# Synthesis and Characterization of A New Series of "Mesogen-Jacketed Liquid Crystal Polymers" Based on the Newly Synthesized Vinylterephthalic Acid

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ABSTRACT: The synthesis and characterization of a new series of mesogen-jacketed liquid crystal polymers, poly{2,5-bis[(para-substituted phenyl)oxycarbonyl]styrene}s, based on 2-vinylterephthalic acid are reported. These polymers formed very stable liquid crystal phases above the glass transition temperatures. A brief comparison of the properties of the new polymers with those of some previously reported counterparts is included.

## Introduction

The concept of a "mesogen-jacketed liquid crystal polymer" (MJLCP) was first proposed by Zhou et al. to describe the side-chain liquid crystalline polymers in which the mesogenic units were attached laterally to the main chain via a direct connection or via short spacers.[1,2] According to this model, the spatial requirement of the bulky and rigid mesogenic units causes the main chain of the polymer to take extended and stiffened conformations. The idea has been repeatedly supported by studies of, e.g., Hardouin,[3] Gray,[4] Richardson,[5] Schrock,[6] Mauzac,[7] Xu,[8] Zhou,[9−12] and, most recently, Ober and co-workers.[13] For example, small-angle neutron scattering experiments have shown that the polymer chains have in the nematic phase prolate conformations with a large shape anisotropy.[3] The X-ray diffraction studies have suggested that there is a tendency for the side groups to spiral around the backbone.[5] The morphological studies have shown that these polymers form banded textures as do the semirigid main-chain liquid crystalline polymers.[8] The large values of the persistent length in good solvent of MJLCPs have been found in light scattering studies.[9,11] However, the number of the studied MJLCPs has been small. The two series of MJLCPs synthesized in this laboratory[2,10−12] are one based on 2-vinylhydroquinone (VHQ) and another based on 2-vinyl-1,4-phenylenediamine (VPDA). New polymers are desired for further study and better understanding of the structure−property relationships of these unique polymers. Besides, even for the few studied MJLCPs, the structure and property studies are also limited because the polymers have only been synthesized with difficulty in very small amounts in research laboratories. In this paper, we report a new series of MJLCPs which were synthesized via the new precursor 2-vinylterephthalic acid (VTA). We found not only that these new polymers are all liquid-crystalline as other MJLCPs but also that these VYA-based polymers are easier to synthesize than our previous MJLCPs based on VHQ or VPDA.

## Experimental Section

**Instrumental Characterization.** $^1$H NMR spectra were obtained with a Bruker ARX400 spectrometer by using $DCCl_3$ as solvent and TMS as internal standard. The elemental analyses were carried out by means of a Carlo Erba 1106 instrument. The mass spectra were taken by a VG−ZAB−HS mass spectrometer. Differential scanning calorimetry (DSC) curves were recorded on a Shimadzu DSC-50 or TA DSC 2010 for the monomers and a Perkin-Elmer 7 series instrument for the polymers. The liquid crystal properties were also studied by means of a Leitz Laborlux 12 Pol polarizing optical microscope (POM) with a Leitz 350 hot stage. Powder X-ray diffraction studies were carried out with a Rigaku Dmax-2400 diffractometer.

**Materials.** The key precursor 2-vinylterephthalic acid (VTA) was synthesized by four steps (Scheme 1) starting from 2-methylterephthalic acid.[14−15] The *p*-(*n*-alkoxyl)phenols were prepared from the reaction of hydroquinone with corresponding alkyl bromides as described by Klarmann et al.[16] All other reagents and solvents were commercial products.

