

Synthesis of mesogen-jacketed liquid crystalline polymers with long symmetry mesogenic core containing two biphenyls

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ABSTRACT

A series of mesogen-jacketed liquid crystalline polymers, poly {2,5-bis[(4-alkoxybiphenyl)oxycarbonyl]styrenes} (P-C_m, *m* = 8, 10, 12, 14 and 18) were designed and successfully synthesized via free radical polymerization. The chemical structures of the monomers were confirmed by ¹H NMR, ¹³C NMR and Mass Spectrometry. The molecular characterizations of the polymers were performed with ¹H NMR, GPC and TGA. The phase structures and transitions of the polymers were investigated by the combination of techniques including DSC, POM, temperature-variable FT-IR spectroscopy, 1D WAXD and SAXS. The experimental results suggest that the polymers with symmetry mesogenic core containing two biphenyls can develop into a well-defined smectic A (S_A) phase. This implies that MJLCPs molecules shape can be modulated from rod-like to ribbon-like by simply changing the length of the mesogenic group.

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1. Introduction

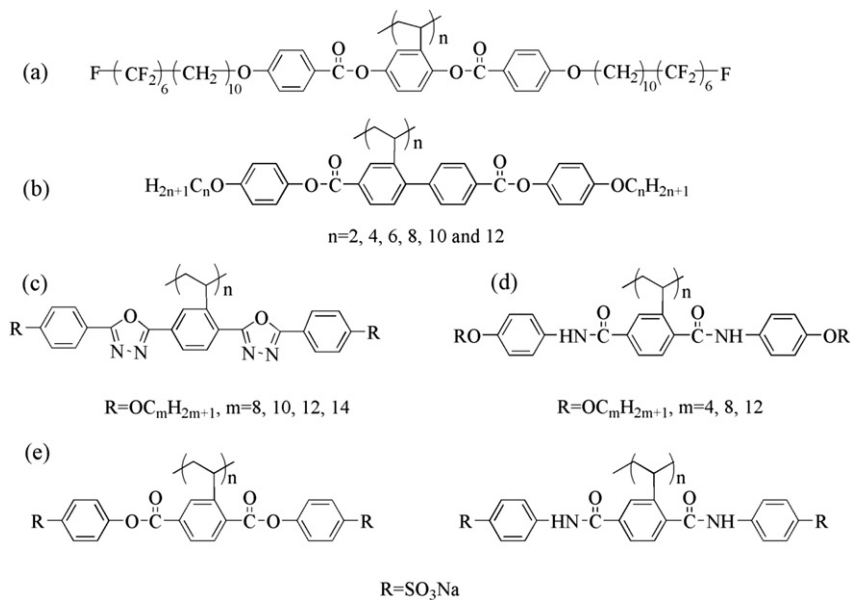
Liquid-crystalline polymers (LCPs) have attracted long standing attention for their potential applications in many fields, including optical data storage, optic, electro-optic, nonlinear optic devices, photomechanical and so on [1–7]. Generally speaking, LCPs have two main categories: main-chain liquid crystalline polymers (MCLCPs) with mesogen units located in the main chain [8–10] and side-chain liquid crystalline polymers (SCLCPs) with mesogens attached to the main chain as side groups [11,12]. For SCLCPs, Finkelmann pointed out that the flexible spacer inserted between main chain and mesogenic side groups was indispensable in order for a SC-LCP to achieve LC phase since it decoupled the interaction of side chain and polymer backbone, which disrupted the ordered packing of the side mesogens [13]. However, as proposed by Zhou et al., in 1987, mesogen jacketed liquid crystal polymers (MJLCPs), which were a special class of SCLCPs with their mesogenic units attached laterally to the main chain through a short spacer or with a single covalent bond, could also form stable LC phases [14–25]. Unlike the conventional SCLCPs whose backbones usually take a random-coil chain conformation, MJLCPs are somewhat rigid and exhibit some features of MCLCPs because the strong coupling

between the polymer main chain and the highly crowded, rigid, and bulky side groups. So, the LC phase structures are found to be columnar nematic phase and hexagonal columnar phase in which each cylinder is formed by a single MJLCPs chain molecule.

However, the rod-like chain shall not be the only molecular shape of MJLCPs. Smectic phases have been found in laterally attached side-chain LC polymers by changing several variables, including the length or type of the terminal flexible substituent, chemical structures of mesogens, hydrogen bonding and the electrostatic interactions. For example, Padma Gopalan has reported the design, synthesis and characterization of MJLCPs with semi-fluorinated mesogenic groups (see Scheme 1(a)) [26]. Authors pointed out that the polymers could form S_A phase because of the microphase separation. Through changing chemical structures of mesogens, Chen et al. have researched the phase behavior of MJLCPs with unbalanced mesogenic core and different terminal flexible substituents (see Scheme 1(b)) [27]. The results showed that well-defined S_A phase was formed when the carbon number for the flexible substituents were shorter than four (butoxy groups); whereas the one reached four, well-defined S_C phase was observed. Chai et al. also have found that the MJLCPs containing the 1,3,4-oxadiazole unit exhibited S_A phase (see Scheme 1(c)) [28]. Cheng et al. have found that the polymers contained amide linkages in the side groups formed S_A phase due to hydrogen bonding (see Scheme 1(d)) [29]. Meantime, when the terminal groups were replaced by ionic groups, the polymers still presented S_A phase because of the electrostatic interactions (see Scheme 1(e)) [30].

