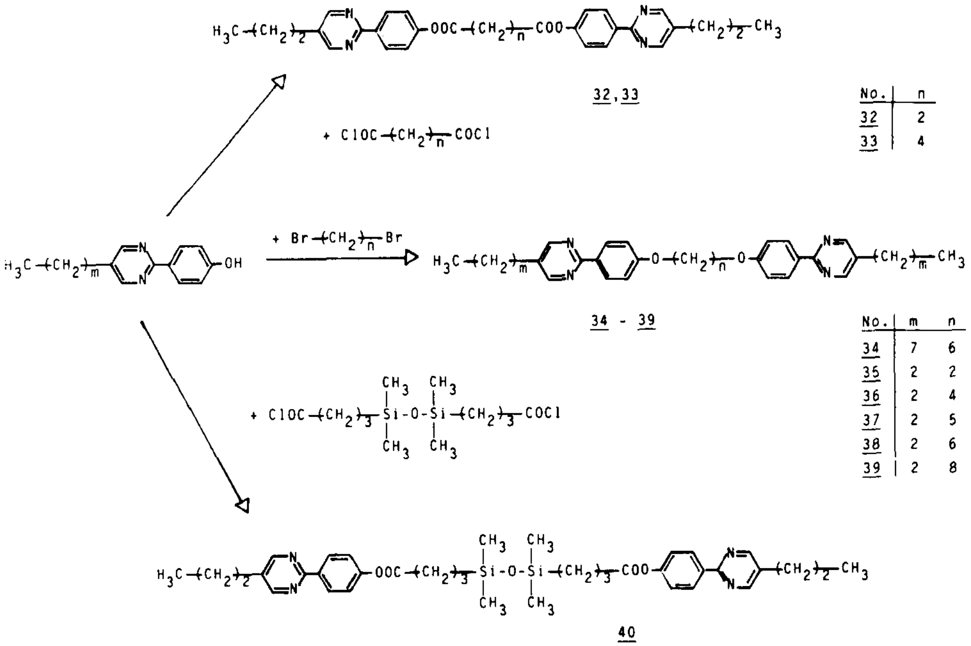
Scheme 4.

as sketched out in scheme 1. The synthetic route to polysiloxanes is given in scheme 2, to polyacrylates and polymethacrylates in schemes 3 and 5 and to dimers in scheme 6. An alternative route starting from a cyanophenylpyrimidine to obtain a polymethacrylate with an ester linkage between the mesogen and spacer is given in scheme 4.

The transition temperatures and enthalpies for the monomers, the dimers and the polymers are summarized in tables 1–3. The molecular weights for the polymers in table 3 were measured by analytical GPC calibrated against polystyrene standards. For the polysiloxanes, the magnitudes of the molecular weights correspond to the values predetermined by the poly(methylhydrogensiloxane) which was used.



Scheme 5.



No.	n
32	2
33	4

No.	m	n
34	7	6
35	2	2
36	2	4
37	2	5
38	2	6
39	2	8

Scheme 6.

3. Results and discussion

3.1. *Mesomorphic properties of the precursors*

The low molecular weight phenylpyrimidines containing a terminal alkyl group on one side and a functional ether group on the other side (**1–5**, **13–21**, schemes 2, 3) show the following phase behaviour.

Table 1. Properties of the monomers and the precursors (see schemes 2–5)

Number	Phase transition temperatures/°C (*a*)	Transition enthalpies/J g^{-1}
1	K 47 I	91
2	K 52 I	93
3	K_1 41 S 49 N 52·5 I (K_2 26)(*b*)	109/6·9/4·1 (75)
4	K 72 I	87
5	K 59 I	99
11	K 98 I (*c*)	91
13	K 62 I	69
14	K 71 I	97
15	K 103 I	107
16	K 70 I (S 61 N 65)	64 (5/6)
17	K 48 I	94
18	K 62 I	99
19	K 97 I	104
20	K (*d*) −9 S 42 N 52 I	38/10/2
21	K 45–50 N 53 I (S 52,5)(*e*)	80–130/11 (33)(*e*)
27	K 66 (S 55 N 58) I (*f*)	
28	K 45 I (*f*)	
30	K_1 83 K_2 87 N 156 I (*g*)	83(*h*)/1·9

(*a*) K, K_1, K_2, crystalline phases; S, smectic phase; N, nematic phase.

(*b*) A second, unstable crystalline modification exists melting at 26°C.

(*c*) Only 8–10°C supercooling.

(*d*) Only 5°C supercooling: K is probably a higher ordered smectic phase.

