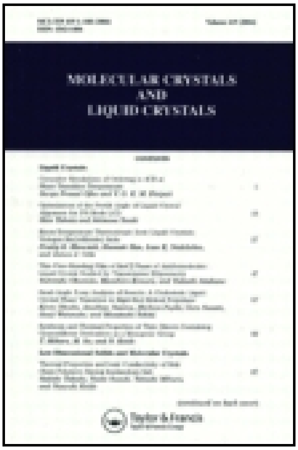

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Thermotropic Behavior of Side-Chain Liquid-Crystalline Polymers with a Pendant Terphenylene Mesogen

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Thermotropic Behavior of Side-Chain Liquid-Crystalline Polymers with a Pendant Terphenylene Mesogen

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The synthesis and the thermotropic behavior of new monomers and side-chain liquid-crystalline polymers were studied. For the functionalization of the methacrylic and acrylic monomers, a bromine end-functionalized dialkoxyterphenylene, showing both liquid-crystalline and light emission properties, was used. Monomers were polymerized by AIBN-initiated and thermal polymerizations. The thermotropic behavior of compounds was studied by DSC, POM and XRD. Results indicate a well-defined thermotropism, which was attested by the multiple thermal transitions and different optical textures. X-ray diffraction patterns showed several equidistant sharp reflections at low angles following monolayer and bilayer structures of tilted smectic phases for the monomers and polymers, respectively.

Keywords: mesogenic group; terphenylene; thermotropic behavior

INTRODUCTION

Side-chain liquid-crystalline polymers (SCLCP) combine the properties of polymers with those of liquid crystals and during the last two decades have been an attractive matter to study [1]. SCLCP are composed by three basic components: a main polymeric chain, a spacer and a mesogenic group. Since the spontaneous organization of the mesogenic groups causes the liquid crystal behavior, perhaps these groups

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are the most important part of a SCLCP. Let us consider the particular case of the dialkoxy-terphenylene [2] derivatives, which are mesogens of particular interest because of the high anisotropy of their chemical structure, especially if the dialkoxyterphenylene is functionalized at one chain-end to be further grafted into a polymer backbone to produce novel macromolecular structures showing particular liquid crystalline properties. Recently, we reported a series of interesting bromine end-functionalized dialkoxyterphenylene [3] molecules, which develop a rich mesomorphism with tilted smectic type mesophases (SmC and SmF/SmI). A second interesting property of these oligophenylene molecules emerges from their π-conjugated core, which can produce a high-energy light emission with potential applications in optoelectronic devices like the organic light emitting diodes (OLEDs). It should be mentioned that SCLCP with an acrylic or methacrylic backbone are easy to synthesize [4] and show a relatively high thermal stability [5]. Also, these polymer backbones show a very low interaction with the UV-vis radiation emitted by the π-conjugated mesogens in the OLED devices. In this work we present and discuss the synthesis and the thermotropic characterization of new side-chain liquid-crystalline methacrylic and acrylic polymers with alkoxy-terphenylene pendant groups.

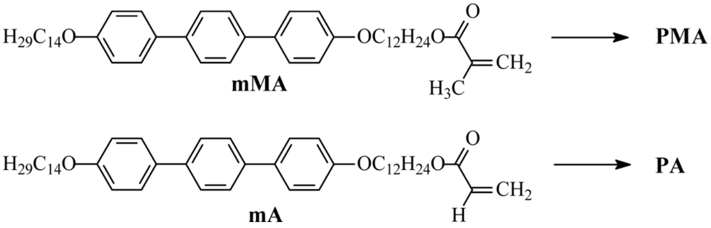
EXPERIMENTAL

Measurements

^{1}H-NMR spectra were recorded in a 300 MHz with a Jeol NMR spectrometer ($CDCl_3$ and THF-d_8 as solvents). Differential scanning calorimetry (DSC) traces were registered in a TA MDSC 2920 at 10°C/min. Elemental analyses (C and H) were performed in a Carlo Erba (1106) instrument at the Charles Sadron Institute, Strasbourg, France. Optical textures of liquid crystal phases of all intermediates were obtained by polarizing optical microscopy (POM) by using an Olympus microscope coupled with a Mettler FP82 hot stage. The X-ray diffraction (XRD) patterns on unaligned samples were recorded with a Guinier focusing camera, using a bent quartz monochromator, $K\alpha_1$ copper radiation from a Philips PW 1009 X-ray generator, and a home-made electrical oven.

Monomer Synthesis and Polymerization

Chemical structures of the functionalized acrylic (**mA**) and methcrylic (**mMA**) monomers studied in this work are shown in Scheme 1.



SCHEME 1 Chemical structures of methacrylate (**mMA**) and acrylate (**mA**) monomers.