**Synthesis of Monomers and Polymers.** The syntheses and structures of the monomers are shown in Scheme 1. The

**Scheme 1. Synthesis of VTA and the Monomers**

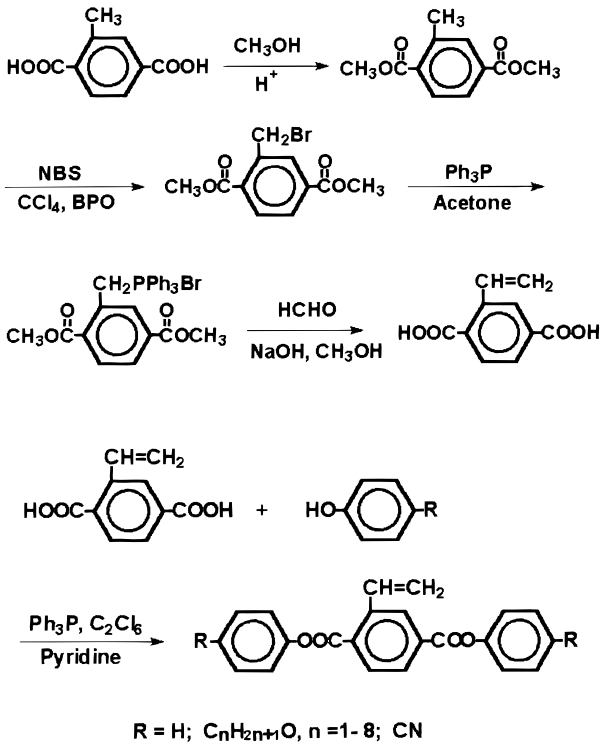


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**Table 1. Melting Points of the Monomers**

| monomers | R | mp (°C) | monomers | R | mp (°C) |
|---|---|---|---|---|---|
| $M_0$ | H | 100−101 | $M_5$ | $n$-$C_5H_{11}O$ | 92−93 |
| $M_1$ | $CH_3O$ | 109−110 | $M_6$ | $n$-$C_6H_{13}O$ | 63−64 |
| $M_2$ | $C_2H_5O$ | 121−122 | $M_7$ | $n$-$C_7H_{15}O$ | 76−78 |
| $M_3$ | $n$-$C_3H_7O$ | 123−125 | $M_8$ | $n$-$C_8H_{17}O$ | 77−78 |
| $M_4$ | $n$-$C_4H_9O$ | 107−109 | $M_{CN}$ | CN | 217−218 |

**Table 2. Property of the Polymers**

| polymers | $M_n \times 10^{-4}$ | $M_n/M_w$ | $T_g$ (DSC, °C) | $T^*$ (POM, °C)[b] | $T_i$ (POM, °C) |
|---|---|---|---|---|---|
| $P_0$ | 8.6 | 1.8 | 131 | ∼175 | >300 |
| $P_1$ | 2.0 | 2.5 | 118 | $\sim T_g$ | >300 |
| $P_2$ | 5.1 | 3.8 | 104 | $\sim T_g$ | >300 |
| $P_3$ | 5.8 | 3.4 | 98 | $\sim T_g$ | >300 |
| $P_4$ | 6.5 | 3.5 | 98 | $\sim T_g$ | >300 |
| $P_5$ | 5.0 | 3.4 | 98 | ∼200 | >300 |
| $P_6$ | 4.8 | 3.0 | 95 | ∼228 | >300 |
| $P_7$ | 5.9 | 3.4 | 102 | ∼234 | >300 |
| $P_8$ | 4.1 | 3.6 | 117 | ∼274 | >300 |
| $P_{CN}$ | *a* | *a* | 178 | ∼235 | >300 |

[a] $P_{CN}$ did not dissolve in THF and the molecular weight was not determined by GPC. [b] The temperature at which the birefringence develops noticeably, which may be higher than $T_g$.

