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Liquid-crystalline side chain polymethacrylates II. Variation of spacer and central linkage in nitro-terminated polymers

R. Lorenz[a][b]
[a] Central Research Units, F. Hoffmann-La Roche, Basle, Switzerland [b] BASF, Kunststoffiabor, Ludwigshafen, F. R. Germany

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Liquid-crystalline side chain polymethacrylates

II. Variation of spacer and central linkage in nitro-terminated polymers

by R. LORENZ†
Central Research Units, F. Hoffmann-La Roche, CH-4002, Basle, Switzerland

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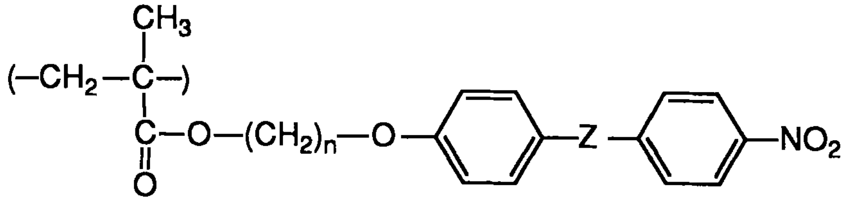
The thermal behaviour and the mesogenic properties of liquid-crystalline side chain polymers with the structure



are described with n = 3, 6, 8 or 11 and Z = -COO-, -CONH- or -N=N-. The polymers were made by radical chain polymerization. Most of them exhibit smectic phases, nematic phases were not observed. The amide linkage which has not yet been described as a structural element in such polymers gives rise to polymers of high polarity and high glass transition temperatures (T_g). In all cases the amide polymers produced the highest T_g values, the ester polymers showing the lowest. The azo polymers exhibited the largest mesophase ranges and the highest clearing temperatures (T_{cl}) of all the materials investigated. Whereas the T_{cl} values for the azopolymers are nearly independent of the length of the spacer those of the amide and ester polymers show rising clearing points with increasing spacer length.

1. Introduction

Only a few liquid-crystalline side chain polymers with nitro-terminated mesogenic groups have been described in the literature [1–3]. These polymers were synthesized mainly for investigations in the field of non-linear optics with the prime interest being in second order effects, e.g. frequency doubling of laser light or linear electrooptical modulation. To show these effects a polymer has to have moieties which exhibit a pronounced second order hyperpolarizability. Molecules or moieties with this property contain an electron donating and an electron withdrawing group with both groups connected by a conjugated system [4–6]. A further condition has to be fulfilled for second order non-linear optical behaviour: the molecule or the moiety itself and the ensemble of molecules or moieties must not be centrosymmetric. While the first prerequisite can be easily fulfilled the second is difficult to achieve. The highly polar molecules or moieties tend to orient antiparallel in most cases and so form more or less centrosymmetric crystals or clusters.

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† Present address: BASF, Kunststofflabor, ZKV/D, Gebäude B1 D-6700 Ludwigshafen, F.R. Germany.

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In consequence, considerable effort has been made to prepare non-crystalline polymers containing non-linear optical moieties. The aim is to orient these highly polar moieties in a DC electric field above the glass transition temperature, thereby reducing the centrosymmetric antiparallel orientation and increasing the non-centrosymmetric parallel alignment. This field-induced equilibrium is then frozen in by cooling. In order to slow down relaxation processes as much as possible the material should be used far below T_g and, in consequence, high glass transition temperatures are essential. For theoretical reasons polymers possessing non-linear optical moieties, in combination with liquid-crystalline properties, are expected to give larger effects than comparable isotropic materials [7].

