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Living tandem free radical polymerization of a liquid crystalline monomer

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Summary

In order to synthesize liquid crystalline polymers with controlled structure, the stable free radical polymerization (SFRP) technique was employed to obtain homopolymers and block copolymers based on mesogenic acrylates. By the use of the stable free radical 2,2,6,6-tetramethyl-piperidinyl-l-oxy (TEMPO) we have obtained resins with polydispersity index (PDI) below the limiting theoretical value of 1.5, established for conventional free radical polymerization of acrylates.

Introduction

Thermotropic liquid crystalline polymers (LCPs) are an important class of materials due to their good mechanical properties when compared to conventional thermoplastics, what makes them useful as reinforcing agents for ordinary plastics. The linkage of an LCP to an amorphous polymer as a block copolymer is of special interest since this type of polymer may be used as a compatibilizer in a blend of LCPs and ordinary plastics, improving the adhesion between the LCP and the amorphous matrix.

Side chain liquid crystalline polymers (SCLCPs) have been sinthesized by several methods as anionic polymerization (1), group transfer polymerization (GTP) (2), free radical polymerization (3) and chemical modification of a conventional polymeric backbone by a liquid crystalline group (4). The anionic and GTP methods provide polymers with controlled structure but have some practical difficulties like severe reaction conditions and great monomer selectivity. The free radical method can be easily applied to many kinds of monomer but do not permit the control of the polymer structure. Living free radical techniques can combine the advantages of these methods in one. The most successful system employed to living free radical polymerization of conventional monomers is the one based on the use of a nitroxyl radical that reversibly caps the polymer chain (5). In this work we evaluate the application of this technique for the preparation of homopolymers and block copolymers, outlined in Scheme 1.

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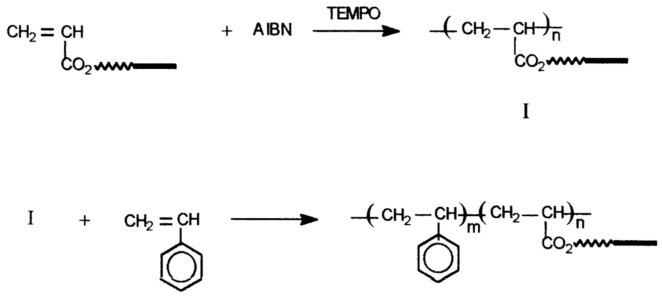


Scheme 1 Preparation of liquid crystalline homopolymers and block copolymers by SFRP

Experimental

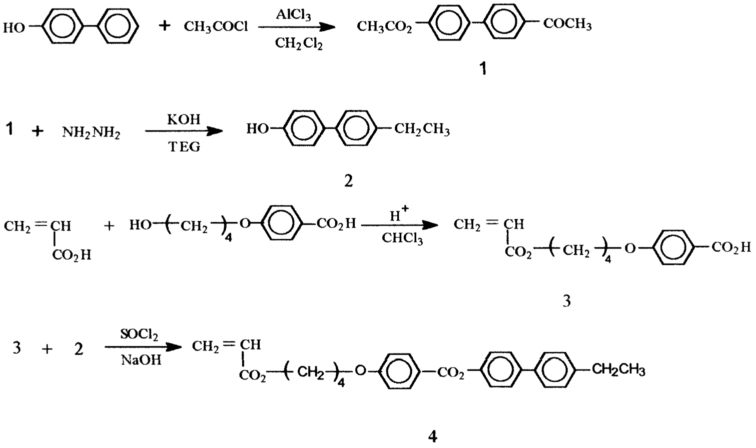
Materials

2,2,6,6-Tetramethyl-piperidinyl-l-oxy (TEMPO) was purchased from Aldrich Co. Inc., Diethyl ether, dioxane and chloroform were purchased from Vetec S. A. Styrene was purchased from Petroflex S.A. Azoisobutyronitrile (AIBN) was purchased from Metacril S.A.

Synthesis

Liquid crystalline monomer

The acrylate monomer was prepared by following the route depicted in Scheme 2.