experimental details are described below using 2,5-bis[(*p*-methoxylphenyl)oxycarbonyl]styrene ($M_1$) as an example: VTA (4.0 mmol, 0.77 g) and triphenylphosphine (2.2 g, 8.4 mmol) were dissolved in 10 mL dried pyridine to obtain solution A. *p*-Methoxylphenol (1.04 g, 8.4 mmol) and hexachloroethane (2.1 g, 8.8 mmol) were dissolved in 10 mL of dried pyridine to obtain solution B. B was slowly added into A. The mixture was stirred at 60 for 5 h. After the mixture had cooled to room temperature, it was poured into a methanol/water solution to precipitate the product. The precipitate was collected and purified using column chromatography on silica gel with chloroform as eluant. The product was further purified by recrystallization from benzene/petroleum ether (yield 66%, mp 109−110). The characterization data of this monomer were as follows. IR: 1720 cm-1(C═O). Mass spectrum: 404 (parent), 281 (base), 158, 130, 102. $^1$H NMR: 3.83 and 3.84 (2 s, 6H of $-OCH_3$), 5.47−5.86 (2 d, 2H of $=CH_2$), 6.95−7.18 (m, 8H of phenyl), 7.51−7.54 (q, 1H of $-CH=$), 8.18−8.44 (m, 3H of phenyl). Anal. Found (calcd): C, 71.30 (71.28); H; 4.79 (4.98).

All the other monomers were obtained and characterized similarly. Because the syntheses were straightforward, the characterization results of the monomers are not included in this short report.

The polymerizations of the monomers were carried out in THF solution at 60 using 0.5% molar equiv of AIBN as initiator. The polymers were precipitated in and washed with methanol.

## Results and Discussion

**The Monomers.** All the structures of the monomers were confirmed as shown in previous section. The phase transitions of the monomers were studied by DSC and POM. All the monomers formed a liquid crystalline phase upon melting. However, because of the ready thermal polymerization of the monomers, the mesophase was not stable. Therefore, no further discussion is made of the property of the monomers except for a simple collection of the melting points (Table 1, recorded from POM observations).

**The Polymers.** All the monomers polymerized reasonably well by radical solution polymerization. In Table 2 the polymers were denoted by P with $P_1$ for the polymer of monomer $M_1$, $P_2$ for $M_2$, $P_{CN}$ for $M_{CN}$ and so forth. Also given in the table are molecular weight and polydispersity of each polymer measured by GPC with polystyrene as standard and THF as solvent. The molecular weights are on the order of $10^4$. These results show once more that the large mesogenic substituent on one of the vinyl carbons does not eliminate the polymerizability of the monomers as found in other MJLCP systems.[10−12] Although no kinetic study has ever been carried out for this polymerization, the remarkable polymerizability is understandable by presuming a hindered chain termination as disclosed by Otsu et al. for the polymerization of 1,2-disubstituted fumarates.[19]

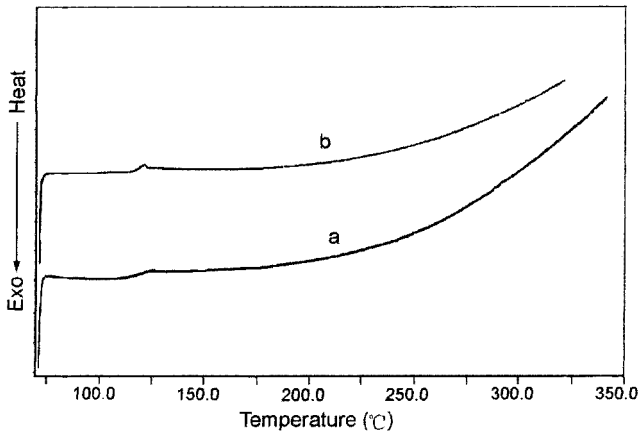


**Figure 1.** DSC heating curves for the polymers $P_1$ (curve a) and $P_8$ (curve b).

Similar to our previous MJLCPs based on 2-vinylhydroquinone[10] or 2-vinyl-1,4-phenylenediamine,[12] these new polymers based on VTA are also noncrystalline. The DSC measurements from room temperature to 300 showed only a glass transition step but no endothermic peak correlative to any melting of crystals (Figure 1). The lack of any crystallinity indicates that the bulky substituents along the polymer chains hinder crystallization as the phenyl groups do for atactic polystyrenes. Since the stereoregular polystyrenes do crystallize, we expect that the stereoregular polymers of our monomers be also crystallizable. However, our effort to synthesize such polymers has not been successful.

