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SYNTHESIS OF A NEW CLASS OF SIDE CHAIN LIQUID CRYSTAL POLYMERS——POLYMERS WITH MESOGENS LATERALLY ATTACHED VIA SHORT LINKAGES TO POLYMER BACKBONES

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Abstract New monomers, 2,5-(4-alkoxybenzoyloxy)benzyl acrylates were synthesized. Upon radical polymerizations of these monomers thermotropic liquid crystalline polyacrylates with mesogens laterally attached to polymer backbones via short linkages were obtained. The polymers were found non-crystalline by WAXS measurements. Above glass transition all the polymers had a stable mesophase as revealed by DSC and a polarizing microscope. The glass transition and the isotropization temperatures were about 100 °C and about 165°C respectively, both varying with the size of the R substituents in the mesogens. The term "mesogen-jacketed polymer" is proposed to describe this type of polymers of which the main chains are jacketed with laterally substituted mesogens and to distinguish this new class of side chain liquid crystal polymers from the conventional ones.

INTRODUCTION

Liquid crystal polymer molecules can be constructed by incorporation of mesogenic moieties into polymer molecules by different ways.[1,2,3] The polymers are of the main chain class if the mesogens are present as part of the molecular backbones, while those with mesogens as the substituents or side chains are of the side chain class. The meso-

gens are generally rodic, but the discotic mesogens have also been successfully employed[1] and the bowl shaped or the bowlic mesogens may have offered us new opportunities to make more fancy liquid crystalline polymers. In this paper is reported a series of new class of side chain liquid crystalline polymers of which the mesogens are rodic but laterally attached to the polymer backbones vis short linkages (Fig.1). The results of this study have been partly reported as a communication to the Macromolecules[3].

Conventional side chain LCP:

The new type:

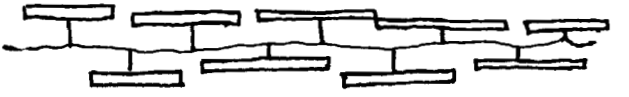
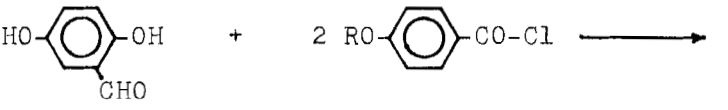
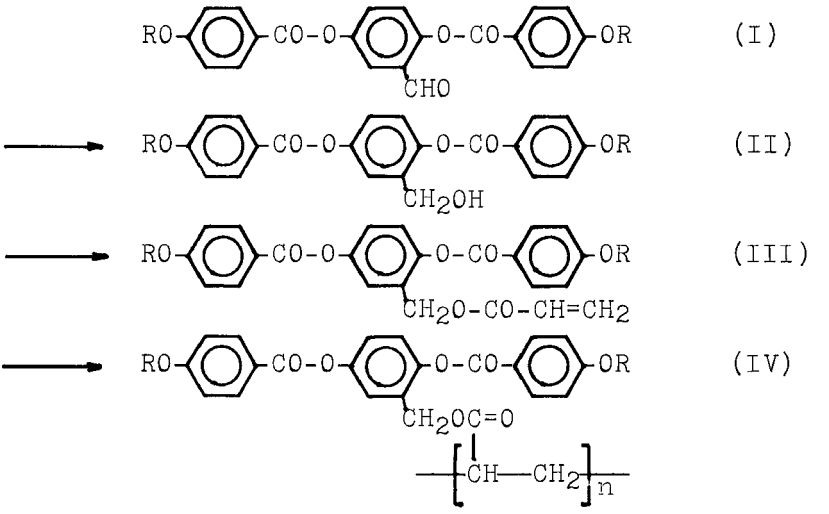


FIGURE 1. A sketch showing the difference between a conventional side chain LCP and the new type with mesogens laterally attached to the main chain backbones.

The polymers were synthesized according to the following sequence of reactions and have a general chemical structure of (IV):





EXPERIMENTAL

In this section the syntheses of the compounds I-III and the polymers IV are separately discussed.

2,5-Bis(4-methoxybenzoyloxy)benzaldehyde (I,R=CH_3)

A solution of 2,5-dihydroxybenzaldehyde (2.8g) in 20 ml THF was added dropwise with vigorous stirring to a solution of 4-methoxybenzoyl chloride (15g) in 110ml THF and 12ml triethylamine. Because the reaction is exothermic an ice bath was used to cool the system to about 10 °C. After the addition the reaction was allowed to continue at room temperature for 24 hours. The product and the triethylamine-HCl salt precipitated. It was filtered, washed with water, 500ml 5% Na_2CO_3 solution and water again. The product was dried in vacuo and recrystallized in toluene (yield 79%).

