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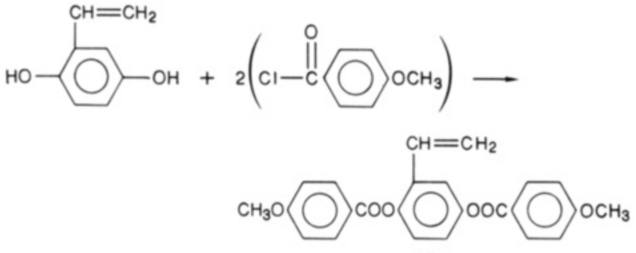
Communications to the Editor

Liquid-Crystalline Side-Chain Polymers without Flexible Spacer

It is well-known that the systematic realization of liquid-crystalline side-chain polymers requires a flexible linkage of the rigid mesogenic moieties to the polymer backbone via a flexible spacer. According to Finkelmann,[1] if rigid mesogenic side chains are directly attached to the polymer backbone, motions of the polymer segments and mesogenic groups are directly coupled. In the liquid state above T_g, the polymer tends to adopt a statistical chain conformation that hinders anisotropic orientation of the mesogenic side chains. Also, steric hindrance prevents mesogenic order. The flexible spacer decouples motions of the main chain and side chain and alleviates steric hindrance. Under these conditions, the mesogenic side chains can be anisotropically ordered in the liquid state even though the polymer main chain tends to adopt a statistical chain conformation. This idea of Finkelmann has been proved by many experiments and has become a useful guide for molecular design of liquid-crystal side-chain polymers. However, we[2] have predicted that for our new type of side-chain polymers the introduction of flexible spacers to decouple the motions of the main chain and the mesogens is likely not as necessary, because in this case the gravity center of the mesogen is the position bonding to the main chain. Our first polymers still have, though very short, flexible linkages. In this short communication, we report the synthesis of poly(2,5-bis((*p*-methoxybenzoyl)oxy)styrene) in which only a single covalent bond is used to connect the mesogens and the main chain, offering the first example for the new type of side chain polymers to show its ability of forming liquid crystals in the absence of flexible spacers.

Monomer. The monomer 2,5-bis((*p*-methoxybenzoyl)oxy)styrene was synthesized by the reaction of 2-vinyl-1,4-dihydroxybenzene and 4-methoxybenzoyl chloride in the presence of pyridine using THF as solvent:



(I)

The structure of the product was proved by elemental analysis, MS, IR, and NMR. Elemental analysis: calcd 71.26% C, 4.99% H; found 71.51% C, 4.91% H. Mass spectrum (FI ZAB-HS): *m*/*e* 404 (parent), 135 (base), 107, 77, 31, 27. IR (Shimadzu IR 408): C=O 1725, $CH{=}CH_2$ 1430 cm^{-1}. NMR (Varian FT-80 A, solvent $CDCl_3$): 3.83, singlet for CH_3O, 6 H; 5.15–5.40 and 5.55–5.90, two doublets for vinyl $=CH_2$, 2 H; 6.55–8.25 ppm, multiplet, 12 H for vinyl =CH and phenyl rings.

This compound melts at 172–173.5 °C and forms a liquid-crystalline state which becomes isotropic at 175–175.5 °C. Figures 1 and 2 are photomicrographs of the liquid-crystalline state of the monomer.

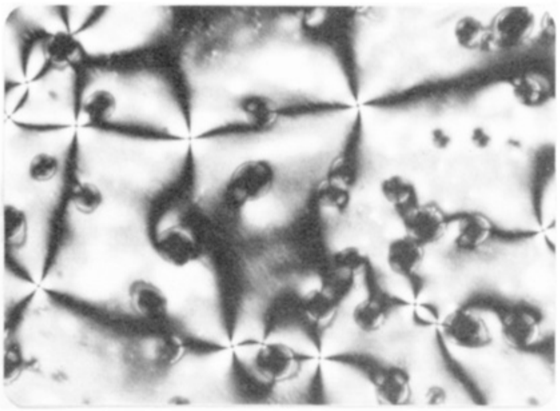


Figure 1. Microphotograph of the monomer, taken at 175 °C.

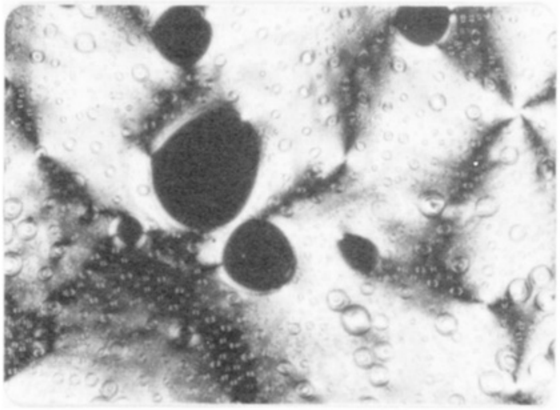


Figure 2. Isotropization process of the liquid-crystalline melt of the monomer shown at 175 °C.

