

Synthesis, structure and mesomorphic properties of side-chain chiral liquid crystalline polysiloxanes based on (*S*)-(+)-2-methyl-1-butanol derivatives

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Abstract

The synthesis of five chiral liquid crystalline monomers (M_1 – M_5), and their corresponding side-chain polymers (P_1 – P_5) based on (*S*)-(+)-2-methyl-1-butanol derivatives is described. The chemical structures of the monomers were confirmed by FT-IR, ^1H NMR, and elemental analyses. The structure-property relationships of the monomers and polymers obtained are discussed. The mesomorphic properties were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), polarizing optical microscopy (POM), and X-ray diffraction (XRD) measurements. All monomers showed a cholesteric phase. For M_2 , M_3 , and M_5 , besides a cholesteric phase and a smectic A (S_A) phase, M_2 also revealed an enantiotropic chiral smectic C (S_C^*) phase and a monotropic smectic B (S_B) phase, and M_3 also showed a S_B phase. The polymers P_1 – P_5 exhibited a S_A phase, moreover, P_2 , P_3 and P_5 also revealed a S_C^* phase. The experimental results demonstrated that a flexible siloxane backbone and a long flexible spacer tended to exhibit a low glass transition temperature, high thermal stability, and wide mesophase temperature range.

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1. Introduction

Chiral liquid crystalline polymers (LCPs) have attracted considerable interest, because of their unique optical and electrical properties, including the selective reflection of light, thermochromism, ferroelectricity, and their potential applications such as non-linear optical devices, full-color thermal

imaging, electro-optical materials, and fast switching [1–18]. The rod-like, chiral molecules responsible for the macroscopical alignment of the mesogenic domains can produce a cholesteric or S_C^* phase. Depending on the chemical structure, it may be feasible to achieve a macroscopic alignment of the chiral mesophase domains. Many side-chain chiral LCPs, mostly adopting commercially available chiral compounds such as cholesterol, menthol, and (*R*)-(-)-methyl mandelate, have been studied [19–25]. The aims of our research are: (i) to study structure-property relationships of side-chain chiral

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LCs based on (*S*)-(+)-2-methyl-1-butanol derivatives; (ii) to supply the necessary data to synthesize piezoelectric and ferroelectric liquid crystalline (LC) materials; and (iii) to explore their advanced applications.

In this study, chiral LC monomers and their corresponding side-chain LC polysiloxanes based on (*S*)-(+)-2-methyl-1-butanol derivatives were synthesized and characterized. Their mesomorphic properties and phase behavior were investigated with DSC, TGA, POM, and XRD. The effect of the rigidity of the mesogenic core and the bridge bond on the mesomorphic properties is discussed.

2. Experimental procedures

2.1. Materials

Polymethylhydrosiloxane (PMHS, $\overline{M}_n = 700$ –800) was purchased from Jilin Chemical Industry Co. (*S*)-(-)-2-methyl-1-butanol, $[\alpha]_D^{20} -6.2^\circ$ (from Merck) and 4,4'-dihydroxybiphenyl (from Aldrich) were used as received. Undecylenic acid was purchased from Beijing Jinlong chemical Reagent Co., Ltd. H_2PtCl_6 catalyst was obtained from Shenyang Chemical Reagent Co. Toluene used in the hydrosilylation reaction was purified by treatment with LiAlH_4 and distilled before use. All other solvents and reagents were purified by standard methods.

2.2. Characterization

FT-IR spectra were measured on a Perkin–Elmer spectrum One (B) spectrometer (Perkin–Elmer, Foster City, CA). ^1H NMR (400 MHz) spectra were obtained with a Varian WH-90PFT spectrometer (Varian Associates, Palo Alto, CA). The elemental analyses were carried out with a Elementar Vario EL III (Elementar, Germany). The optical rotations were obtained on a Perkin–Elmer 341 polarimeter. The phase transition temperatures and thermodynamic parameters were determined with a Netzsch DSC 204 (Netzsch, Germany) equipped with a liquid nitrogen cooling system. The heating and cooling rates were 5–10 °C/min. The thermal stability of the polymers under atmosphere was measured with a Netzsch TGA 209C thermogravimetric analyzer. The heating rates were 20 °C/min. A Leica DMRX POM (Leica, Germany) equipped with a Linkam THMSE-600 (Linkam, England) cool and hot stage was used to observe the phase transition temperatures and analyze the mesomorphic proper-

ties through the observation of optical textures. XRD measurements were performed with a nickel-filtered Cu-K_α ($\lambda = 1.542 \text{ \AA}$) radiation with a DMAX-3A Rigaku (Rigaku, Japan) powder diffractometer.

2.3. Synthesis of the intermediate compounds

The synthesis of the main intermediate compounds is outlined in Scheme 1. Yields, structural characterization and some physical properties of the intermediate compounds are summarized in Table 1. 4-[(*S*)-2-methyl-1-butoxy] benzoic acid (**1**), 4-[(*S*)-2-methyl-1-butoxy]-4'-hydroxybiphenyl (**2**) and 4-(10-undecylen-1-yloxy) benzoic acid (**5**) were prepared according to the method reported previously [26–28].

4-Hydroxyphenyl-4'-(10-undecylen-1-ate) (**3**), 4-hydroxybiphenyl-4'-(10-undecylen-1-ate) (**4**), 4-hydroxyphenyl-4'-(10-undecylen-1-yloxy)benzoate (**6**), 4-hydroxy-biphenyl-4'-(10-undecylen-1-yloxy)benzoate (**7**).

Four compounds **3**, **4**, **6** and **7** were prepared by the same method. The synthesis of **7** is described below as an example.

4-(10-Undecylen-1-yloxy)benzoyl chloride was prepared through the reaction of compound **5** with excess thionyl chloride according to the reported literature [28]. The acid chloride obtained (16.1 g, 50 mmol) was dissolved in 10 mL of dry tetrahydrofuran (THF), and then added dropwise to a cold solution of 4,4'-dihydroxybiphenyl (46.5 g, 250 mmol) in 150 mL of THF and 4 mL of pyridine under quick stirring. After the mixture was heated to reflux for 12 h, the reaction solution was poured into a beaker filled with 500 mL of water. The crude product, obtained by filtration, was washed with 5% NaOH solution and ethanol, and then recrystallized from acetone. A white solid **7** was obtained. Yield 48%, mp 175 °C.

2.4. Synthesis of the monomers

The synthetic route to olefinic monomers is shown in Scheme 2.

4-(10-Undecylen-1-yloxy)phenyl-4'-[(*S*)-2-methyl-1-butoxy]benzoate (**M**₁), 4-(10-undecylen-1-yloxy)-biphenyl-4'-[(*S*)-2-methyl-1-butoxy]benzoate (**M**₂), 4-[(*S*)-2-methyl-1-butoxy]biphenyl-4'-(10-undecylen-1-yloxy)benzoate (**M**₃), 4-(10-undecylen-1-yloxy)benzoyloxy)phenyl-4'-[(*S*)-2-methyl-1-butoxy]benzoate (**M**₄) and 4-(10-undecylen-1-yloxy)benzo-

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