

Rapid Communications

SYNTHESIS AND PROPERTIES OF NEW SIDE-CHAIN LIQUID
CRYSTALLINE POLYMER WITH Laterally ATTACHED
MESOGENS BY ESTER GROUP*

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Abstract New liquid crystalline monomer, 2,5-bis[(4'-methoxyphenoxy)carbonyl]phenyl acrylate was successfully synthesized. Polyacrylate with laterally attached mesogens *via* ester linkage was also derived. This polymer forms an enantiotropic liquid crystal phase while its monomer exhibits a metastable nematic phase with respect to the crystalline state. However, its liquid crystallinity is very low as compared to that of poly{2,5-bis[(4'-methoxyphenoxy)carbonyl]-styrene}.

Keywords Poly{2,5-bis[(4'-methoxyphenoxy)carbonyl]phenyl acrylate}, Hydroxyterephthalic acid, Mesogen-jacketed liquid crystalline polymers

The concept of "mesogen-jacketed liquid crystalline polymers" (MJLCPs) was first proposed by Zhou *et al.*^[1, 2]. This idea was supported in succession by Hardouin^[3], Gray^[4], Richardson^[5], Schrock^[6], Xu^[7], Mauzac^[8] and Zhou^[9, 10]. Various results showed that the MJLCPs have special characteristics as compared with the conventional side-chain liquid crystal polymers containing long flexible spacers. For example, The MJLCPs strongly promote the nematic state^[1, 2, 11-14] and yield the banded texture^[7] by shear flow in mesophase. They have prolate conformations^[3] with large anisotropy in the nematic state and larger persistent length^[10] in solution etc. However, there is little knowledge concerning the laterally attached mesogenic polymers with very short linkage except polyacrylate^[1, 15] and polynorbornene^[16] containing 2,5-bis[(4'-*n*-alkoxybenzoyl)oxy] mesogens with $-\text{COOCH}_2-$ group as the spacers. In this communication, we report the synthesis of a new laterally attached mesogenic polymer with only $-\text{COO}-$ group as the spacer. The liquid crystallinity of this polymer was also studied. The result obtained is helpful for further understanding the role of the spacer in affecting the liquid crystallinity and the "Jacket Effect" of MJLCPs.

SYNTHESIS

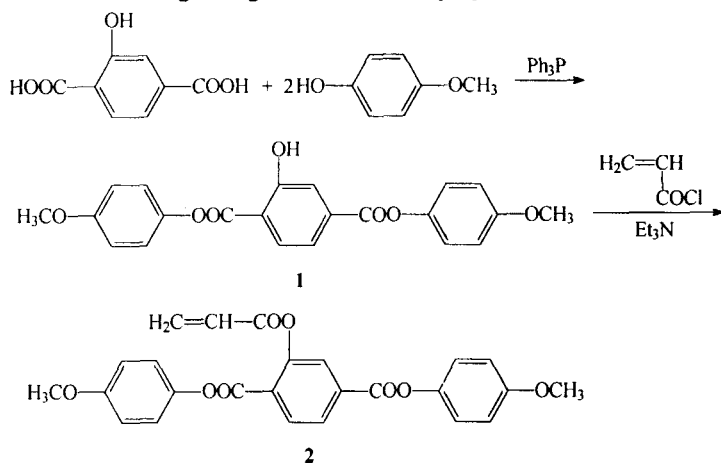
The monomer, 2,5-bis[(4'-methoxyphenoxy)carbonyl]phenyl acrylate (**2**) was synthesized in two steps by condensing hydroxyterephthalic acid with *p*-methoxyphenol, and then by the esterifying of the resulting product with acryloyl chloride (Scheme 1). The chemical structure of **2** was identified by means of elemental analysis (Elemental Vario EL), M.S. (VG-ZAB) and NMR. (ARX-400),

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respectively. The results are in good agreement with the proposed structure (Table 1).



Scheme 1

Table 1 Key data for compounds 1 and 2

	Compound	
	1	2
Yield	35%	70%
MS (+EI)	—	448
C, H analyses (%):	—	C 66.96(66.90), H 4.464(4.587)
Found (calcu.)		
¹ H-NMR (δ , CDCl ₃)	10.60 (s, 1H), 8.20 (d, 1H, J = 8.2 Hz), 7.85 (s, 1H), 7.74 (d, 1H, J = 8.2 Hz), 7.10~7.20 (m, 4H), 6.89~7.01 (m, 4H), 3.85 (s, 3H), 3.84 (s, 3H)	8.32 (d, 1H, J = 8.0 Hz), 8.19 (dd, 1 H, J = 8.0 Hz, J = 1.6 Hz), 8.03 (d, 1H, J = 1.6 Hz), 7.15 (d, 2H, J = 7.2 Hz), 7.09 (d, 2 H, J = 7.2 Hz), 6.95 (d, 2H, J = 7.2 Hz), 6.92 (d, 2 H, J = 7.2 Hz), 6.65 (d, 1H, J = 17.2 Hz), 6.36 (dd, 1 H, J = 17.2 Hz, J = 10.4 Hz), 6.04 (d, 1H, J = 10.4 Hz), 3.83 (s, 3 H), 3.81 (s, 3H)
Phase transition*	k 162.2 n 242.1 (0.94) i	k 122.7 n 53.8 (0.40) l
(ΔH , kJ · mol ⁻¹)	i 229.9 (−0.35) n	i 49.8 (−0.79) n

* k = crystalline, n = nematic, i = isotropic, (monotropic); thermal transitions were read from first or second heating scans with a heating rate of 20°C and first cooling scans with a cooling rate of 20°C.