Scheme 2. Route to the synthesis of liquid crystalline monomer

4-Acetoxy-4’-acetylbiphenyl (**1**)

This compound was synthesized according to a procedure described by Tanigaki *et al.* (6). The product **1** was a white solid, melting point 124.5°C.

4-Hydroxy-4’-ethylbiphenyl (**2**) was prepared by the general method of a Wolff-Kishner reduction (7) under conditions that lead to the alkalyne hydrolysis of the acetoxy portion. The white solid obtained showed a melting point of 150°C.

4-(4-propenoyloxybutyloxy)benzoic acid (**3**) was prepared by a procedure described by Whitcombe *et al.*(8), yielding a product with melting point 119°C.

4’-Ethylbiphenyl-4-(4-propenoyloxybutyloxy)benzoate (**4**) was synthesized by a method established in the literature (9). After purification the product melted at 104°C.

Polymerizations

Homopolymers were prepared in sealed ampoules degassed by freeze-thaw technique from a mixture of monomer (**4**), AIBN, TEMPO and dioxane, heated to 135°C, in a 48-hour reaction. In a typical experiment were reacted 0.5 g (1.1 x 10^{-3} mol) of the liquid crystalline monomer, 0.0009 g (5.5 x 10^{-6} mol) of AIBN and TEMPO in a proportion of 3:1, 1:1 and 1:3 related to the molar amount of AIBN, in 1.5 ml of dioxane. Copolymers were obtained by reacting 0.5 g of the macroinitiator of poly-4 with 0.5 g (4.8 x 10^{-3} mol) of styrene in sealed ampoules at the same conditions, in the absence of initiator (AIBN) and TEMPO. Purification of homo and copolymers was made by sequential precipitations onto ethyl ether from chloroform solutions.

Characterization

Thermal characteristics were examined by means of a Perkin-Elmer DSC-7, with samples weighing from 4 to 7 mg. The thermograms were obtained at both heating and cooling rates of 20°C/min under nitrogen atmosphere.

Molecular weights were determined by gel permeation chromatography (GPC) on a Waters chromatograph using Ultrastyragel® columns calibrated against monodisperse polystyrene standards, eluted with THF.

^{1}H-NMR spectrum was obtained using a 300 MHz Bruker spectrometer.

Results and discussion

The homopolymerization of monomer **4** by the SFRP technique gave polymers with the characteristics shown in Table 1.

The variation on the ratio between [I] and [TEMPO] was investigated due to the controversial results that have been reported about this technique. Some works state that for a good efficiency an excess of initiator is required (10), while others claim that the nitroxide must be in excess for better results (11). In this work we can conclude that both situations and equimolar amounts of initiator and nitroxide can be successfully used, as long as the ratio between them is near unity.

Table 1- Characteristics of LC polymers obtained by SFRP

	[I]/[TEMPO]	Conversion (%)	M_n (g/mol)	PDI
Polymer 1	1.2	78	6800	1.49
Polymer 2	1.0	76	6900	1.47
Polymer 3	0.83	76	6900	1.47

I is the initiator: AIBN; time of polymerization: 48 h; solvent: dioxane

The GPC trace of polymer 2 (Figure 1) shows a very interesting behaviour for a radical polymerization of liquid crystalline monomer, with a PDI wich is below that one predicted for conventional free radical polymerization (1.5) and indicates a controlled reaction.

The ^{1}H-NMR spectrum, shown in Figure 2, confirms the structure of the polymer with multiple absorptions near to $\delta = 1.0$ ppm, related to the protons of the piperidine system, an indication of the incorporation of the nitroxide at the chain end.

The technique was used for the preparation of a homopolymer (polymer 4) with a molecular weight of 6800 and PDI of 1.67 that was further copolymerized with styrene to yield a copolymer with the following characteristics, after a 16-hour reaction: conversion:34%; M_n:9700; PDI: 2.61. This results show the incorporation of the charge of the second monomer, as an indication of the living fashion of the reaction.

