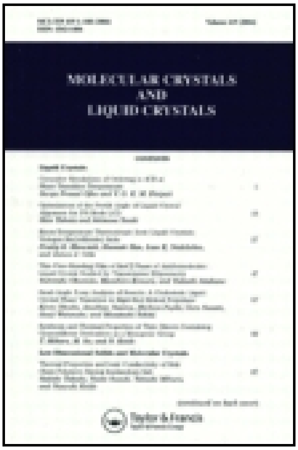

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Synthesis of Liquid Crystalline Side Chain Polymers Via Phase-Transfer Catalysis

P. Keller [a]

[a] Laboratoire Léon Brillouin C.E.N, Saclay 91191 Gif sur Yvette, Cedex, (France)

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SYNTHESIS OF LIQUID CRYSTALLINE SIDE CHAIN POLYMERS VIA PHASE-TRANSFER CATALYSIS

P.KELLER
Laboratoire Léon Brillouin
C.E.N. Saclay
91191 Gif sur Yvette Cedex (France)

Abstract: Among the various synthetic ways used to prepare mesomorphic side-chain polymers,the transformation of "reactive polymers" via polymer-analogous reactions is a very interesting approach. We describe the use of phase-transfer catalyzed esterification reaction for the synthesis of various families of mesomorphic side-chain polymers:polyacrylates, polymethacrylates, polyitaconates, polymaleates and poly(methylvinyl ether co maleates) starting from, respectively, polyacrylic, polymethacrylic, polyitaconic, polymaleic and poly(methylvinyl ether co maleic) acids. We discuss the effect of changes in chemical structure of the macromolecular backbone on the mesomorphic properties.

INTRODUCTION

During the last years an increasing interest has been devoted to liquid crystalline side-chain polymers. This interest is justified both by the eventual technological applications of these materials and by the fundamental problems they arise.

A variety of synthetic approaches have been utilized to prepare these mesomorphic side-chain polymers. These include free-radical polymerization of mesogenic methacrylates[1], acrylates[2] and chloroacrylates[3]; anionic[4] and group-transfer[5] polymerizations of methacrylates; cationic polymerization of vinyl and propenyl ether monomers[6]; ring-opening polymerization of glycidyl esters to side-chain poly(ethylene oxide)s[7]; polycondensations to give side-chain polyesters[8]; and transformation of "reactive polymers" by reaction with terminally functionalized mesogens to give mesomorphic polymers (this type of reaction is known as a polymer-analogous reaction).

This last synthetic method has some advantages one being that known polymers are used as starting materials for liquid crystalline polymer synthesis. It could also permit the preparation of nonclassical mesomorphic polymers with new macromolecular backbones no easily accessible by other routes. However, until recently, this way to obtain liquid crystalline side-chain polymers has not been extensively investigated. The most popular application of this method is the synthesis of mesomorphic polysiloxanes[9-13], the only other example described in the litterature being the synthesis of polyacrylates starting from poly(acryloyl chloride)[14].

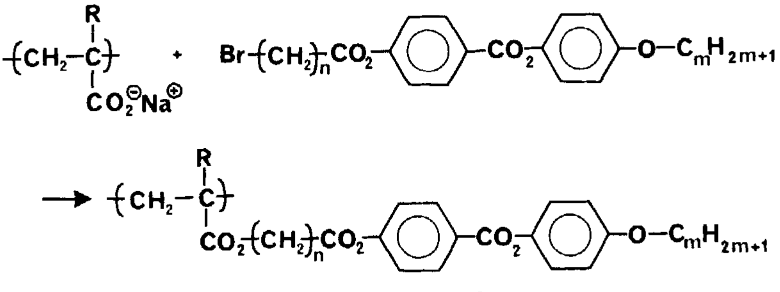
Following this way, i.e. synthesis of liquid crystalline side-chain polymers by polymer-analogous reactions, we have recently developped a new procedure for the preparation of liquid crystalline polymers[15] by grafting of mesogenic monomers on various polymers using phase-transfer catalyzed esterification reactions.

RESULTS AND DISCUSSION

Starting from polymers bearing one (or several) carboxylic fonctions by monomeric unit (such as polyacrylic acid, polyitaconic acid...), the synthesis of mesomorphic polymers is achieved by displacement of bromide ion from bromide-terminated mesogenic monomers with the sodium salt of the polycarboxylic acid under liquid-liquid phase-transfer conditions[15] (Scheme 1; the synthesis of mesomorphic polyacrylates is taken as an example). Formally, this substitution reaction is similar to the well-known displacement of bromide ion by acetate anion (or methacrylate-acrylate anions) under phase-transfer conditions to give esters[16].

Liquid crystalline polyacrylates[15] (1) and polymethacrylates[17] (2) have been prepared in a first step to demonstrate the potentialities of this new synthetic route.