This compound is liquid crystalline, m.p.192°C and i.p.224 °C. Elemental analysis: calc.67.99% C, 4.46% H; found 67.79% C and 4.39% H. IR absorption: ester C=O 1725 cm^{-1}, -CH=O 1695 and the aldehyde C-H stretching 2900 cm^{-1}. ^{1}H-NMR spectrum: a singlet at 10.08 for -CH=O, a singlet at 3.89 for CH_3 and a multiplet at 6.82 to 7.97 for the benzene rings.

Compound I with R=C_2H_5

Compound I with R=C_2H_5 and R=C_4H_9 were prepared in the same manner.

Elemental analysis: calc. 69.91% C, 5.10% H; found 69.82% C and 5.01% H. It is also liquid crystalline, m.p. 186, i.p. 228 °C. IR absorptions: ester C=O 1725, -CH=O 1687 cm^{-1}. ^{1}H-NMR: a singlet at 10.08 for -CHO, a quartet at 4.03-4.29 for the ethoxy -CH_2- and a triplet at 1.29-1.47 for the ethoxy CH_3-.

Compound I with R=C_4H_9

Elemental analysis: calc. 71.01% C, 6.17% H; found 70.83% C and 6.09% H. It is liquid crystalline too, m.p.104 and i.p. 203 °C. IR absorptions: ester C=O at 1725, -CH=O at 1690 cm^{-1}. ^{1}H-NMR: a singlet at 10.09 for -CHO, a triplet at 4.19-4.02 for RCH_2O, a multiplet at 1.18-1.84 for CCH_2CH_2C and a triplet at 1.03-0.95 for the CH_3-.

2,5-Bis(4-methoxybenzoyloxy)benzyl alcohol (II)

1.2g I (R=CH_3) was dissolved in 60 ml DMSO, to which a solution of 0.6g $NaBH_4$ in 5 ml H_2O was

added dropwise with vigorous stirring at 0 °C.The mixture was stirred for 4 hrs at 0 °C. The reaction solution was poured with stirring into 400ml H_2O to precipitate the product. The product was filtered out, washed with H_2O, dried in vacuo and recrystallized in toluene (yield 57%).

Unlike its precursor this compound is not liquid crystalline, m.p. 159-160 °C.

Elemental analysis: calc. 67.65% C, 4.94% H; found 67.38% C and 4.82% H. IR absorptions: O-H stretching at 3495 and the ester C=O at 1710 cm^{-1}. ^{1}H-NMR: a singlet at 2.14 for $-CH_2OH$ and another singlet at 3.94 for the CH_3O-.

Compound II with R=C_2H_5

The compounds II with R=C_2H_5 and R=C_4H_9 were prepared in a similar way.

It is also non-liquid-crystalline, m.p.158 °C.

Elemental analysis: calc. 68.81% C, 5.51% H; found 68.72% C and 5.47% H. IR absorptions: O-H stretching at 3430 and the ester C=O at 1710 cm^{-1}. ^{1}H-NMR: a singlet at 2.13 for $-CH_2OH$, a triplet at 1.25-1.44 for the alkoxy CH_3 and a quartet at 4.04 -4.17 for the alkoxy -CH2O-.

Compound II with R=C_4H_9

It is non-liquid-crystalline too, m.p. 125 °C.

Elemental analysis: calc. 70.72% C, 6.55% H; found 70.51% C, 6.61% H. IR: O-H stretching at 3490 and the ester C=O at 1710 cm^{-1}.^{1}H-NMR: a singlet at 2.13 for $-CH_2OH$, a multiplet at 1.02-1.92 for the alkoxy C_3H_7 and at 4.03-4.12 a triplet for

the alkoxy $-CH_2O-$.

2,5-Bis(4-methoxybenzoyloxy)benzyl acrylate (III)

4g II(R=CH_3) was dissolved in 40 ml THF and 10 ml Et_3N, to which 5ml acryloyl chloride in 20ml THF was added dropwise with stirring at 0 °C. The reaction was continued at 0 °C for 4 hrs. The Et_3N-HCl salt was precipitated. It was filtered. The solvent was removed from the filtrate by vacuum. The residual liquid was poured with stirring into 100ml water to precipitate the product. Recrystallization was carried out in 95% ethanol (yield 84%).

The monomer thus obtained is also non-liquid-crystalline, m.p. 102 °C.

Elemental analysis: calc. 67.54% C, 4.80% H; found 67.35% C and 4.90% H.

^{1}H-NMR: a multiplet at 6.19-6.57 for the vinyl protons in addition to a singlet at 2.14 for the ester $-CH_2OCO-$ and another singlet at 3.87 for the CH_3O-.

Compound III with R=C_2H_5

Compounds III with R=C_2H_5 and R=C_4H_9 were prepared in the same manner.

It is also non-liquid-crystalline, m.p. 120 °C.

Elemental analysis: calc. 68.58% C, 5.34% H; found 68.27% C and 5.51% H.

