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Liquid-crystalline side-chain polyacrylates and polymethacrylates I. Variation of the terminal group

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Liquid-crystalline side-chain polyacrylates and polymethacrylates

I. Variation of the terminal group

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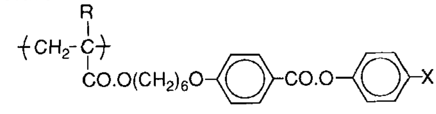
Liquid-crystalline side-chain polyacrylates and polymethacrylates were prepared having the structure



with X = alkyl, $-CH_2CN$, $-CF_3$, halogen, $-OCH_3$, $-SCH_3$ or the 3,4-methylendioxy group and $R = -H$ or $-CH_3$. The substituent X exerts a strong effect on the properties of the polymer. The influence of the polarizability of X was particularly pronounced; increasing the polarizability raised both the glass transition temperature T_g and to greater extent the clearing point T_{cl}, and also enhanced the formation of smectic phases. In the polyacrylate series, partial crystallization of the mesogenic side groups as well as a broadening of the two phase liquid crystal–isotropic region were observed with increasing polarizability of X. Polar (e.g. CF_3) and bulky (e.g. tertiary-butyl) substituents increase T_g; non-linear substituents diminish the liquid-crystalline phases. As expected the polyacrylates exhibited lower values of T_g but higher clearing temperatures than the analogous polymethacrylates. The more flexible polyacrylate chain also facilitates the formation of smectic phases.

1. Introduction

The first liquid-crystalline polymers having mesogenic groups attached directly to the polymer backbone were synthesized and characterized in the early seventies. In a few cases, these materials exhibited liquid-crystalline phases particularly when the polymers were made by bulk polymerization of the monomers in the liquid-crystalline state [1, 2]. However, there was no systematic approach to the synthesis of liquid-crystalline side-chain polymers until the concept of spacers had been introduced [3, 4]. The idea is to decouple the motions of the main-chain and of the mesogenic groups by spacers consisting of oligomethylene groups. It is now wide accepted that the spacers allow a special morphology; the backbone and the mesogenic groups form separate domains [4, 5].

It is the side-chain domains that give rise to the liquid-crystalline properties of the polymer which are quite similar to those of low molar mass liquid crystals. Liquid-crystalline side chain polymers have analogous electric [6, 7], magnetic [6] and elastic properties [8, 9] to low molar mass liquid crystals and show the same mesomorphic optical textures [4, 6]. The main difference is the greatly increased viscosity of liquid-crystalline side-chain polymers [6, 8, 9] which is accompanied by a high stability of the orientation. Many dynamic processes such as viscous flow, orientation in external fields or on surfaces, occur at a far lower speed. Thus, these polymers are not suitable for use in common electrooptic devices. Interesting new applications for liquid-crystalline side-chain polymers are under investigation and these are mainly in the fields of information storage and processing [10, 11, 12] and in the area of nonlinear optics [13, 14].

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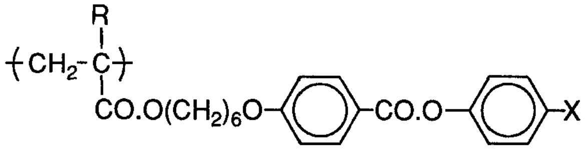
Numerous papers are to be found in the literature concerning modifications of the structure of liquid-crystalline side-chain polymers and the effects of such structural changes on the glass transition temperature T_g, the mesophases exhibited, the clearing point T_{cl} and certain electrooptical properties. The influence of the main-chain, the length and type of the spacer and the structure of the mesogenic group have all been investigated in detail [4, 6, 15–17].

In addition to the structure of the polymer, the molecular weight has a pronounced influence on liquid-crystalline behaviour; for example, T_{cl} depends markedly on the degree of polymerization up to a critical value which in certain cases is in the range of about ten [18]. For certain polymethacrylates with structures very similar to the polymers investigated in this work, it was found that T_{cl} increased by 2°C if the number average molar mass was raised from 12 000 to 20 000 g/mol [19]. It was also reported that the type of mesophase formed can depend on the degree of polymerization resulting in different mesophases at the same temperature for polymers with broad molar mass distributions [20].