(*e*) Complex melting behaviour: depending on pre-treatment several melting and recrystallization processes occur. Employing a special treatment it is possible to obtain a mobile smectic phase changing to the nematic phase just below the clearing point.

(*f*) Measured by polarizing microscopy.

(*g*) The sample changes during measurement; probably it starts to polymerize.

(*h*) ΔH_{K_1-N}

Table 2. Properties of molecules containing two phenylpyrimidine groups as mesogenic units (see scheme 6)

Number	Phase transition temperatures/°C (*a*)	Transition enthalpies/J g^{-1}
32	K 184 I	102
33	K_1 143 K_2 170 N 173 I	26/68/12·2
34	K 66 S 143 N 147 I	46/75/12
35	K 235 I	127
36	K 198 I (S 183 N 194) (*b*)	140(78/15)
37	K 133 I	83
38	K_1 108 K_2 152 N 171 I	4,6/80/16·5
39	K_1 128 K_2 155 S 158 I	17/5·0/78
40	K 102 I	63

(*a*) K, K_1, K_2, crystalline phases; S, smectic phase; N, nematic phase.

(*b*) Monotropic liquid-crystalline phases; the transition temperatures are taken from the D.S.C. cooling curve.

Table 3. Properties of the polymers (see schemes 2–5).

Number	Phase transition temperatures/°C (*a*)	Transition enthalpies/J g^{-1} S_yS	SS	LC-I	Molecular weight (*b*)/g mol^{-1}
6	g −11 N 14 I			1·5	12 000 (*c*)
7	g −11 N 44 I			2·2	16 000 (*c*)
8	g −8 S_x 12 S 110 I		6·3	9·7	17 500 (*c*)
9	g −7 S 56 I			1·1	8 000 (*c*)
10	g −10 S_y 26 S_x(*d*) 31 S 79 I	1·1	0·6	6·1	17 500 (*c*)
12	g 167 S 263 I			4·7	22 000
22	g 27 N 42 I			2·3 (*e*)	17 000
23	g 39 N 62 I			2·2	30 000
24	g 83 I				10 000
25	g 29 S 96 I			9·5	45 000
26	g 7 S_A 97 I			13	7 000
29	g 37 S 133 I			14·5	27 000
31	g 21 N 165 I (*f*)			3	12 000

(*a*) S, disordered smectic phase (S_A or S_C); S_A, smectic A; S_x, S_y, smectic phases not further specified; N, nematic; g, glassy.

(*b*) Values determined by GPC based on polystyrene as standard.

(*c*) The values calculated from the oligosiloxane used (DP-35; Merck) are **6**, 12 000; **7**, 12 500; **8**, 14 900; **9**, 11 000; **10**, 14 900.

(*d*) The D.S.C. heating and cooling curves do not reach the base line between the two endothermic transition peaks at 26° and 31°C.

(*e*) An endothermic transition at the clearing temperature could only be detected by D.S.C. by annealing the sample in the glass transition.

(*f*) Broad biphasic region at about 155–170°C.

The phenylpyrimidines with two short terminal groups (**4**, **15**, **19**) are characterized by relatively high melting points and the absence of a liquid-crystalline phase. Lengthening the alkyl portion of the ether group causes the melting points to drop (**1**, **2**, **5**, **13**, **14**, **17**, **18**); however, a liquid-crystalline phase could only be obtained from phenylpyrimidines containing two longer terminal groups **3**, **16**, **20**, **21** in spite of their different functional ends. The alcohol **16** shows monotropic liquid-crystalline phases as does the alcohol **27** (scheme 4) with an ester linkage between the central rings and the terminal group. The monomers **20**, **21** and the precursor **3** possess enantiotropic liquid-crystalline phases, all clearing at about 53°C. This is several degrees lower than the clearing point of the 5-*n*-octyl-(4-*n*-hexyloxy-phenyl)-pyrimidine described by Schubert and Zaschke (K 27·5 S_C 44·5 S_A 57·5 N 65 I) [25]. It would appear that a functional end group diminishes the stability of the liquid-crystalline phases. In case of the methacrylate **20** with a branched terminal group, the melting point drops significantly in comparison to that for the acrylate **21**.