The polymer (P-1), which was obtained from radical polymerization (Chart 1), has the molecular weight (M_n) of 1.1×10^4 and polydispersity (M_w/M_n) of 2.22 as determined by gel permeation chromatography (GPC) on a PL-GPC 210 instrument.

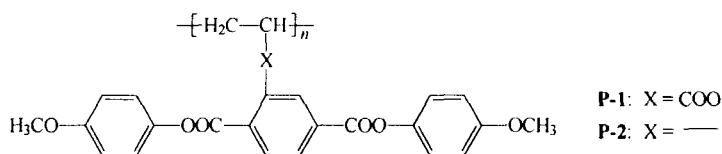


Chart 1

Phase Behavior

Compound 2 forms a monotropic liquid crystal phase, which is metastable with respect to the crystalline state. Its m.p. is 122.7°C and its clearing temperature is only 53.8°C (Fig. 1). The textures shown from polarized optical microscope (Fig. 2) (Leitz Laborlux 12 Pol) and the small enthalpy changes ($< 1 \text{ kJ} \cdot \text{mol}^{-1}$) measured by DSC (Perkin-Elmer DSC-7) (Table 1) are typical of a nematic phase^[12].

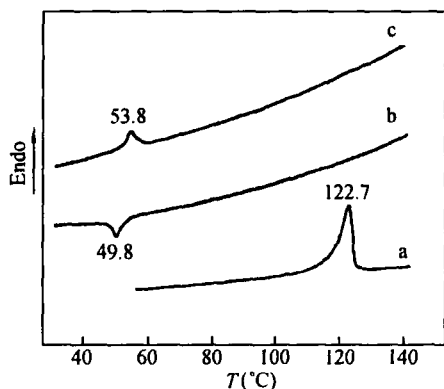


Fig. 1 DSC curves of the first heating scans a), the first cooling scans b) and the second heating scans c) of compound **2**

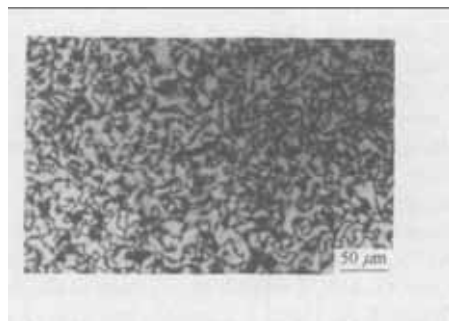


Fig. 2 Optical polarizing micrograph of compound **2** obtained at 30°C

Interestingly, **P-1** exhibits a stable enantiotropic liquid crystalline phase. From the polarizing optical microscope (Fig. 3), we observed that **P-1** was non-crystalline but softened at around 80°C to form a liquid crystalline phase. The clearing temperature is 125°C. The DSC heating curve of the polymer (Fig. 4) also showed the same results. This indicates that the linkages formed between the laterally substituted nematic monomer units and the polymer backbone “stabilize” the liquid crystalline state^[11].



Fig. 3 Optical polarizing micrograph of **P-1** obtained at 70°C

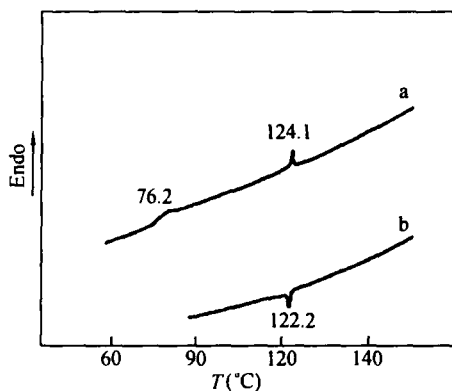


Fig. 4 DSC curves of the heating scans a) and the cooling scans b) of **P-1**

If the ester units of the **P-1** are removed, the mesogenic units will connect directly with the polymer backbone with no spacer, and **P-2** will be obtained (Chart 1), and its liquid crystallinity would be significantly improved^[17]. No clearing temperature of **P-2** was observed below 320°C. That is, the clearing temperature of **P-2** is higher than that of **P-1** by at least 195°C. These results are consistent with the study of Hardouin *et al.*^[8], and they also indicate that the “Jacket Effect” is much weakened by the introduction of even a very short —COO— spacer.

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