*Macromolecules* **1987,** *20,* 233–234

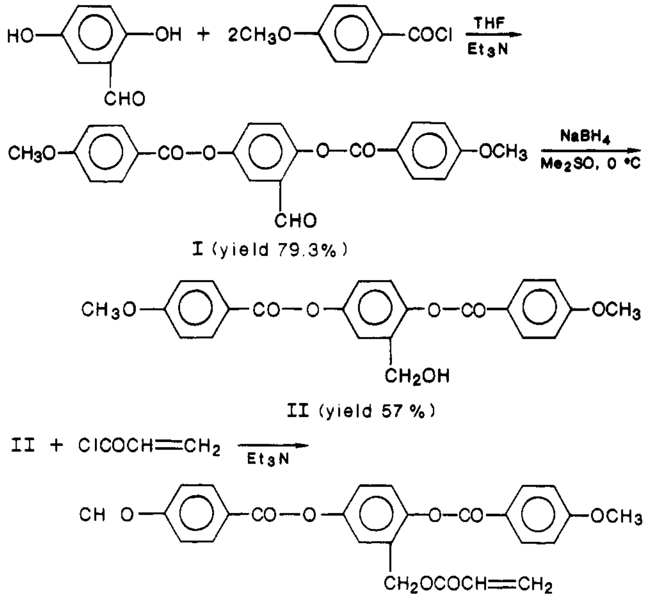
# Communications to the Editor

## Synthesis of Liquid-Crystalline Polyacrylates with Laterally Substituted Mesogens

It is possible to incorporate mesogenic units into polymer molecules in different ways and thus to construct different types of liquid crystal polymers. Figure 1 shows some of the possibilities.

Most recently, Hessel and Finkelmann[1] reported the synthesis of a new class of liquid crystal side-chain polymers where the mesogenic groups are laterally attached to the polymer backbones. Independently, we have also succeeded in making this new type of side-chain polymer (Figure 1, case 2B).

*Monomers.* The first new monomer of this series, 2,5-bis[(4-methoxybenzoyl)oxy]benzyl acrylate, was synthesized according to the following sequence of reactions:



I (yield 79.3%)

II (yield 57%)

III (yield 83.5%)

Compound I is a yellow crystal with a melting point of 192 °C. Above this point a stable nematic phase is formed (revealed by both DSC and polarizing microscopy). The clearing temperature of this mesophase is 224 °C.

Surprisingly, the reduction of compound I to compound II destroyed the liquid crystallinity of the compound. Compound II is a white crystal that melts at 159–160 °C, resulting in no mesophase. Hydrogen bonding between the hydroxyl groups of the compound may have prevented the molecules from being parallelly orientated in the melt.

Monomer III was obtained as a white crystal by reaction of compound II with acryloyl chloride in the presence of triethylamine. The monomer melts at 102 °C and is also non-liquid-crystalline as would be expected from the large lateral substitution.

Monomers with alkoxy groups other than methoxy can be synthesized in the same manner.

*Polymer.* The polymerization was conducted in a THF solution at refluxing temperature (~70 °C) with AIBN as the initiator (1 mol % of AIBN).

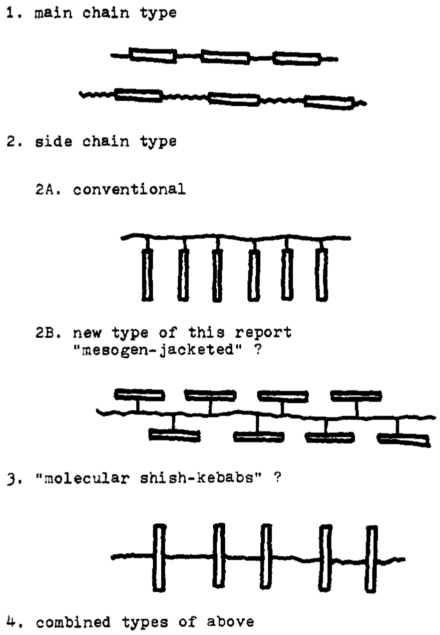
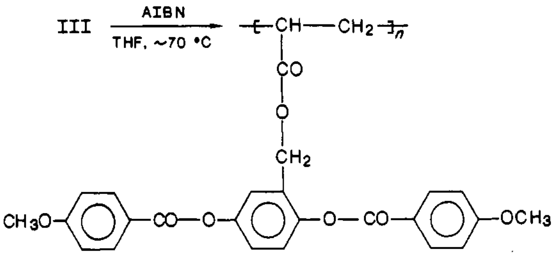


**Figure 1.** Some possible placements of mesogens in polymer molecules.



The polymer is a white powder with $\bar{M}_n = 8000$ and $\bar{M}_w = 13\,000$ as measured by GPC with polystyrenes as the calibrating standards. It is noncrystalline as determined by WAXS. However, the polymer shows a stable liquid-crystalline state in the range 140–180 °C as revealed by DSC and a polarizing microscope. The preliminary DSC measurements cannot suggest an accurate $T_g$ for the polymer yet; however, the sample "melts", flows, and becomes birefringent at 140 °C upon heating, and there is at 180 °C an endothermic isotropization peak in the DSC thermogram. Figure 2 shows the texture of the liquid-crystalline state of this polymer, which suggests that the liquid crystal is probably nematic.

