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A New Class of Liquid Crystal Side Chain Polymers
Mesogenic Groups Laterally Attached to the Polymer Backbone

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Summary

A new class of liquid crystal side chain polymers has been synthesized, where the mesogenic groups are laterally attached to the polymer backbone. The monomeric liquid crystals are laterally substituted with an alkyl chain having a methacrylic ester group in the ω-position. While the monomers exhibit a metastable nematic phase with respect to the crystalline state, the polymers are liquid crystalline in a broad temperature range above the glass transition temperature.

Introduction

According to the classical concept of low molar mass liquid crystals, liquid crystal side chain polymers have been synthesized by attaching a rigid rod-like mesogenic moiety at its end to the polymer backbone via a flexible spacer (1), (schematically presented in Fig. 1a). Detailed investigations on chiral nematic (cholesteric) phases of these systems indicate that the linkage of the l.c. molecules to the polymer main chain restricts rotational and translational motions, which is directly reflected in the helicoidal structure of the phase (2). According to the theory of Goossens (3), the restriction of rotational motions around the long molecular axis of the l.c. moiety should mainly be responsible for the strong increase in the cholesteric twist angle when comparing the monomeric and polymeric phases. Having this concept in mind, the next step is to look for systems which are hindered in a rotational motion around the long axis of the rods.

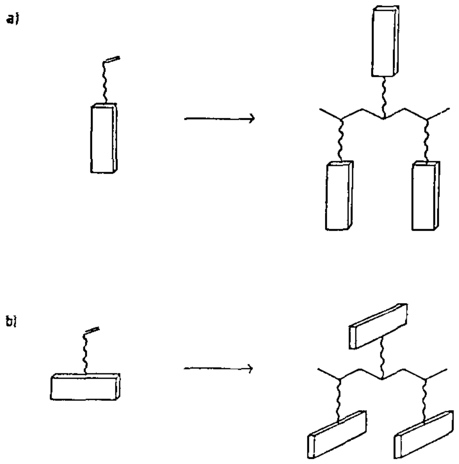


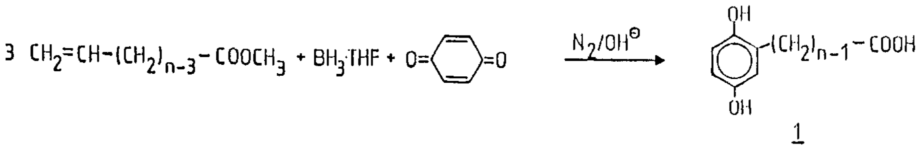
Fig. 1:
Liquid crystal side chain polymers:
Mesogenic moities attached
a) conventionally,
b) laterally to the polymer main chain

Recently Weissflog et al. 4) succeeded in preparing nematic liquid crystals, where the mesogenic groups are laterally substituted with long aliphatic alkyl chains. These systems perfectly match the condition to restrict long axis rotational motions by attaching them to a polymer backbone via a laterally substituted alkyl chain, shown in Fig. 1b). In this paper we describe the synthesis and phase behavior of two monomers and the corresponding polymers which fit this concept.

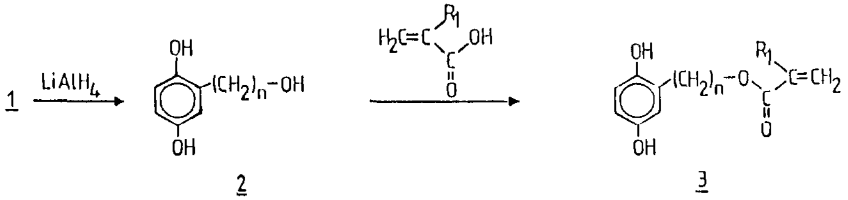
Synthesis

The synthesis of the new systems followed basically the route described by Weissflog et al. 4), modified by the introduction of the polymerizable group via the following reaction scheme:

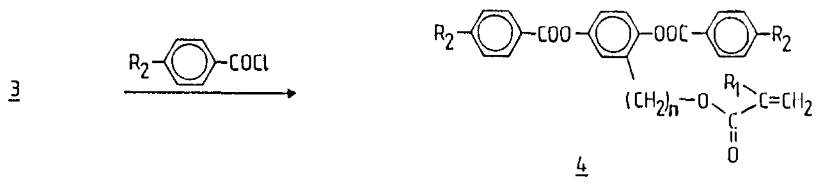
In the first reaction step, quinone is substituted via the boron adduct of undecenoic acid methylester (n = 11) to the hydroquinone derivative 5). Under the basic conditions employed for the separation of the product, the ester group is hydrolyzed, thus yielding directly the desired acid 1.