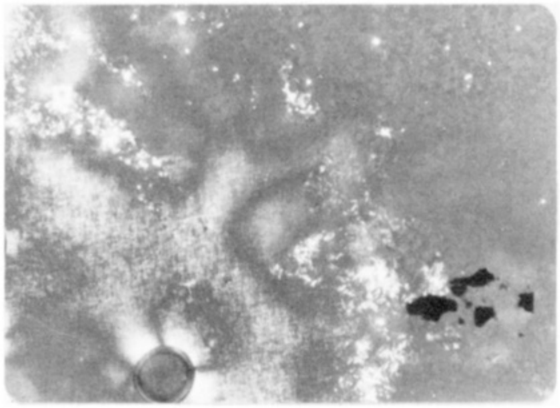


Figure 3. Recurrence of birefringence after 5 min of polymerization at 178 °C.

Polymer. An interesting property of this monomer is its high polymerizability, even though a bulky group is attached to the double bond. On the hot stage on a polarizing microscope, the extinguished monomer melt becomes birefringent again on further heating for a few minutes at a temperature above the clearing point of the monomer melt. Figures 3 and 4 show this phenomenon. Figure 3 was taken at 178 °C about 5 min after the extinction and shows the recurrence of birefringence. After about 10 min of polymerization at about 180 °C, the sample droplet becomes highly birefringent, as shown by Figure 4 which was taken at 180.5 °C. If a press is put on the sample, a thinner specimen with an optical texture similar to that shown in Figure 5 is obtained.

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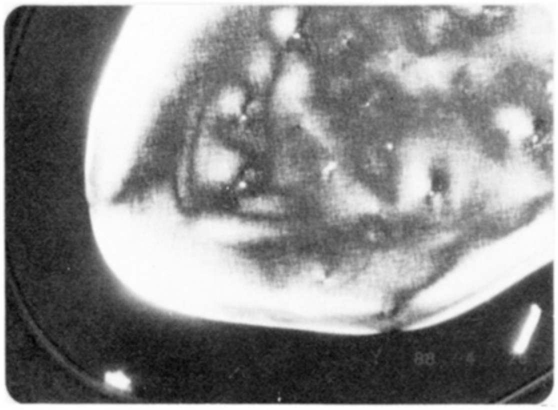


Figure 4. Sample droplet becoming highly birefringent after 10 min of polymerization.

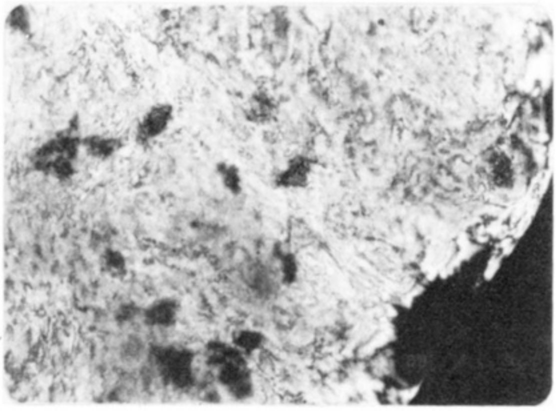
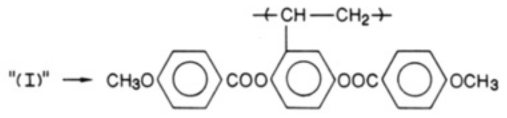


Figure 5. Polymer melt birefringence, even at 320 °C.

Following the above observation, a polymer was obtained by bulk polymerization of the monomer sealed in a glass tube which was immersed in a bath. The bath temperature was kept at 172 °C for 10 min and then slowly raised to 220 °C in 12 h. No initiator was used in this process:



(II)

The molecular weight of the polymer thus obtained was determined by a Waters 201 GPC instrument with polystyrene as the calibrating standard at $\bar{M}_n = 1.33 \times 10^5$, $\bar{M}_w = 3.13 \times 10^5$. The solid-to-liquid crystal transition of the polymer occurs at about 125 °C. A TGA test (Shimadzu DT-30, in N_2, 20 °C/min) found that the polymer started to decompose at 310 °C; a 5% weight loss was obtained at 380 °C. A liquid-crystalline phase can be observed even at temperatures as high as 330 °C (which disappears gradually with decomposition of the polymer at such a high temperature). Figure 5 is a microphotograph of the polymer taken at 320 °C. The optical texture suggests that the liquid-crystalline phase is probably nematic, because no typical texture of a smectic phase is observed.