A sketch is given in Figure 3 to illustrate the *speculated* structure of the polymer. For every second carbon atom (or every 2.5 Å) along the polymer main chain there is a mesogenic group approximately 20 Å in length. The spatial requirements of the long mesogenic groups necessitate that the mesogens be parallel to each other as well as to the polymer main chain. As a result, they form a more or less cylindrical "mesogen-jacket" around the main chain. In

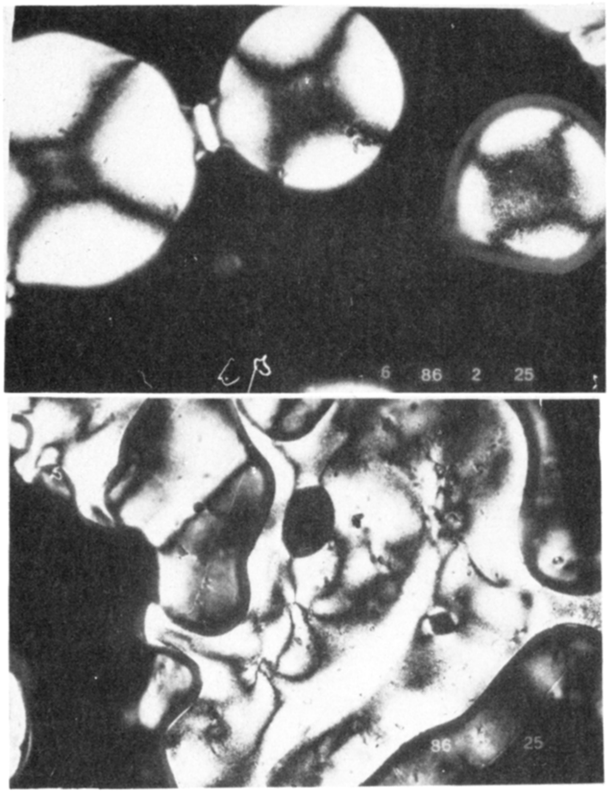


**Figure 2.** Textures of the polymer observed at 150 °C on a polarizing microscope.

Figure 3 connections between the main chain and mesogens are deleted for clarity.

A distinct feature of this "mesogen-jacketed polymer" is that the gravity centers (or the nearby positions) of the mesogens are positions bonding to the main chain. Consequently, the motion of the main-chain segments should have only minor coupling effects on the motion of the mesogens, in contrast to the cases of conventional liquid crystal side-chain polymers where the mesogens are connected perpendicularly to the main chain. Therefore, the introduction of flexible spacers to decouple the motions of the main chain and the mesogens is likely not as necessary. In fact, the polymer molecules reported here have only short linkages, $-COOCH_2-$, between the main chain and the mesogens. It occurs to the authors that with the linkages to the gravity centers of the mesogens the main chains hold the mesogens together, draw them closer, and help the formation of an ordered mesophase. As in the case of this report, monomer III is non-liquid-crystalline while the polymer has a stable liquid-crystalline state. Detailed information about the new series of monomers and polymers will be presented in our forthcoming papers.

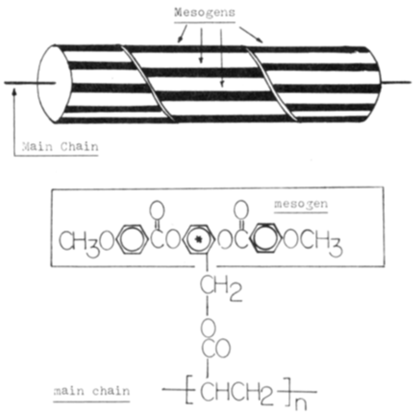


**Figure 3.** Speculative model showing a "mesogen-jacket" around a polymer main chain (top); the asterisk indicates the gravity center of the mesogen.

**Acknowledgment.** Financial support of this work by the National Science Foundation of China is gratefully acknowledged.

**Registry No.** I, 105252-90-2; II, 105252-91-3; III, 105252-92-4; III (homopolymer), 105280-90-8; $4\text{-}H_3CO_6H_4COCl$, 100-07-2; $ClCOCH{=}CH_2$, 814-68-6; 2,5-dihydroxybenzaldehyde, 1194-98-5.

## References and Notes

(1) Hessel, F.; Finkelmann, H. *Polym. Bull. (Berlin)* **1986**, *14*(3–4), 375–378.

**Qi-Feng Zhou,* Hui-Min Li, and Xin-De Feng**

*Chemistry Department, Peking University*
*Beijing 100871, People's Republic of China*

*Received July 17, 1986*