This paper reports the effect of the terminal-group X on the liquid-crystalline behaviour of polymethacrylates and polyacrylates having the structure;

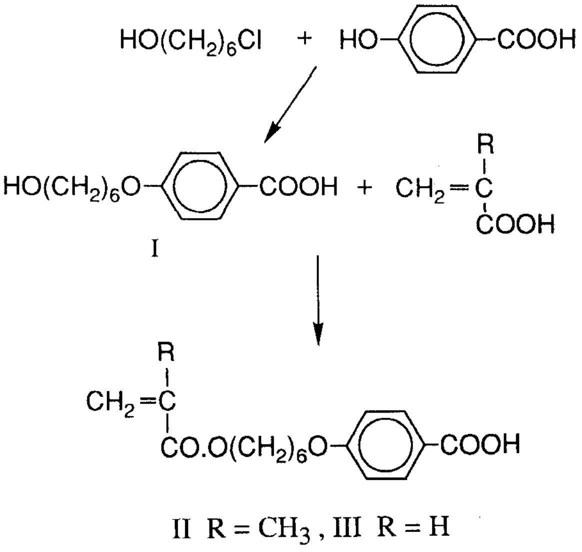


Scheme 1

with X = alkyl, $-CH_2CN$, $-CF_3$, halogen, $-OCH_3$, $-SCH_3$ or the 3,4-methylendioxy group and R = $-H$ or $-CH_3$.

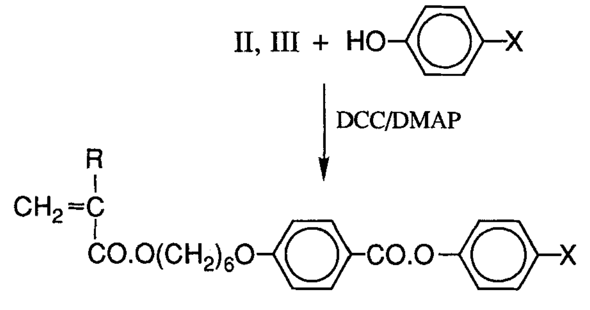
2. Synthesis

The monomers were prepared in three steps according to the scheme [16, 17];



II R = CH3 , III R = H

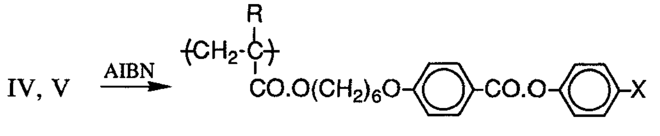
Scheme 2



IV $R = CH_3$, V $R = H$

Scheme 3

The menemonic DCC refers to dicyclohexylcarbodiimide and DMAP to 4-(dimethylamino)pyridine. The monomers **IV** and **V** were homopolymerized in toluene using 2,2′-azobisisobutyronitrile (AIBN) as initiator



Scheme 4

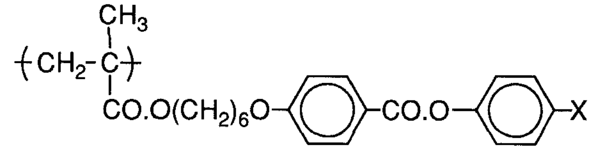
The properties of the polymers as well as those of the monomers are listed in table 1 (methacrylates) and table 2 (acrylates).

3. Results and discussion

A comparison of the polymethacrylates with alkyl substituents (polymers **1–5** in table 1) reveals the marked influence of the structure of the alkyl group on the formation of liquid-crystalline phases and on the glass transition temperature T_g. While the polymers **1–3** having a methyl, ethyl or *n*-propyl substituent form liquid-crystalline phases none are observed for the polymethacrylates containing an isopropyl or tertiary-butyl group. Branching of the alkyl group at the α-carbon atom disturbs the linearity of the side chains and apparently prevents the formation of liquid-crystalline phases. The bulkier alkyl groups of **4** and **5** increase T_g considerably in comparison with that of **2** and **3**. The T_g and the clearing point T_{cl} of polymer **1** should not be considered as being representative (because of its low degree of polymerization). For polymer **1** the T_{cl} values determined by D.T.A. and optical microscopy differ by 8°C. The reason for this may be the low degree of polymerization of **1**. All the other polymethacrylates show reasonably good agreement in the T_{cl} values measured by the two methods although the heating rates differ by a factor of ten (table 1).