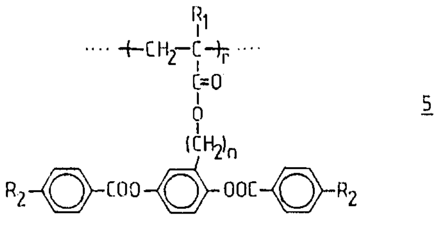
After reduction of the hydrocarbon acid 1 with $LiAlH_4$ the alcohol 2 is esterified with methacrylic acid (R_1 = CH_3) to the ester 3.:



Finally, 3 is esterified with p-substituted benzoic acids to the monomer 4:



The monomers 4 can be radically polymerized in THF or benzene solution yielding the desired polymers 5:



According to gel permeation chromatographic measurements, under the experimental conditions (initiator 1 mol%, 1 molar solution of monomer in benzene at 60°C), the elution volumes of the polymers appear at a volume which corresponds to polystyrene having a molar mass of about 10^6 g/mole.

The properties of monomers 4 and polymers 5 will be described, where $R_1 = CH_3$, $n = 11$ and $R_2 = -OCH_3$ or $-OC_6H_{13}$.

Phase behavior

The phase behavior of the monomers and polymers was determined by polarizing microscopy and differential scanning calorimetry. Additionally, x-ray measurements were performed on the polymers to confirm the results of the previous methods.

The monomers exhibit a monotropic nematic phase, which is metastable with respect to the crystalline state (Table 1).

Table 1

Phase transitions of monomers 4 and polymers 5

R_2	Phase Transitions (in K) Monomer 4	Polymer 5	
$-OCH_3$	k (336) n 296 i	g 312 n 337 i	$\Delta H_{n,i}$=1,0 J/g
$-OC_6H_{13}$	k (322) n 319 i	g 282 n 335 i	$\Delta H_{n,i}$=0,9 J/g

Because of the ease of supercooling, the monomers, the nematic phase can be clearly identified by the ±1/2 singularities of the nematic texture. Compared to the derivatives which are laterally substituted only with alkyl chains $^{4)}$, the methacryl end groups clearly depress the nematic to isotropic phase transformation temperature. Furthermore, the end groups of the mesogenic moiety affect the phase transformation as expected. The methoxy derivative exhibits a lower nematic to isotropic phase transformation temperature than the hexyloxy derivative.

Most interestingly, the polymers exhibit a stable liquid crystalline phase. As established for l.c. side chain polymers which have been investigated so far $^{6)}$, the l.c. phase transformation temperatures of the polymers 5 are higher than those of the corresponding monomers 4. This clearly indicates that the linkage of the laterally substituted nematic monomers to the polymer backbone also "stabilizes" the liquid crystalline state. It has to be noted that the liquid crystalline to isotropic phase transformations, as observed in DSC experiments, are characterized by a sharp endothermal heat flow. The half width of the peaks is only 1-2 K when the samples are heated or cooled at 5° K/min.

At low temperatures the polymers exhibit the glassy state, which changes into the liquid crystalline state at the glass transition accompanied by the characteristic change in the specific heat. According to preliminary results based on the absolute value of the change of the specific heat at the glass transition, the polarizing microscopic texture, the x-ray pattern and the liquid crystalline to isotropic phase transformation enthalpy (see Table 1), the polymers exhibit a nematic phase. Furthermore, their flow behavior and viscosity is similar to those of conventional nematic side chain polymers.

These polymers prove that the liquid crystalline state can also be observed for systems which have the mesogenic groups laterally attached to the polymer main chain. Beside the aspects of packing effects of the mesogenic groups in the l.c. state as mentioned by Diele et al. 7), these polymers will be extremely interesting with respect to the state of order and molecular motions of the mesogenic moieties as described above. Detailed information about the physical properties of this type of polymer will be presented in a forthcoming paper.

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