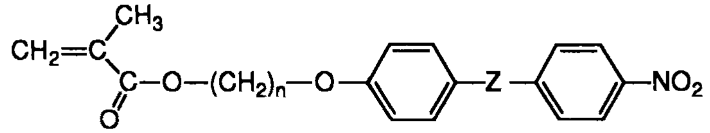
Liquid-crystalline side chain polymethacrylates were chosen in this work as they exhibit comparatively high T_g values [8]. The mesogenic side groups possess an electron withdrawing terminal nitro group with the aromatic system acting as donor. The central linkage of the aromatic system was varied, therefore, in order to study its influence on the non-linear optical properties of the polymers. The length of the spacer mainly determines the mobility and orientability of the mesogen. Both influence T_g and the liquid-crystalline behaviour as is shown in this work. The results for the non-linear optical properties will be presented in a forthcoming paper.

2. Results and discussion

The monomers used are listed in table 1. As expected the amide monomers (**4**–**6**) exhibit the highest melting points. The azobenzene monomers (**7**–**10**) as well as their polymers (**17**–**20**) are red. The homopolymers prepared (**11**–**20**) are listed in table 2. For comparison the thermal data of four 4-nitrobiphenyl polymers (**21**–**24**) are also given, which were synthesized and characterized by Leslie *et al.* [1].

In the series of polymers with the phenylbenzoate moiety (**11**–**13**) the polymer with the shortest spacer does not form a liquid-crystalline phase. The broadness of the mesophase range as well as the absolute value of the clearing temperature T_{cl} increase with increasing spacer length. As in all other series (**14**–**16**, **17**–**20** and **21**–**24**) the glass transition temperature decreases with increasing spacer length.

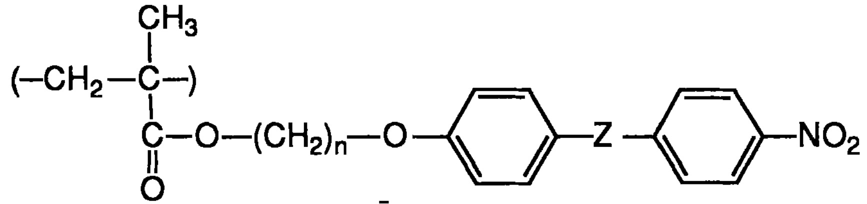
Table 1. Monomers.



No.	n	Z	T_m/°C
1	3	-COO-	101·4–102·9
2	6	-COO-	72·5–74·0
3	11	-COO-	86·8–88·9
4	3	-CONH-	128·9–131·8
5	6	-CONH-	136·0–138·5
6	11	-CONH-	127–132
7	3	-N=N-	119·3–121·7
8	6	-N=N-	88·5–91·0 (82·7–84·1)(*a*)
9	8	-N=N-	86·4–88·7
10	11	-N=N-	87·7–89·5

(*a*) Monotropic modification.

Table 2. Properties of the polymers



No.	*n*	*Z*	M̄n (*a*)/g mol^{-1}	M̄w (*a*)/M̄n	*T*(*b*)/°C (calorimetric data)	T_{cl}/°C (microscopic data)
11	3	-COO-	21000	2·10	g 85 I	—
12	6	-COO-	25400	2·69	g 50 S(*c*) 107 I	S(*c*) 104·0–105·0 I
13	11	-COO-	23000	1·99	g 40 S_A 133 I	S_A 128·6–130·0]
14	3	-CONH-	(*d*)	—	g 118 I	—
15	6	-CONH-	(*d*)	—	g 95 I	— (*e*)
16	11	-CONH-	(*d*)	—	g 57 S_A 135 I	S_A 133·6–136·3 I
17	3	-N=N-	12300	2·34	g 95 S_A 158 I	S_A 154·5–155·5 I
18	6	-N=N-	16600	1·86	g 55 S_A 173 I	S_A 166·0–168·0 I
19	8	-N=N-	14600	2·62	g 37 S_A 164 I	S_A 158·4–160·4 I
20	11	-N=N-	11300	4·36	c 67 S_A 165 I	S_A 151–168 I
21	3	—			g 85 N 100 I(*f*)	
22	6	—			g 40 N 64 I(*f*)	
23	8	—			g 35 N 75 I(*f*)	
24	11	—			g 20 S_A 95 I(*f*)	

(*a*) The number and the weight average molecular weight (M̄n and M̄w respectively) were determined by GPC relative to polystyrene standards using THF as a solvent.