The introduction of a polar substituent such as cyanomethyl (polymer **6**) or trifluoromethyl (polymer **7**) results in nematic polymethacrylates with reasonably high T_g values compared to polymers **1–3**. This increase in T_g is obviously the result of interactions between the polar groups. The halogenated polymethacrylates **8–11** reveal the distinct influence of the nature of the halogen atom on the properties of the

Table 1. Melting points of the methacrylate monomers and properties of the corresponding methacrylate polymers.



No.	X	m.p.† °C	$\overline{Mn}$ g/mol	$\overline{Mw}/\overline{Mn}$	T‡/°C (calorimetric data)	T§/°C (microscopic data)
1	CH_3	75	6500	3·38	g 33 L.C.‖ 51 N 70 I	N 78·1–78·8 I
2	C_2H_5	35	52200	2·04	g 43 N 77 I	N 76·0–76·4 I
3	*n*-C_3H_7	43	31500	3·30	g 38 L.C. 76 N 86 I	N 85·0–86·2 I
4	*i*-C_3H_7	54	41900	2·20	g 53 I	
5	*t*-C_4H_9	69	29900	2·31	g 71 I	
6	CH_2CN	67	15800	2·40	g 52 N 72 I	N 73·6–76·6 I
7	CF_3	65	25700	3·04	g 52 N 85 I	N 83·8–85·5 I
8	F	50	25800	2·39	g 43 N 57 I	N 58·3–61·0 I
9	Cl	60	18200	2·28	g 47 N 100 I	N 99·5–100·2 I
10	Br	45	24700	2·25	g 52 S_A 110 I	S_A 108·2–110·5 I
11	I	60	40400	3·75	g 72 S_A 134 I	S_A 132·0–133·0 I
12	OCH_3	55	13300	3·78	g 47 L.C. 68 N 107 I	N 108·6–109·0 I
13	SCH_3	62	43100	3·43	g 65 N 116 I	N 115·3–115·6 I
14	OCH_2O¶	89	15500	2·83	g 51 N 64 I	N 66·5–69·0 I

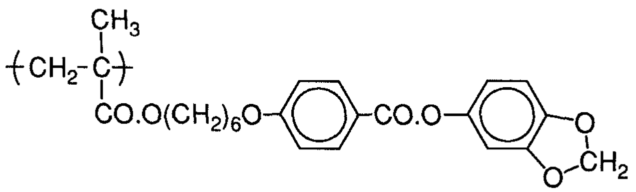
† Melting point of monomer.

‡ The DTA measurements were made with a heating rate of 10°C/min. The temperature values given for the endothermic events are the onset points.

§ The microscopic determinations were carried out using heating or cooling rates of 0·1 to 1·0°C/min. The identification of the nematic and S_A phases was possible after annealing for 2 to 72 hours.

‖ L.C. denotes liquid crystalline phases not yet identified.

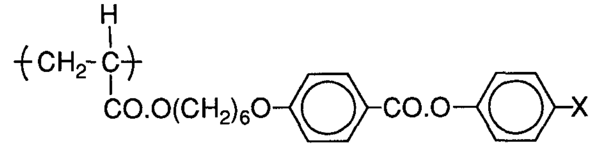
¶ Structure of polymer 14:



polymer. While nematic polymers result with the less polarizable fluorine and chlorine substituents (**8** and **9**), polymers with smectic A phases are formed in the case of the more polarizable bromine and iodine substituents (**10** and **11**). The width of the mesophase range as well as the absolute value of the clearing temperature T_{cl} increase from the fluoro to the iodo substituted polymethacrylate, for T_g a similar shift to higher values is also found. The most pronounced rise in the mesophase range is observed between the fluorinated and the chlorinated polymer (table 1).