^{1}H-NMR: a multiplet at 6.24-6.57 for the vinyl protons in addition to a triplet at 1.29-1.49 for the alkoxy CH_3-, a multiplet at 4.11-4.20 for the alkoxy $-CH_2O-$ and a singlet at 2.13 for the ester $-CH_2OCO-$.

Compound III with $R=C_4H_9$

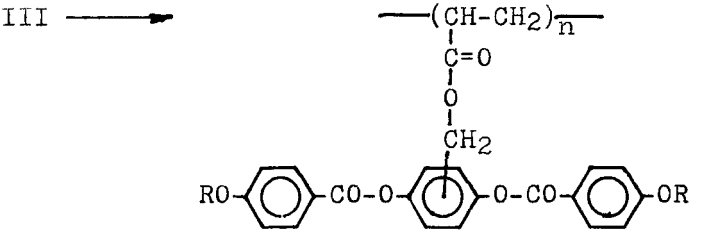
It is again non-liquid-crystalline, m.p. 87 °C.

Elemental analysis: calc. 70.32% C, 5.19% H; found 70.13% C and 5.41% H.

^{1}H-NMR: a multiplet at 6.24-6.57 for the vinyl protons in addition to a multiplet at 0.95-1.90 for the alkoxy C_3H_7, a triplet at 4.01-4.09 for the alkoxy $-CH_2O-$ and a singlet at 2.13 for the ester $-CH_2O-CO-$.

Preparation of the polymers

The polymers were prepared in THF solutions of the monomers at refluxing temperature with AIBN as the initiator (1 mol% AIBN).



Where $R=CH_3$, or C_2H_5 or C_4H_9. As an example of the preparations, 2,5-bis(4-methoxybenzoyloxy)benzyl acrylate (2.31g) was dissolved in 15ml THF, 1 mol% AIBN was added to the solution. The reaction was conducted at refluxing temperature under N_2 with stirring for 5 hrs. The polymer was then precipitated in 300ml methanol. The product was filtered and thoroughly washed with methanol and dried at room temperature under vacuum.

In this study all the elemental analyses were performed by the microanalysis laboratory of the

Chemistry Department, Peking University. The melting temperatures and the liquid crystal properties were determined by a polarizing microscope and a DSC instrument. A Varian FT-80A NMR was used to obtain the NMR spectra of the compounds, IR spectra of the monomers were made on a Shimadzu IR-408 instrument.

RESULTS AND DISCUSSION

Molecular Weights Of The Polymers

In Table 1 are molecular weights of a series of the polymers, measured by a Waters 201 GPC instrument with polystyrene as the calibrating standards. The molecular weights are relatively low presumably because that the huge mesogenic substituent on the C=C of the monomer molecules has imposed strong hindrance on the addition polymerization process.

Thermal Analysis And The Liquid Crystal Properties

The compounds I are crystalline. Above the melting point a stable nematic phase is formed with the butoxy derivative having the widest liquidcrystalline range from 104 to 203 ^{o}C.

Surprisingly the reductions of compounds I to compounds II have destroyed the liquid crystallinity of the compounds. Compounds II are non-mesomorphic. The hydrogen bonding between the hydroxyl groups of the compounds may have prevented the molecules from being parallelly orientated in the melt.

The monomers III were also non-liquid-crystal-

line as would be expected from the large lateral substitution.

The WAXS analysis using a D/Max 3B X-ray diffractometer revealed that all the polymer samples including those annealed or otherwise heat-treated are noncrystalline.

The glass transition temperatures of the polymers as shown in Table 1, are around 100 °C which is much higher than that of such normal polyacrylates as poly(methyl acrylate) of which the glass transition temperature is only 6 °C, indicating that the polymer main chain has been stiffened significantly by the laterally substituted rodic mesogens.

Above the glass transition all the polymers have a stable mesophase in a temperature range of about 60 °C.

A distinct feature of this new class of polymers ("mesogen-jacketed")[3] is that the gravity centers(or the nearby position) of the mesogens are positions bonding to the main chain. Consequently, the motion of the main chain segments should have only minor coupling effects on the motion of the mesogens in contrast with the cases of conventional liquid crystal side chain polymers where the mesogens are connected via the ends to the main chain. Therefore, the introduction of flexible spacers to decouple the motions of the main chain and the motions of the mesogens is likely not as necessary. In fact, the polymers reported here have only short linkage between the main chain and the mesogen. It occurs to the authors

that with the linkages to the gravity centers of the mesogens the main chains hold the mesogens together, draw them closer and help the formation of an ordered mesophase. As in the case of this report, all the polymers are truely liquid crystalline although their monomers are not.

TABLE 1 Properties of the polymers

R	M_n	M_w	T_g °C	T_i °C
CH_3	5,500	16,000	103	160
C_2H_5	7,000	14,000	98	165
n-C_4H_9	8,000	15,000	97	163

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