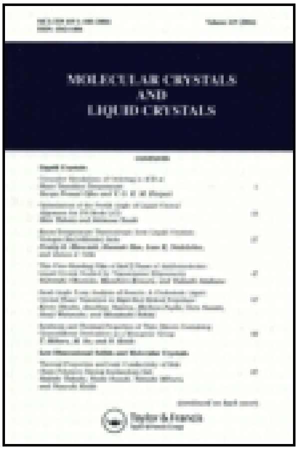

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Restudy of the Old Poly-2,5-di(benzoyloxy)styrene as a New Liquid Crystal Polymer

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The 40 year old polymer, poly-2,5-di(benzoyloxy)styrene, has been restudied from the view point of the "mesogen-jacketed liquid crystal polymer." This old polymer was synthesized in 1952 as a precursor of an electron exchange polymer and is now found to be thermotropically liquid crystalline, from which the characteristic banded texture of rigid and semi-rigid liquid crystal polymers may be obtained. The monomer of this polymer, 2,5-di(benzoyloxy)styrene, was then also not realized as liquid crystalline, is now found to be liquid crystalline forming too. This finding offers probably the first example of liquid crystal rigid rod-like molecules with lateral but without terminal substitutions. The synthesis and primary characterization of a series of the closely related polymers poly-2,5-bis[(4-substituted-benzoyl)oxy]styrenes are also reported.

Keywords: mesogen jacketed liquid crystal polymers, rigid side chain liquid crystal polymers, liquid crystal monomers, liquid crystal polymers, 2,5-bis[(4-alkoxybenzoyl)oxy]styrene, 2,5-bis[(4-alkylbenzoyl)oxy]styrene, 2,5-bis[(4-cyanobenzoyl)oxy]styrene, 2,5-di(benzoyloxy)styrene, poly-2,5-di(benzoyloxy)styrene

INTRODUCTION

The concept "mesogen-jacketed liquid crystal polymers" (MJLCPs) was proposed to describe the side chain liquid crystal polymers which are of the side chain type but with mesogenic units attached laterally to the main chain without or with only short spacers.[1–3] This type of polymers is expected to have the stiffened chain conformation because of the steric requirement of the rigid and bulky mesogenic units. The first experimental support of this concept was given by Hardouin and co-workers.[4] A new concept "rigid side chain liquid crystal polymer" was further proposed for these polymers with emphasis on the side chain type and on the stiffened chain conformation.[5] A success of these efforts would lead to polymers which can be conveniently synthesized by, say, radical chain polymerization to

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obtain high molecular weight, but also show the property of rigid polymers as represented by main chain liquid crystal polymers.

It is well known that rigid and semi-rigid main-chain liquid crystal polymers, both lyotropic and thermotropic, can form banded texture by shear or elongational flow in their liquid crystal state.[6] No banded texture has been observed for flexible chain polymer molecules including that of conventional side-chain liquid crystal polymers having mesogenic groups attached longitudinally to a flexible backbone. This characteristic morphological feature implies the significant chain rigidity of main-chain liquid crystal polymer molecules. It is thus reasonable to expect MJLCPs to form banded texture because their chains are also of certain rigidity. Interestingly, one of the MJLCPs, poly-2,5-bis[(4-methoxybenzoyl)oxy]styrene,[2] has recently been reported to form indeed the banded texture,[7] for which chain rigidity is again suggested.

The monomer 2,5-bis[(4-methoxybenzoyl)oxy]styrene and its polymer[2] were reported to be liquid crystalline. The synthesis and the properties of the homologous monomers and polymers with other alkoxy as well as alkyl or cyano substituents, and that of the corresponding unsubstituted compounds are reported in this paper. The unsubstituted homologue poly-2,5-di(benzoyloxy)styrene was originally synthesized some 40 years ago by Cassidy and co-workers[8] and is now found to be not only liquid crystalline but also banded texture forming.

EXPERIMENTAL

In this study all the elemental analyses were performed by the elemental analysis laboratory of this department. A Varian FT-80A NMR was used with *d*-chloroform as solvent and TMS as internal standard to obtain NMR spectra of the compounds. The mass spectroscopic results were from a VG-ZAB-HS instrument. The thermal and liquid crystal properties were characterized by a Du Pont 1091 DSC and a Leitz Laborlux 12 Pol polarizing microscope with a Leitz 350 heating stage. A Waters 201 GPC was used to find the molecular weights of the polymers with polystyrenes as calibration standards.

SYNTHESIS OF THE MONOMERS

Most of the monomers were synthesized by reaction of 2-vinyl-1,4-dihydroxybenzene and 4-substituted benzoyl chlorides. As an example, the methyl substituted monomer, 2,5-bis[(4-methyl-benzoyl)oxy]styrene, was synthesized as follows:

2.5 g (0.018 mol) of 4-methylbenzoic acid was mixed with thionyl chloride. The mixture was refluxed for about 1 hour to give a clear solution. The excess thionyl chloride was taken off by vacuum. The residues washed twice by petroleum ether. 5 ml dry THF was added to make a solution of the acid chloride.