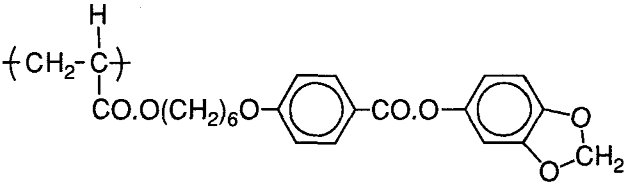
A comparison of the methoxy with the more polarizable methylmercapto-substituted polymethacrylate (polymers **12** and **13**) also demonstrates the effect of increasing polarizability, namely the shifting of T_{cl} and T_g to higher values. While the mercaptomethyl substituted polymethacrylate forms only a nematic mesophase, two

Table 2. Melting points of the acrylate monomers and properties of the corresponding acrylate polymers.



No.	X	$\frac{\text{m.p.}\dagger}{^\circ\text{C}}$	$\frac{\overline{\text{Mn}}}{\text{g/mol}}$	$\frac{\overline{\text{Mw}}}{\overline{\text{Mn}}}$	$\frac{T\ddagger}{^\circ\text{C}}$ (calorimetric data)	$\frac{T\S}{^\circ\text{C}}$ (microscopic data)
8a	F	50	11900	2·32	g 23 N 63 I	N 62·0– 63·2 I
9a	Cl	59	10100	2·24	g 26 L.C. 93 S_A 109 I	S_A 108·0–113·5 I
10a	Br	64	13200	2·81	g 37 L.C. 74 L.C. 87 S_A 129 I	S_A 126·0–134·0 I
11a	I	67	7900	2·87	c 72 L.C. 93 L.C. 110 S_A 135 I	S_A 131·0–152·0 I
12a	OCH_3	65	8200	1·90	g 33 S_A 97 N 120 I	N 118·8–119·9 I
13a	SCH_3	63	16000	2·51	c 53 S_A 129 I	S_A 127·7–131·0 I
14a	OCH_2O¶	53	11000	1·81	g 36 S_A 84 I	S_A 87·3– 87·9 I

†, ‡, §, ∝, see footnotes to table 1.
¶ Structure of polymer **14a**:



mesophases are formed in the case of the methoxy-substituted polymer. Introduction of the 3,4-methylendioxy group (polymer **14**) distorts the linearity of the mesogenic group which causes a strong depression of T_{cl} as compared to polymer **12**; T_g is not affected in this case.

The halogenated polyacrylates (table 2, polymers **8a** to **11a**) show similar trends in the transition temperatures as the analogous polymethacrylates. T_{cl} and T_g are shifted to higher values from the flourinated to the brominated polyacrylate. The increase of T_{cl} and T_g is coupled with an increase in the mesophase range. While the fluorinated polyacrylate possesses a nematic mesophase the chlorinated analogue exhibits a smectic A phase. In comparison the bromine and the iodine substituted products show three mesophases. In contrast to the other halogenated polyacrylates, the iodine substituted product is partially crystalline as revealed by D.T.A. The D.T.A. diagrams show an endothermic peak during heating and an exothermic one during cooling but no glass transition. The same is observed for polymer **13a**. Crystallization is restricted to the side chains (since radical chain polymerization leads to atactic, amorphous polymers). In the case of the polyacrylate, crystallization is facilitated by the higher mobility of the main-chain as compared to the analogous polymethacrylate. Another interesting feature is the broadening of the two phase liquid crystal—isotropic liquid region for the halogenated polyacrylates which exhibit a smetic A phase observed by optical microscopy. The temperature range from the fully formed fan texture of the S_A phase to the solely isotropic liquid varies from 5·5° C for the chlorine substituted polymer to 21°C for the iodine terminated one. Other polymers with a S_A phase (**10**, **11**, and **14a**) do not show this increase in the width of the biphasic region. Broad two phase regions as well as the crystallization of the side chains have also been observed for liquid crystal side-chain polysiloxanes [21].