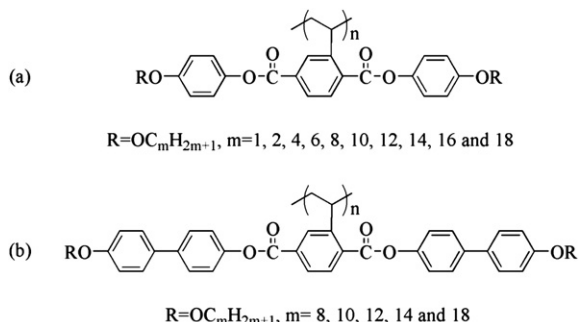
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Scheme 1. Chemical structures of MJLCPs synthesized previously.

In our previous studies, we have systematically researched the influence of alkoxy tail length on the self-organization of poly{2,5-bis[4-alkoxyphenyl]oxycarbonyl]styrenes} (P-OC $_m$, m is the number of the carbons in the alkoxy groups, $m = 1, 2, 4, 6, 8, 10, 12, 14, 16$ and 18) based on 2-vinylterephthalic acid and 4-alkoxyphenyl (see Scheme 2(a)) [31]. The experiments results demonstrated that the polymers could form smectic phase, isotropic phase and columnar phase when $m \geq 10$. The attachment of long flexible alkyl side chains to the polymer backbone can lead to layered structures due to the unfavorable interaction between mesogens and the apolar alkyl side chains, and it was considered that the smectic phase was proposed to form by the driving force of the enthalpy. Interesting point arises concerning the properties of MJLCPs when 4-alkoxyphenol was replaced by 4-alkoxybiphenol. One hand, compared with the rigid of core of the P-OC $_m$, the new MJLCP (poly{2,5-bis[4-alkoxybiphenyl]oxycarbonyl]styrene}, P-C $_m$) has a larger aspect ratio, leading to the stronger interaction between the side on rigid mesogens. The other hand, the phase behaviors of P-OC $_m$ were strongly alkyl length dependent due to the competing of the steric effect, the microphase separation and the driving force of the entropy. Of particular interest is to ask in whether the alkyl tails length has also influence on the phase behaviors of P-C $_m$. So, in this paper, we reported the synthesis and characterization of a series of vinyl monomers with different numbers of alkoxy terminal groups and their corresponding homopolymers. The chemical structures of polymers are shown in



Scheme 2. Chemical structures of P-OC $_m$ (a) and P-C $_m$ (b).

Scheme 2(b). However, the monomers M-C $_m$ ($m < 8$) were found to be difficultly dissolved in common organic solvents or be polymerized to a sufficiently high M_n . Our experimental results proved that the polymers could develop into a stable S $_A$ phase, whatever the alkyl tail length is short or long. Therefore, through studying the phase behavior of these polymers, we can deeply understand the relationship between a simple structural variable of the monomer and the change in the phase structure of MJLCPs.

2. Experimental section

2.1. Materials

The precursor 2-vinylterephthalic acid (VTA) was synthesized according to previous paper [25]. Chlorobenzene (Acros, 99%) was purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with distilled water, once with 5% sodium carbonate solution, and again with distilled water before being dried with anhydrous calcium chloride and then distilled. 4-(dimethylamino)pyridine (DMAP, 99%, ACROS), 4, 4'-Diphenol (98%, Alfa Aesar) and the corresponding octadecaoyl bromides together with other reagents and solvents were used as received without further purification.

2.2. Synthesis of monomers

The synthetic route of monomers of 2,5-bis [(4-alkoxybiphenyl)oxycarbonyl]-styrenes (M-C $_m$, $m = 8, 10, 12, 14, 18$) is shown in Scheme 3. The experimental details are described as follows using 2,5-bis[(4-octanoxybiphenyl)oxycarbonyl]-styrene (M-C8) as an example.

2.2.1. Synthesis of 4-octanoxybiphenol

4, 4'-biphenol (20 g, 0.1074 mol), octyl bromide (3.5 g, 0.0182 mol), K_2CO_3 (14.964 g, 0.1086 mol) and 200 ml were added into a 500 ml round-bottom flask. The mixture was heated for 12 h in 55 °C, next the reaction mixture poured into a large amount of water to precipitate products. The products were purified by precipitation in water from THF solution three times. At last, the crude products were purified by column chromatograph (silica gel,

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