The terphenylene mesogenic moiety was synthesized trough a palladium-catalyzed boronic acid coupling reaction as reported elsewhere [3]. Monomers were prepared reacting bromine end-functionalized terphenylene with the acrylic or methacrylic acid according to well known methods described in the literature [6]. Side-chain acrylic **PA** and methacryic (**PMA**) polymers were obtained by thermal polymerization in a DSC running and by AIBN-initiated free radical polymerization of **mA** or **mMA** using dried tetrahydrofuran (1% mol AIBN) as solvent. It is worth to mention that, in solution, only low molecular weight polymers were obtained. All these compounds were obtained with high purity as demonstrated by the NMR characterization.

RESULTS AND DISCUSSION

The multiple thermal transitions exhibited by monomers and polymers were first determined by DSC. The optical texture and structure of each mesophase were then studied by POM and powder XRD, respectively. DSC thermograms presented in Figure 1 show that both monomers **mA** and **mMA** exhibit a rich polymorphic behavior during both the heating (h) and cooling (c) processes. A similar behavior was reported for the bromine end-functionalized dialkoxyterphenylene precursor [3]. Furthermore, these DSC traces do not indicate any thermal polymerization of monomers, probably because of the presence of undetectable traces of inhibitor. After a thoroughly purification, the inhibitor was removed from the monomers and then, the thermal polymerization has occurred in the DSC running as it is observed in Figure 2. As expected, the thermal transitions in polymers are less-defined compared to their respective monomers and the clearing temperatures of monomers occur near 170–180°C, whereas those of polymers occur around 230°C. These data clearly indicate that the main polymeric chain perturbs the possible LC arrangements developing the mesogenic groups by themselves.

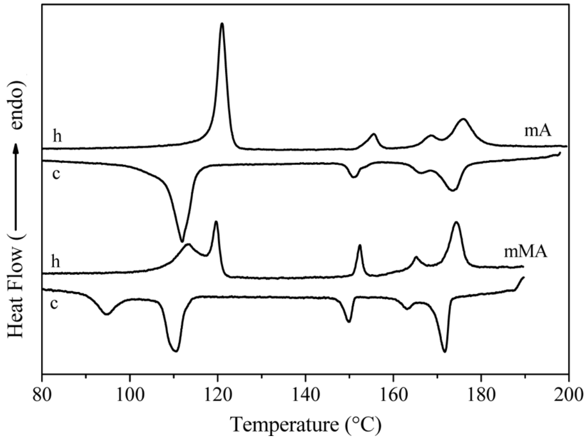


FIGURE 1 Heating (h) and cooling (c) DSC traces for monomers **mMA** and **mA**.

The transition temperatures, determined by DSC and described above, were used as reference for recording the optical textures of all mesophases, which were sequentially obtained upon cooling from the isotropic state. Regarding the monomer **mMA**, it concurrently

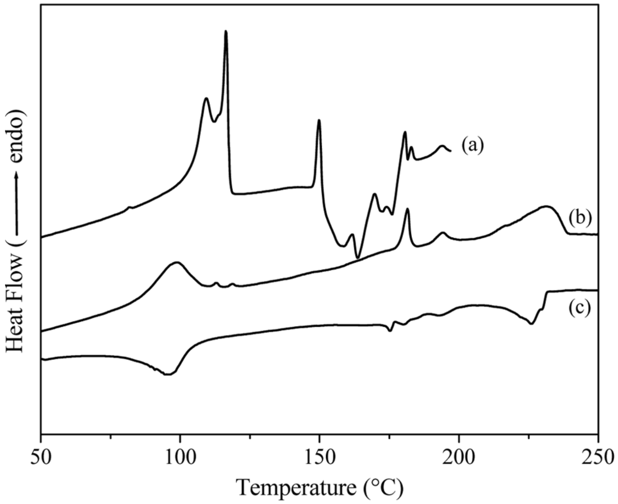


FIGURE 2 (a) Thermal polymerization of monomer **mMA** by DSC; and (b) heating and (c) cooling DSC traces for polymer **PMA**.