The influence of the methoxy, methylmercapto and 3,4-methylendioxy groups on the properties of the polyacrylates (**12a–14a**) is similar to that of the analogous polymethyacrylates (**12–14**). However, the methylmercapto substituent causes crystallization of the side chains (polymer **13a**).

A comparison of the polymethacrylates with the analogous polyacrylates reveals that in general the polyacrylate has a lower T_g but higher T_{cl} [4, 6, 15]. This effect is most pronounced for polymers **10** and **10a**, and **14** and **14a**. The more flexible polyacrylate main-chain also facilitates the formation of S_A phases (compare polymers **9** and **9a**, **13** and **13a**, and **14** and **14a**) as well as the crystallization of side chains if other prerequisites (e.g. high polarizability) are satisfied. It should be noted that the polymers **12** and **12a** are well known standard liquid crystalline side-chain polymers. The results of this work are in good agreement with data published in the literature (**12** g 47 N/S 74 N 111 I; **12a** g 35 S_A 97 N 123 I; [22]).

4. Experimental

4.1. *Characterization of the monomers*

The purity of the compounds recorded in the tables was verified by thin layer chromatography (T.L.C.). Pre-coated T.L.C. plates, silica gel 60 F_{254}, layer thickness 0·25 mm, Art. 5715 (Merck, Darmstadt, Germany) were used. For the analysis of the substituted benzoic acids pre-coated T.L.C. plates, RP-18 F_{254S}, layer thickness 0·25 mm, Art. 15683 (Merck) were used with a *p*-dioxane/water 15:5 eluent. The structure of the products was confirmed by spectroscopic methods. Mass spectra were recorded on a MS9 spectrometer (AEZ Manchester), I.R. spectra on a FTIR-7199 spectrometer (Nicolet) and ^{1}H-N.M.R. spectra on a HX-270 spectrometer (Bruker) at 270 MHz.

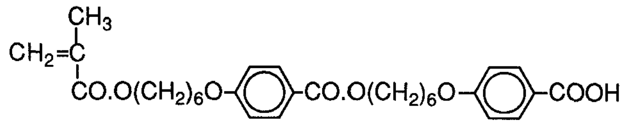
4.2. *Synthesis of the monomers*

4.2.1. *4-(6-Hydroxyhexyloxy)benzoic acid* **I**

This intermediate was synthesized according to a well-known literature procedure [16].

4.2.2. *4-((6-Methacryloyloxy)hexyloxy)benzoic acid* **II** and *4-((6-acryloyloxy)-hexyloxy)benzoic acid* **III**

A mixture of 4-(6-hydroxyhexyloxy)benzoic acid **I** (29·8 g, 0·125 mol), methacrylic acid (172·2 g, 2·0 mol), hydroquinone (8·6 g, 0·078 mol), 4-toluene-sulphonic acid-mono hydrate (8·6 g, 0·045 mol) and chloroform (300 ml) was refluxed in a Dean–Stark apparatus for 36 hours. A solution of sodium acetate-trihydrate (6·2 g, 0·046 mol) in water (15 ml) was added to neutralize the reaction mixture. The solvent was removed under slightly reduced pressure and the excess of methacrylic acid was carefully distilled off (approximately 130 ml were collected) (78–80°C, 26–28 mbar). The crude product was redissolved in chloroform (1·5 l). The solution was filtered, washed with water (4 × 400 ml) and dried over anhydrous sodium sulphate. As the hydroquinone had already been removed by washing the solvent had to be distilled off very carefully (maximum water bath temperature 40°C). Two crystallizations one from toluene (500 ml) and a second from methanol (180 ml) gave a product of 98 per cent purity



IIa

or better (yield 26·8 g, 70 per cent; C 92°C N 101°C I). The large excess of methacrylic acid is necessary to minimize the formation of the diester, which was found in the crude product (2–2·5 per cent under the conditions described). For comparison, when a four fold excess of methacrylic acid (0·5 mol) was used approximately 7 per cent of **IIa** was found. The first recrystallization from toluene removed most of **IIa**, the second from methanol most of the starting product **I** that was partly formed after the reaction by hydrolysis during washing. The purity was determined quantitatively by H.P.L.C. (RP-18 column, dioxane/water). 4-(6-(Acryloyloxy)hexyloxy)benzoic acid, **III**, was prepared by the described method using acrylic acid (1.25 mol) (yield 26·3 g, 72 per cent; C 93°C N 110°C I).