The thermal analysis of the homopolymer, made by Differential Scanning Calorimetry (DSC), (Figure 3) showed liquid crystalline properties between 115-263°C, with an endotherm at 141°C, characterized as a nematic transition. The copolymer showed similar behaviour (Figure 4), with transitions not well defined, due to the spreading of the liquid crystalline moieties in the amorphous matrix of the copolymer. The appearance of thermal characteristics of the copolymer wich are similar to those shown by the homopolymer is an indication of the good phase separation achieved in the block copolymer.

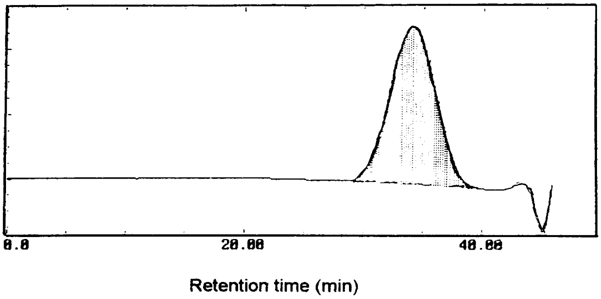


Figure 1. GPC plot of Polymer 2

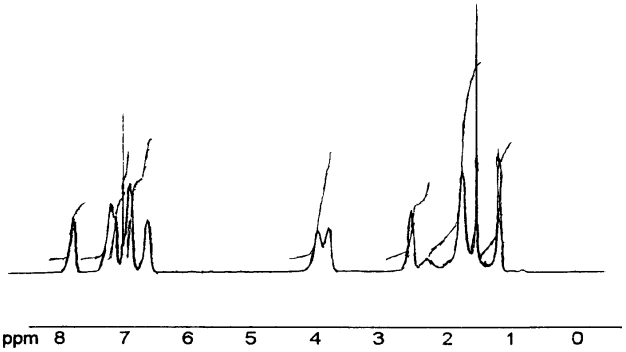


Figure 2. ^{1}H-NMR spectrum of Polymer 2

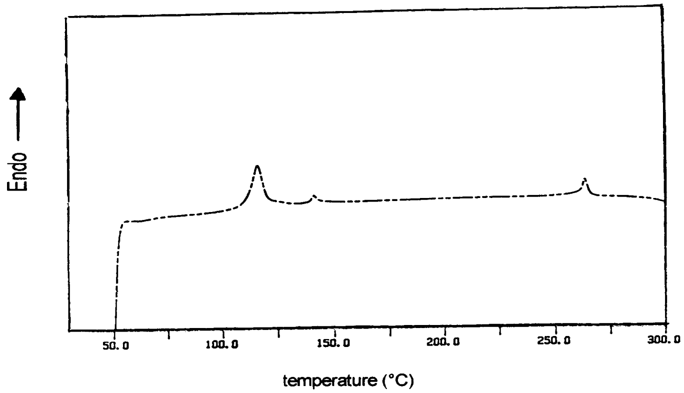


Figure 3. DSC curve of the homopolymer

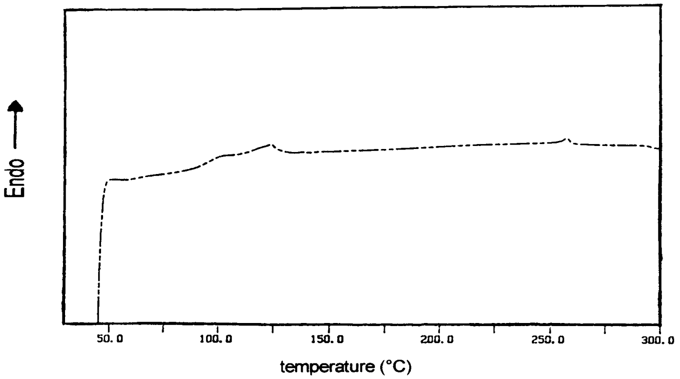


Figure 4. DSC curve of the copolymer

In conclusion, we report in this paper, an effort towards the preparation of a liquid crystalline polymer with controlled structure by a free radical technique. As the structure of the polymer and its molecular weight influences the type and range of the LC microphases, this control permits its utilization as materials with tailored properties for practical applications.

Acknowledgements

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