In order to prove the chemical structure of the polymer, careful IR analyses were carried out for both the monomer (I) and the polymer (II) with a sophisticated Bruker-IFS-113V FTIR spectrometer. This instrument has a vacuum-type interferometer so that moisture, carbon dioxide, and other environmental interferences are essentially eliminated during the experiment. The spectrometer detector is a liquid nitrogen cooled MCT. For the experiment, the scan velocity was set at 0.47 cm/s. Each spectrum was 64 scans averaged to increase the S/N ratio. The resolution was 2 cm^{-1}. The specimen was prepared by the KBr bullet technique. The spectra thus obtained of the monomer and of the polymer are shown in Figures 6 and 7 and in Table I, and the results are discussed as follows:

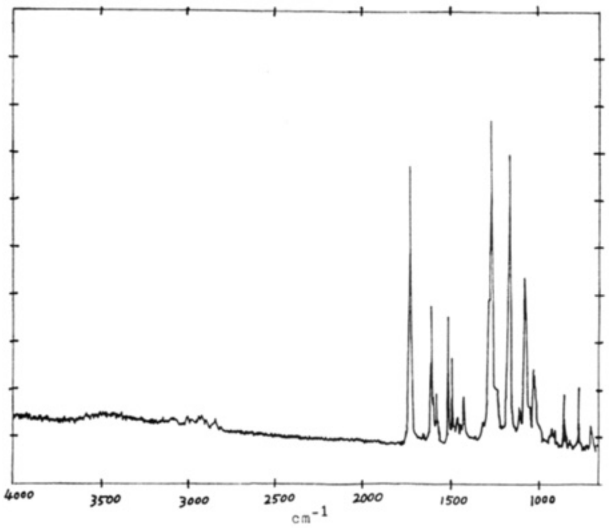


Figure 6. IR spectrum of the monomer.

Table I
Main IR Bands of the Monomer and the Polymer

monomer		polymer	
frequency, cm^{-1}	intensity	frequency, cm^{-1}	intensity
		2936	m
		2840	m
1728	vvs	1730	vvs
1625	vw		
1608	m	1606	s
1581	m	1582	m
1512	m	1511	s
1486	m	1489	m
		1461	m
		1440	w
1423	m	1420	m
		1317	m
1259	vvs	1253	vs
1154	vs	1161	vvs
1072	m	1070	s
1022	m	1028	s
1011	w	1008	w
920	vw		
904	vw	895	w
846	m	845	m
764	m	762	m
692	w	690	m

One of the main differences between the IR spectrum of the monomer and that of the polymer is that there are bands at 2936 and 2840 cm^{-1} in the polymer spectrum but not in the monomer spectrum. These bands are due to the methylene stretching and are characteristic of the methylene structure in the polymer main chain. Also there are bands at 1461 and 1440 cm^{-1} for the polymer owing to the main-chain methylene deformation mode. On the other hand, the very weak band at 1625 cm^{-1} of the alkenyl group of the monomer disappeared in the polymer spectrum. The two weak bands at 920 and 904 cm^{-1} of the monomer changed to a single band at 895 cm^{-1} of the polymer, which are of the C–H out-of-plane deformation mode of the isolated hydrogen of the trisubstituted benzene ring and is very sensitive to the change in the molecular environment of the ring.

Bands which are associated with the mesogenic unit are present both in the monomer spectrum and in the polymer spectrum. However, there are also significant differences in frequency, intensity, and width of the corresponding

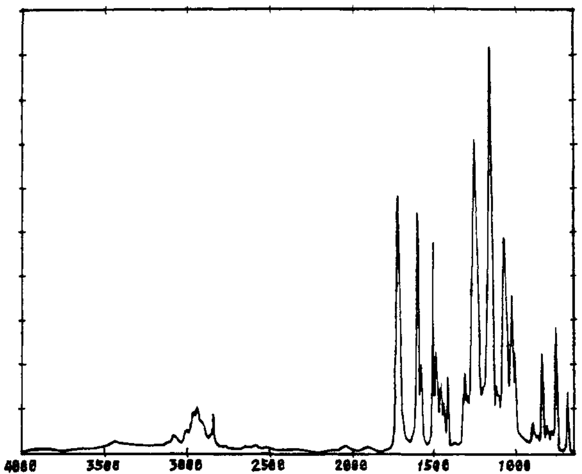


Figure 7. IR spectrum of the polymer.

bands between the two spectra. For example, the carbonyl stretching mode is at 1728 cm^{-1} for the monomer but is at 1730 cm^{-1} with an increased width for the polymer. The benzene C=C stretchings at 1608 (m), 1581 (m), 1512 (m), and 1486 (m) cm^{-1} of the monomer have shifted respectively to 1606 (s), 1582 (m), 1511 (s), and 1489 (m) cm^{-1} of the polymer. The C–O stretchings at 1259 (vvs) and 1154 (vs) cm^{-1} of the monomer have shifted to 1253 (vs) and 1161 (vvs) cm^{-1}. These results and others not described here indicate that the chemical structure of the mesogenic unit of the monomer did not change during the thermal polymerization, but the molecular conformation of the mesogens might have changed to fulfill the spatial requirement in the polymer.