4.2.3. *3,4-(Methylendioxy)phenyl-4-(6-methacryloyloxy)hexyloxy)benzoate (monomer* **14***)*

4-((6-Methacryloyloxy)hexyloxy)benzoic acid, **II** (2·0 g, 0·0065 mol), 3,4-(methylendioxy)phenol (0·83 g, 0·0060 mol) and 4-(dimethylamino)pyridine (0·04 g, 0·0003 mol) were dissolved in anhydrous dichloromethane (20 ml). Dicyclohexylcarbodiimide (1·48 g, 0·0072 mol) was added and the solution was stirred at room temperature over night. After filtration to remove precipitated material, silica gel 60 (20 g) was added and the mixture was evaporated to dryness under reduced pressure. The residual dry powder was put on a silica gel column (200 g) and chromatography carried out using a 3 : 17 ethyl acetate/hexane mixture as eluent. The material was recrystallized once from an ethyl acetate (15 ml)/isopropanol (25 ml) mixture yielding a pure product (yield 2·33 g, 91 per cent; m.p. 88·5–89·3°C). The other monomers were prepared using this method.

4.3. *Characterization of the polymers*

The molecular weights of the polymers were determined by G.P.C. using a Waters 840 system equipped with a Waters 490 multiwavelength detector and a Waters 410 differential refractometer. A set of three Waters Ultrastyragel columns (500 Å, 1000 Å and 10000 Å) was employed with tetrahydrofuran (THF) as solvent at a flow rate of 1 ml/min. The evaluation of the chromatograms was performed using the Waters 840 software. The number and weight average molecular weights ($\overline{Mn}$ and $\overline{Mw}$ respectively) were determined relative to polystyrene standards, Art. 15723 (Merck). The liquid-crystalline behaviour and the transition temperatures of the polymers were investigated using optical microscopy and by differential thermal analysis (DTA). A Zeiss Axioplan microscope with crossed polarizers was used in conjunction with a Mettler FP82 heating stage and FP80 control unit. The liquid-crystalline phases formed below the clearing point were identified using the technique in which a thin film of the polymer between glass plates was heated to just above the clearing point and then slowly cooled until the texture appeared. In all cases subsequent tempering (2–72 hours) yielded textures that allowed an unequivocal determination of nematic and smectic A mesophases. The D.T.A. measurements were performed using a Mettler FP85 calorimeter controlled by the FP80 unit. The thermograms were recorded in the range from -15 to 160°C. The glass transitions corresponded to steps and the liquid crystal transitions corresponded to peaks in the plot of ΔT versus T. In the former case the steepest point was determined and recorded in the tables and in the latter case the onset points were evaluated.

4.4. *Synthesis of the polymers*

The monomer (0·500 g) and 2,2′-azobisisobutyronitrile (0·020 g) were dissolved in toluene (6 ml). The solution was degassed by combined stirring and evacuation (30 mbar) for 3 minutes. Afterwards it was ventilated with nitrogen (99·999 per cent). This procedure was repeated once. The flask was then evacuated again and placed in a water bath (60°C) for 12 hours in the case of an acrylate monomer or for 24 hours in the case of a methacrylate monomer. The solution was dropped into cooled methanol (500 ml, -20°C) and the suspension was stirred for 5 hours at room temperature. The precipitated polymer was filtered off and redissolved in tetrahydrofuran (20 ml). In order to remove all the particles this solution and the methanol used for the second precipitation were filtered through 1·2 μm teflon filters, type 11803 (Sartorius, Göttingen, Germany). The polymer was dried in vacuum (~ 0·05 mbar) at room temperature for 12 hours. Two precipitations were sufficient to remove all monomer as checked by G.P.C.

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