When examined on POM, the powder samples were only slightly birefringent presumably because of the presence of a low degree of mesomorphic order formed during preparation of the samples. When they were heated to above $T_g$, no immediate development of birefringence was observed for some samples. The birefringence developed in noticeable rate only when the temperature was significantly higher than $T_g$. This temperature was identified as $T^*$ in Table 2 to distinguish it from $T_g$.

To make sure that the increased birefringence was a result of the increased mesomorphic order but not because of crystallization, WAXD experiments were carried out on samples which had been annealed and had become highly birefringent. The representative results were shown in Figure 2 which indicated that the samples did not crystallize. The diffraction patterns were similar to those of other MJLCPs,[17,18] showing a diffused halo at larger angles and a relatively sharp peak at lower angles. According to Xu et al.[18] and Ober et al.,[13] the mesophase could be assigned to the nematic phase. However, this assignment is still not conclusive because there is no enough information about the relative orientational arrangement among the side groups.

The slow increase in birefringence is therefore attributable to a slow process of molecular ordering. The

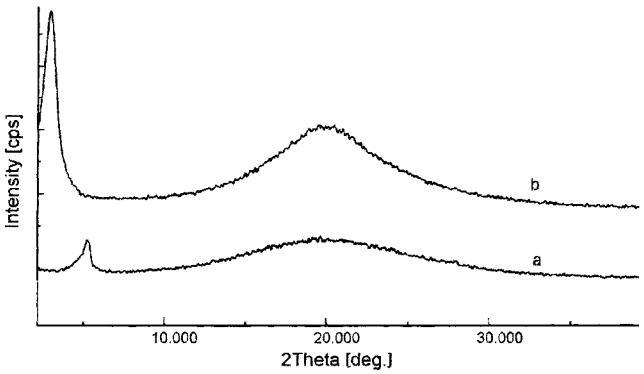


**Figure 2.** Powder X-ray diffraction patterns for $P_1$ (curve a) and $P_8$ (curve b).

process is slow because the viscosity of the sample at temperatures just above $T_g$ can be very high. Only after the temperature is raised to such a point that the viscosity is significantly reduced can the molecules reorganize readily to form an ordered mesophase at a notable rate. This is understandable especially when the significant chain rigidity of MJLCPs is considered.[8,9,11] Although the high rigidity and the slow motion of the polymer molecules may have delayed the formation of the mesophase, they have on the other hand a positive impact on stabilizing the mesophase once it is formed. The mesophase is indeed so stable that no clearing transition is observed until 320 when the samples start to decompose. Therefore, no real $T_i$ in the meaning of the phase transition from a liquid crystal to an isotropic liquid has been detected for these polymers. The results of the preliminary characterizations of this new series of MJLCPs were collected in Table 2.

In conclusion, we have successfully synthesized a new series of mesogen-jacketed liquid crystalline polymers starting from the newly synthesized 2-vinylterephthalic acid. The polymers were noncrystalline but all formed a liquid crystalline phase at temperatures above $T_g$. The mesophases of these polymers gave X-ray patterns which include a very diffused scattering halo at wide angles but a sharp diffraction peak in the lower angle region. The mesophases were very stable, and no clearing temperature was observed before onset of thermal decomposition of the samples. Thus, not only are these polymers based on 2-vinylterephthalic acid and our previously reported MJLCPs based on 2-vinylhydroquinone very similar in molecular structure but also they are similar in properties. However, since VTA is easier to synthesize than VHQ, it is convenient for further study of these new polymers.

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