The IR studies thus suggest that the chemical structure of the mesogenic units in the monomer molecules was untouched during polymerization and that the polymer molecules were built up presumably by thermally initiated addition polymerization of the vinyl monomer. A polymer with mesogens laterally attached to the main chain via only a single covalent bond (no flexible spacer) was thus obtained.

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Registry No. I, 117439-39-1; I (homopolymer), 117439-40-4.

References and Notes

(1) Finkelmann, H.; Wendorff, H. J. Structure of Nematic Side Chain Polymers. In *Polymeric Liquid Crystals*: Blumstein, A., Ed.; Plenum Press: New York, 1985; p 295.
(2) Zhou, Q. F.; Li, H. M.; Feng, X. D. *Mol. Cryst. Liq. Cryst.* 1988, *155*, 73.

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Evidence by Neutron Diffraction of Ordered Structures in Atactic Polystyrene/Carbon Disulfide Physical Gels

Atactic polystyrene (aPS) should be, by nature, an uncrystallizable polymer, and so far, there has been no evidence of any trace of crystallinity in the bulk state. Accordingly, the report on the propensity of this polymer to give physical gels in some solvents came as a surprise,[1] often followed by disbelief. However, different types of experiments carried out with different techniques[2–6] have all pointed to a genuine phenomenon. A thermal analysis study of the gel formation and fusion[6] revealed the presence of exotherms and endotherms, respectively, that were interpreted as resulting from the existence of three-dimensional objects, possibly possessing a nematic-like order (order in only one dimension). Here we report on a series of neutron diffraction experiments intended to give direct evidence of the appearance of order in the physical gels of this polymer.

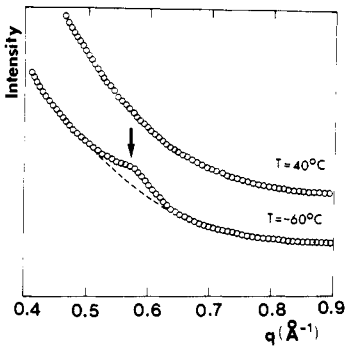

Figure 1. Intensity (in arbitrary unit) as a function of the transfer momentum $q = (4\pi/\lambda) \sin \theta/2$ in Å^{-1}. Temperatures as indicated. Arrow shows the position of the peak maximum.

Neutrons were chosen over X-rays for two essential reasons: (i) by labeling the polymer (deuteriated polystyrene), its diffraction power is significantly increased with respect to the solvent ($b_{\text{deuterium}} = 0.67 \times 10^{-12}$ cm while $b_{\text{sulfur}} = 0.285 \times 10^{-12}$ cm); (ii) as a result, while the use of X-rays would only give the diffraction by the solvent, neutrons are mainly diffracted by the polymer. Due to the low amount of physical junctions, this condition is peremptory (for we do not exactly know what this amount is[6]).

The experiments were carried out on G-6-1 (LLB, further details on request). Only one polymer concentration was investigated (40% w/w). The reasons for using such a concentration are based on the temperature–concentration phase diagram[6] that shows that physical gelation in CS_2 arises from the formation of a polymer–solvent compound whose stoichiometry is defined somewhere between $C_{\text{pol}} \simeq 40\%$ and 50%. Correspondingly, the maximum amount of physical junctions is also in this concentration range.

The solvent used was of high-purity grade. The polymer was characterized by gel permeation chromatography in tetrahydrofuran ($M_w = 1.5 \times 10^5$ and $M_w/M_n \simeq 1.26$).

The polymer–solvent mixture was introduced into an amorphous silica tube (10-mm inner diameter) which was sealed from atmosphere and held at 60 °C for a week in order to obtain a true solution. Then this system was cooled to the desired temperature. At such a concentration, gelation already occurs at room temperature.[1,6] Yet, the maximum amount of physical junctions should be obtained for $T = -60$ °C as deduced from the phase diagram.[6]

A blank sample containing only solvent was prepared under the same conditions.

The diffraction patterns at 40 and −60 °C were accordingly recorded and are drawn in Figure 1. As can be seen, a broad peak is visible at −60 °C. Since the solvent does not display any additional peak at this temperature, this result confirms without ambiguity the presence of ordered structures in this type of gel.