3.2. *Mesomorphic properties of the dimers*

All the phenylpyrimidines containing two mesogenic units (scheme 6, table 2) show markedly increased melting points in comparison to the monomers (cf. table 1). Only for the dimer **34** containing a hexamethylene spacer and two long terminal groups is a broad, highly viscous smectic phase observed. All the other dimeric phenylpyrimidines exhibit liquid-crystalline ranges which are very narrow. The dimers with short spacers (**32**, **35**) do not posess liquid-crystalline phases. Monotropic liquid-crystalline phases are obtained if the two mesogenic units are combined with a tetramethylene spacer and ether linkages (**36**). For those mesogens containing ester linkages, the corresponding dimer (**33**) shows a short nematic phase. Comparing the dimers **36**, **38**, **39** with the phenylpyrimidine **37** containing an odd number of methylene units, a marked odd–even effect can be distinguished. In the same way as the dimer **37**, the siloxane **40** shows a decreased melting point, and no liquid-crystalline phase, not even monotropic, can be observed.

3.3. *Mesomorphic properties of the polymers*

In contrast to some of the dimers, and especially to most of the monomers, all the polymers prepared except **24** possess liquid-crystalline phases (table 3). In particular the siloxanes (**6**–**10**) show distinct textures and transitions although in some cases (**6**, **8**, **10**) the glass transition is close to a smectic–smectic transition or the clearing point. For example, samples of the nematic polysiloxanes **6** and **7** form marbled textures and after annealing for several hours homogeneous textures occur. The polyacrylates (**26**, **31**), and especially the polymethacrylates (**12**, **22**–**25**, **29**), behave differently. At temperatures of 30–50°C above the glass transition samples of these polymers are still quite viscous. For the polymethacrylates **23** and especially **22** this viscosity results in very long annealing times, with sometimes more than a week passing before a texture is observed. In addition, the enthalpy value at the clearing transition of polymethacrylate **22** measured by D.S.C. is the only one dependent on the annealing time. This seems reasonable because of the sluggish reorientation of the mesogenic groups only 10°C above the glass transition. The possibility of a partial crystallinity could be excluded by X-ray measurements. In contrast to the methacrylate **22**, the nematic phase of the polyacrylate **31** with a phenylpyrimidine benzoate unit has quite a wide temperature range. At higher temperatures, a schlieren texture is easily formed and in the biphasic region nematic droplets are observed. The observed smectic phases show mainly fan-shape textures and bâtonnets at the clearing point.

In addition the polyacrylate **26** forms a homeotropic texture suggesting a smectic A phase.

The influence of the terminal groups, the spacer segments and the polymer main chain on the phase behaviour is discussed in the following.

The influence of the terminal group can be appreciated by comparing the polysiloxanes **6**, **7**, **8** or the polymethacrylates **22**, **23**, **25**, which all possess six methylene units in the spacer segment. The phase behaviour changes as expected: if the terminal groups are short (**6**, **7**, **22**, **23**) the liquid crystalline phases are nematic. If the terminal group is an octyl moeity (**8**, **25**), wide smectic ranges (**25**: $d = 17$ Å) with higher transition enthalpies at the clearing point are observed.

To investigate the role of the spacer, the polysiloxanes **7**, **9**, **10** and the polymethacrylates **12**, **23**, **24** all possessing a terminal propyl unit can be compared: if there is no spacer between the main chain and the mesogen (**12**), the glass transition is very high and is followed by a smectic phase ($d = 9{\cdot}2$ Å). One explanation for this behaviour is the strong coupling between the main chain and the mesogenic groups. The polysiloxane **9** with a short spacer shows as well a smectic phase ($d = 11{\cdot}5$ Å) but the glass transition is already located approximately in the range of the other polysiloxanes with longer spacers (**7**, **10**). The corresponding methacrylate **24** shows a different behaviour: the glass transition is significantly higher than the other methacrylates containing a spacer group and also higher than the expected clearing temperature. The introduction of a spacer with six methylene groups (**7**, **23**) results in the occurrence of nematic phases; a long spacer with 11 methylene units (**10**) again causes smectic layers.

A good possibility of studying the influence of the polymeric main chain is provided by comparing the low molar mass analogue 5-*n*-octyl-(4-*n*-hexyloxy-phenyl)-pyrimidine (K 27·5 S_C 44·5 S_A 57·7 N 65 I) [25] with the polysiloxane **8**, the polymethacrylate **25** and the polyacrylate **26** all containing a hexyloxy spacer and the same octyl moiety as the terminal group. All three polymers do not crystallize and possess a much wider liquid-crystalline range. The polymeric chain consequently stabilizes the mesophase. With increasing stiffness of the backbone going from the polysiloxane (**8**) to the polyacrylate (**25**) and then to the polymethacrylate (**26**) the glass transition temperature is increasingly higher and the width of the liquid-crystalline range decreases.