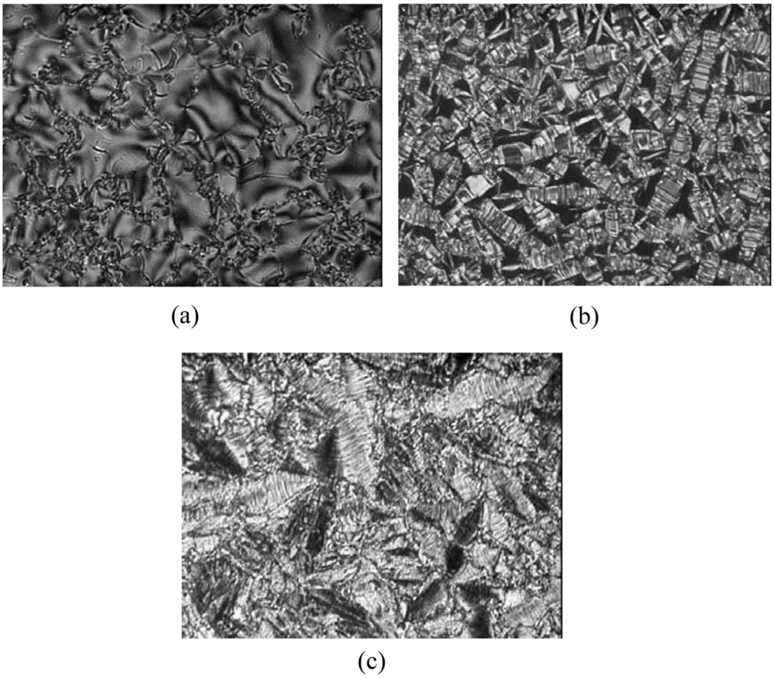


FIGURE 3 Optical texture of monomer **mMA** at (a) 152°C, and polymer **PMA** at (b) 230°C, and (c) 180°C, obtained on cooling.

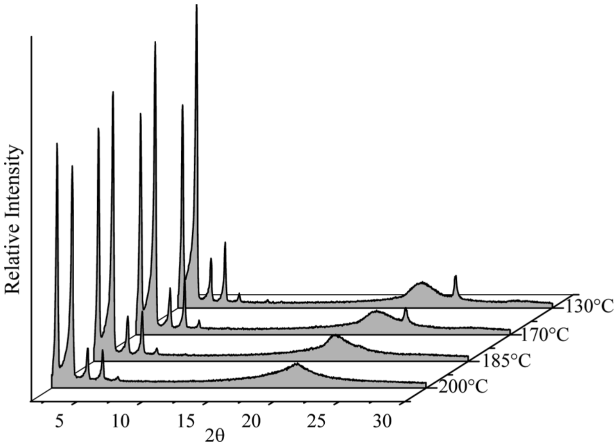


FIGURE 4 XRD pattern of polymer PMA at four different temperatures.

TABLE 1 Experimental Stacking Period d_{001} of Smectic Layer Measured at Temperature T, and Calculated Length L of Monomer **mMA** in its Most Extended Conformation

Temperature °C	LC phase	L, Å calculated	d, Å exp.	Tilt angle, θ
185	I		—	—
166	SmC	49.2	39.9	36°
156	SmF/I		40.3	35°
140	SmX		40.5	35°

showed a Schlieren and a focal-conic fan textures typical of a smectic phase (see Fig. 3a) [7]. On subsequent cooling no evident changes in the optical texture were observed. For the polymer **PMA**, the observed optical textures on cooling from the isotropic state were first a banded bâtonnet texture (Fig. 3b) then, a focal-conic fan texture (Fig. 3c).

The smectic nature of mesophases observed at high temperature for monomers and polymers was characterized in the XRD pattern by the presence of two or more equidistant small angle sharp reflections at low angles (see Fig. 4). These reflections correspond to the stacking period of the smectic layers. The periodicity (d_{001}) measured experimentally was compared with the calculated length L of the mesogenic group (including the methacrylate group) in its most extended conformation (see Tables 1 and 2). Such molecular length (49.2 Å) was calculated using molecular modeling software (Spartan). In contrast to the monomer **MA** in which monolayer tilted smectic phases were observed, the comparison between the distances d_{001} and d_{002} and L in the polymer **PMA** (see Table 2), immediately suggests a bilayer structure with molecules tilted with respect to the normal of the smectic planes. The symmetry change of the mesophases was monitored by the number and shape of the scattering signals in the wide angle

TABLE 2 Experimental Stacking Period d_{001} and d_{002} of Smectic Layer Measured at Temperature T of Polymer **PMA**

Temperature °C	LC phase	L, Å Monomeric unit	d_{001}, d_{002} Å	Tilt angle, θ
>230	I		—	—
230	SmC	49.2	72.6, 36.5	42°
200	SmF/I		74.7, 37.6	40°
170	SmX		77.6, 39.3	37°

region of the XRD pattern. These results suggest a disordered liquid-like arrangement of molecules within the layers. A summary of these observations, the exact phase sequences and the transition enthalpies are gathered in Tables 1 and 2.

CONCLUSIONS

New methacrylic and acrylic monomers modified with a dialkoxyterphenylene mesogen were synthesized and characterized. Monomers were polymerized via thermal polymerization, affording side-chain liquid crystalline polymers. DSC and POM showed that monomers and polymers develop several thermotropic smectic mesophases. By X-ray analysis it was observed that both that monomers and polymers develop tilted smectic mesophases. A comparison between d_{001} and L has indicated a monolayer and bilayer structure for monomers and polymers, respectively. Further studies on these materials are in progress and results will be published soon.

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