(*b*) The DTA diagrams were recorded at a heating rate of 10°C/min. The temperature values given for the transition smectic A (S_A) or smectic (S) to isotropic (I) correspond to peak maximum. The glass transition temperatures (g) were determined by evaluating the inflexion point of the curve. For polymer **20** the maximum of the melting peak is given.

(*c*) The textures obtained did not allow the identification of the mesophase.

(*d*) As polymers **14–16** are not soluble in THF, no GPC measurements were made.

(*e*) Some birefringence was observed around air bubbles. It disappeared at 100–105°C.

(*f*) The data given for the 4-nitrobiphenyl-polymers are reported in [1].

It is worthwhile comparing the phenylbenzoate with the biphenyl polymers (**21–24**). Polymer **21** exhibits a remarkably high T_{cl}, whereas **22** and **24** show T_{cl} values which are 35–40°C below those of **12** and **13**. While the glass transition temperature of **11** and **21** are identical, the T_g values of **22** and **24** are lower than those of **12** and **13** respectively. Obviously, polymer **21** has a special place in this comparison. In the other cases, however, the increased length to width ratio of the phenylbenzoate moiety leads to higher clearing points. In addition the polarity of the ester group causes somewhat higher glass transition temperatures. Surprisingly polymers **21–23** exhibit nematic phases, while all other nitro terminated polymethacrylates are smectic. The analogous low molecular weight 4-alkoxy-4-nitrobiphenyls also show nematic phases [9].

The amide polymers **14–16** are characterized by high glass transition temperatures because of hydrogen bond formation. These polymers should provide a suitable matrix for embedding highly polar guest molecules, e.g. dyes with non-linear optical properties. For polymer **15** it seems that the clearing point is at or just below the glass transition temperature (see table 2, footnote (*e*)). As revealed by DTA polymer **16** does not show side chain crystallization despite its long spacer and the benzamides pronounced tendency to crystallize.

The azo representatives (**17–20**) show a somewhat different behaviour. They exhibit broad S_A phases, the highest clearing points and relatively high T_g values, compared with the esters. There are only small differences in the T_{cl} values and it seems that there is little correlation between the clearing point and the length of the spacer. Polymer **20** shows side chain crystallization, as detected by DTA.

Many cyano- and alkoxy-terminated azo and azoxy liquid crystal side chain polymers with different types of backbones have been described in the literature [10–15]. Broad mesophase ranges and high T_{cl} values are typical for this class of polymer and are obviously brought about by the pronounced polarizability of the azo- and azoxy-benzene moiety.

3. Experimental

The ester monomers **1–3** and their precursors 4-((3-methacryloyloxy)propyloxy)-benzoic acid, 4-((6-methacryloyloxy)hexyloxy)benzoic acid and 4-((11-methacryloyloxy)undecyloxy)benzoic acid were synthesized according to an established route [16–18]. Detailed procedures are given elsewhere [17, 18]. The amide monomers **4–6** were prepared by a standard method utilizing these three intermediates [19]. The azobenzene monomers **7–10** were produced following a well-known three-step synthesis [10]. The analytical methods for checking the purity of the monomers are given in [18].

The polymers **11–20** were made by radical chain polymerization in dimethylformamide (DMF) using 2,2′-azobisisobutyronitrile (AIBN) as initiator. A solution of 9 mass % monomer related to the DMF mass and 2 mass % AIBN related to the monomer mass was heated to 60°C for 10 hours. The polymer was isolated and purified by two precipitations in methanol. The details regarding preparation and characterization by polarization microscopy, DTA and GPC are also described in [18].

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