4. Experimental

4.1. *5-n-alkyl-2-(4-alkenoxyphenyl)-pyrimidines (1–5)*

The starting 2-(4-hydroxyphenyl)-5-alkylpyrimidines were synthesized according to the procedure given by Zaschke and Stolle [27]. The purification of those derivatives with short alkyl substituents is best done by repeated precipitation from basic aqueous solutions with diluted acetic acid. To 5 mmol of the 2-(4-hydroxyphenyl)-5-alkylpyrimidines were added 1 g of dry pulverized potassium carbonate and 20 ml of acetone. Depending on the volatility a 1·2 to 2·0-fold excess of the ω-bromoalkene and a few crystals of potassium iodide was added. After refluxing and stirring vigorously for 1 week, the acetone was evaporated and the residue shaken with ether several times. The ethereal solution was dried over sodium sulphate and the ether evaporated. After recrystallization from acetone the product was further purified by column chromatography (silica gel; chloroform as eluent).

Number	**1**	**2**	**3**	**4**	**5**
m.p. °C	47	52	41	72	59
Yield per cent	92	98	81	55	82

4.2. *5-n-alkyl-2-(4-n-hydroxyalkoxyphenyl)-pyrimidine (**13–16**)*

10 mmol of the 5-*n*-alkyl-2-(4-hydroxyphenyl)-pyrimidine were added to 3 g of dry pulverized potassium carbonate, a trace of potassium iodide, 30 ml of acetone and either 11 mmol of 6-chlorohexanol or 20 mmol of 2-bromoethanol; the mixture was refluxed for 10 days with vigorour stirring. After evaporation of the solvent, the residue was shaken with chloroform. The solution was dried over sodium sulphate, evaporated and the product purified by column chromatography (silica gel; chloroform as eluent) followed by recrystallization from acetone. Of the starting material, 10–30 per cent was recovered.

Number	**13**	**14**	**15**	**16**
m.p. °C	62	71	103	70
Yield per cent	71	54	27	86

4.3. *4-(5-pentyl-2-pyrimidinyl)-benzoic acid 6-hydroxyhexylester (**27**)*

2 g of 5-pentyl-2-(4-cyanophenyl)-pyrimidine (8 mmol) and a 10-fold excess of 1,6-hexanediol were heated at 90°C. A stream of dry hydrogen chloride was introduced and the heterogeneous mixture became homogeneous. Two hours later the reaction mixture turned brown and contained an insoluble precipitate. The mixture was poured into 50 ml of ice-water and twice shaken with ether. The ethereal layer was washed quickly with aqueous sodium bicarbonate. After drying with sodium sulphate the ether and the 6-chlorohexanol ($\text{b.p.}_{\cdot 2\,\text{mm}}$ = 94°C) were removed by evaporation. The residue was purified by column chromatography (silica gel) with chloroform as eluent. The product, having a m.p. of 66°C was obtained in 16 per cent yield.

4.4. *Methacrylic acid esters (**11**, **17–20**, **28**)*

5 mmol of the respective alcohol or phenol were dissolved in 10 ml of dry pyridine. Freshly distilled methacrylic acid chloride, stabilized with di-*t*-butylcresol, was added cautiously in 20 per cent excess while cooling the reaction vessel. Some crystals of 4-dimethylaminopyridine were added and stirred for 10 hours while excluding moisture. The mixtures containing **11** and **19** were treated with dilute, ice-cold sulphuric acid. The resulting crystalline esters were removed and washed with a solution of sodium bicarbonate. The pyridine from all other reaction mixtures was removed and the residues as well as the esters **11** and **19** were purified by column chromatography (aluminia neutral, activity I, chloroform as eluent) and recrystallization from acetone.

Number	**11**	**17**	**18**	**19**	**20**	**28**
m.p. °C	98	48	62	97	−9	45
Yield per cent	24	57	63	41	34	71

4.5. *Acrylic acid ester **21***

1 mmol of 5-*n*-octyl-2-(4-*n*-hydroxyhexylphenyl)-pyrimidine, a few crystals of 4-dimethylaminopyridine and some magnesium shavings were refluxed with a 25-fold excess of freshly distilled acrylic acid chloride, stabilized with di-*t*-butylcresol. The reaction was followed by thin layer chromatography and was stopped before higher

amounts of by-products appeared. The excess of acrylic acid chloride was evaporated in vacuum and the product isolated by column chromatography (aluminia neutral) using chloroform as the eluent. The product, having a m.p. of 50°C was obtained in 72 per cent yield.