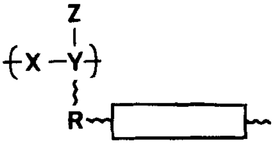
In a second step, this synthetic approach has been used to study the effect of the chemical



R = H **1**

R = CH_3 **2**

Scheme 1



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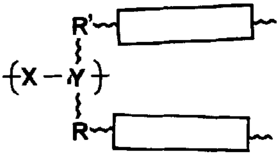

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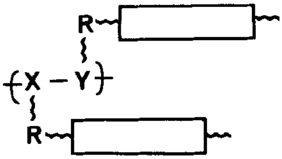

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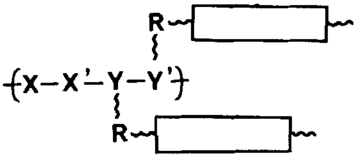

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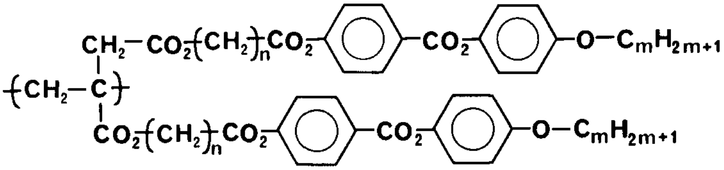

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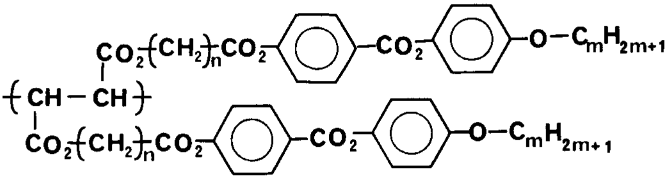

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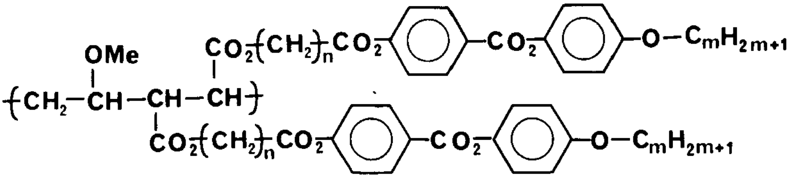

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structure of the polymer backbone on the mesomorphic properties or, more precisely, the effect of the density in mesogenic side group along the backbone on the mesomorphism.

In fact, the most usual chemical structure for a liquid crystalline side-chain polymer is the following[9] (Structure A), in which each monomer unit carries only one mesogenic side group.But, we may ask us the question: what happen to the mesomorphic properties if there is now two (or more) mesogenic side group by monomer unit, such as in the following schematic structures (B), (C)and (D) ?

These hypothetical structures have in fact real counterparts in polymer chemistry: structure (B), (C) and (D) sketch, respectively, a polyitaconate, a polymaleate and a copolymaleate.

The synthesis of such kinds of side-chain polymers appears as quite difficult to realize by using classic preparations like radical polymerizations and so on.

In contrary, polymer-analogous reactions using phase-transfer catalyzed esterification grafting reactions are very well suited for this purpose. Starting from polyitaconic, polymaleic and poly(methylvinyl ether co maleic) acids and using the procedure describe above for the synthesis of mesomorphic polyacrylates[15] (1), we have been able to prepare mesomorphic polyitaconates[18] (3), polymaleates[19] (4) and poly(methylvinyl ether co maleate)s[20]

(5).

All of the polymers (3), (4) and (5) exhibit liquid crystalline behavior as it can be seen from the data given in Table 1 (see also ref. 18-20). For all the series prepared, the mesomorphism is strongly influenced by the structure of the mesogenic side-chain (i.e. length of the flexible spacer; nature of the terminal group).

Table 1: Mesomorphic properties of liquid crystalline polyacrylates (1), methacrylates (2), polyitaconates (3), polymaleates (4) and poly(methylvinyl ether co maleate)s (5).

Polymer	n	m	Phase transitions in xC
1a	4	1	g 120 N 165 I
1b	4	4	g 55 S 100 N 150 I
2a	4	1	g 50 N 150 I
2b	4	4	g 40 S 80 N 190 I
3a	4	1	g 90 N 155 I
3b	4	4	g 132 S 147 N 166 I
4a	4	1	g 50 N 129 I
4b	4	4	K 106 S 126 N 145 I
5a	4	1	g 115 N 200 I
5b	4	4	g 55 S 145 N 165 I

a) g=glass; K=crystal; N=nematic; S=smectic; I=isotropic

In the synthesized series, a doubling of mesogenic units per monomeric unit do not accentuate the liquid crystalline properties of the polymers as we may have expected. Moreover, the influence of the chemical structure of the macromolecular backbones on the mesomorphism do not appear clearly in our studies. These results are not in fact surprising since the mesomorphic properties in these complicated systems might be seen as the result of subtil equilibrium between various interaction forces (mesogenic-mesogenic groups interactions;mesogenic group-macromolecular backbone interactions) which can be attractive or repulsive and also of the obliged cohabitation resulting from the chain connectivity.

In fact, it is difficult at present to predict the properties of the polymers from the chemical structure and properties of either the starting reactant polymers or the mesogenic monomers[21]. Further systematic synthesis must be carried out in order to obtain more informations concerning the mutual interactions of polymeric and liquid crystalline properties in liquid crystalline side-chain polymers.

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