4.6. *4-(6-propenoyloxyhexyloxy)benzoic acid 4-(5-(n-propyl)-2-pyrimidinyl)-phenyl ester **30***

5 mmol of 4-(5-(*n*-propyl)-2-pyrimidinyl)-phenol were added to 10 ml of purified dimethylformamide and an equivalent amount of 4-(6-propenoyloxyhexyloxy)-benzoic acid. While stirring the mixture at 0°C, 5·5 mmol of N,N′-dicyclohexyl-carbodimide were added and the mixture allowed to warm to room temperature. Three hours later, the precipitated urea was removed and the dimethylformamide evaporated *in vacuo*. The residue was dissolved in dichloromethane. The solution was shaken twice with 1 M hydrochloric acid and afterwards with a saturated solution of sodium bicarbonate; it was then dried over magnesium sulphate. After removing the solvent *in vacuo* the product was purified by column chromatography and then recrystallized from acetone. The product, having a m.p. of 87°C, was obtained in 15 per cent yield.

4.7. *Phenylpyrimidines containing two mesogenic groups and an ether spacer (**34–39**)*

The etherification of the 5-*n*-alkyl-2-(4-hydroxyphenyl)-pyrimidines with α,ω-dibromoalkanes was carried out as described in §4.1. The reaction mixtures were treated with water and the residues recrystallized from acetone several times. The insoluable phenylpyrimidine **37** was recrystallized from dioxane.

Number	**34**	**35**	**36**	**37**	**38**	**39**
m.p. °C	66	235	198	133	152	155
Yield per cent	65	5	51	3	57	57

4.8. *Phenylpyrimidines containing two mesogenic groups and an ester spacer (**32**, **33**, **40**)*

The esterification of 5 mmol of 5-*n*-alkyl-2-(4-hydroxyphenyl)-pyrimidines with 2 mmol of α,ω-alkenyldicarboxylic acid dichlorides was carried out as described in §4.3. The esters **32** and **33** were purified by column chromatography (silica gel; chloroform as eluent). The siloxane **40** was recrystallized twice from methanol and once from *n*-hexane.

Number	**32**	**33**	**40**
m.p. °C	184	170	102
Yield per cent	20	46	18

4.9. *Polysiloxanes (**6–10**)*

The alkenic derivatives **1–5** were added by a hydrosilylation reaction to poly-(methylhydrogensiloxane) (Merck; DP-35). 0·1 ml of the poly-(methylhydrogensiloxane) was added to a 20 per cent excess of the alkenic component, 5 ml of dry toluene and 5 μl of a solution containing the platinum catalyst (SLM 86003; Wacker). After treating the mixture with dry nitrogen, the vessel was closed and heated to 80°C for 1 week. The reaction could be monitored by I.R.-spectroscopy (Si–H bond at 2140 cm^{-1}). The toluene was evaporated and the polysiloxanes purified by gel permeation chromatography (preparative GPC with PVA 2000 from Merck) using tetrahydrofuran as the eluent. The products were freeze dried.

Number	**6**	**7**	**8**	**9**	**10**
Yield per cent	82	77	71	68	34

4.10. *Polyacrylates (26, 31) and polymethacrylates (12, 22–25, 29)*

The monomers (**11**, **17–21**, **28**, **30**) were dissolved in 5 ml of toluene, which had been previously distilled from lithium aluminium hydride, and polymerized under nitrogen for 2 days at 70°C with 1 mol-per cent of AIBN as initiator. The polymethacrylate **12** precipitated from the reaction mixture. The solvents were evaporated and the products purified by preparative GPC using a PVA 2000 (Merck) THF system. The polymers were dried *in vacuo* at 60°C or dissolved in benzene and freeze dried.

Number	**12**	**22**	**23**	**24**	**25**	**26**	**29**	**31**
Yield per cent	90	79	82	83	65	50	97	56

4.11. *Characterization methods*

All precursors, dimers and polymers except the siloxanes (which tend to give very stable silicon carbides during the combustion process) gave correct elemental analyses. IR and ^{1}H-N.M.R. spectra of selected members of each group of phenylpyrimidines were all in agreement with the proposed structures. The thermal behaviour of the compounds was investigated by a DSC-2C differential scanning calorimeter (Perkin Elmer). The scan rate was 10 K/min and the peak maxima were taken as transition temperatures. The textures were observed with a POL-BK II polarizing microscope (Leitz) equipped with a FP 5 hot stage (Mettler). The molecular weights of the polymers were measured using an analytical GPC (Waters) equipped with 1000 and 10 000 Å columns (PL gel) and polystyrene standards. The X-ray experiments were performed using nickel filtered Cu Kα-radiation.

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