To the above acid chloride solution 0.8 g (0.006 mol) of vinylhydroquinone in 5 ml THF and 5 ml triethylamine was added slowly. The reaction was kept in an ice/water bath and a magnetic stirrer was used. After about 8 hours the reaction temperature was allowed to rise to the ambient room temperature. The reaction was continued for another 16 hours. Most of the THF was distilled off the system, and distilled water was added to obtain a solid, which was washed sequentially with dilute HCl, water, saturated sodium bicarbonate, and water. 2 g of the raw product was obtained.

The raw product was first purified by column chromatography with 1 to 1 ether/petroleum ether as eluant. The product was further purified by recrystallization from ether. 1.4 g of the product was obtained, which melts at 123°C and gives the following results which characterize the chemical structure of 2,5-bis[(4-methylbenzoyl)oxy]styrene:

C, H analysis: C 77.31%; H 5.29% (cald. 77.42% and 5.38%, respectively).

NMR: δ = 2.45 ppm, 6H for the two methyl, 5.10–5.85 ppm, 2 H for $=CH_2$, 6.55–6.95 ppm, 1 H for $-CH=$, and 7.10–8.18 ppm, 11 H for benzene rings.

Mass spectroscopy: 372 (parent), 119 (base), 136, 91.

The following procedure was used for synthesis of the nonsubstituted homologue 2,5-di(benzoyloxy)styrene. It was found that by this procedure product might be obtained with higher purity than by that used for the methyl substituted homologue.

With stirring 2.4 g benzoic acid and 6 g triphenyl phosphine were dissolved in 10 ml pyridine at room temperature. To the solution 5.6 g hexachloroethane and 1.4 g vinylhydroquinone in 10 ml pyridine were added. The mixture became yellow with the evolution of considerable amount of heat and the formation of a precipitate. The reaction was finished in about half an hour as judged by the cease of heat evolution. Another two hours had passed before the treatment with methanol/water (1:2) and an oily phase was obtained. The oily material was separated by column chromatography with ether/petroleum ether (2:1) as eluant. 1.2 g product with a melting point of 88°C and a clearing point of 95°C (as determined by DSC and discussed below) were obtained, for which the chemical structure was proved

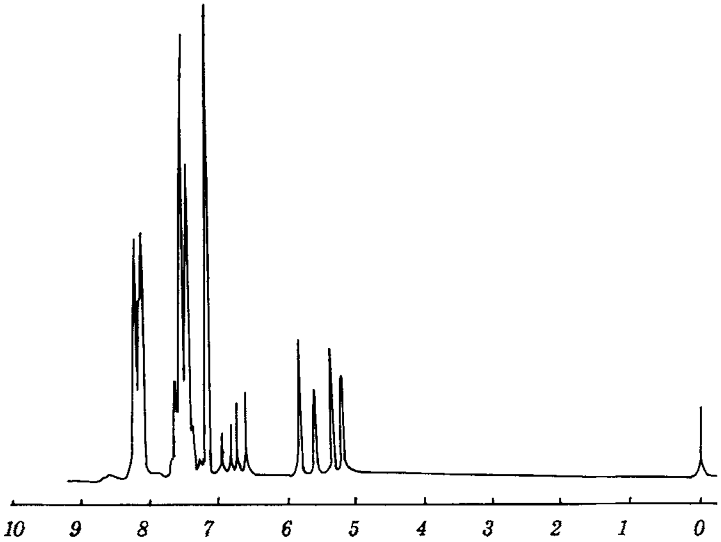


FIGURE 1 NMR of the monomer 2,5-di(benzoyloxy)styrene.

TABLE I

Properties of the monomers

R	*melting and liquid crystal phase transition*
H	*k 88 n 95 i*
CH_3	*k 123 n 128 i*
C_2H_5	*k 106 i (i 102 n 57 k)**
C_4H_9	*k 44 s 98 i*
CN	*k 216 n 257 i*
OCH_3	*k 184 n 195 i***
OC_2H_5	*k 150 n 168 i*
OC_4H_9	*k 109 s 130 n 167 i*

* *monotropic as determined by optical polarizing microscope*

** *These data are somewhat higher than that reported in reference [2] because of higher purity.*

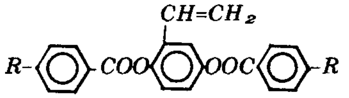
by C, H analysis, NMR and by mass spectroscopy to be the required monomer 2,5-di-(benzoyloxy)styrene:

C, H analysis: C 76.68%; H 4.45% (cald: C 76.74%; H 4.65%).

NMR: δ = 5.25–5.87 ppm, 2 H for $=CH_2$; 6.64–7.00 ppm, 1 H for —CH=; and 7.19–8.29 ppm, 13 H for benzene rings (see also Figure 1).

MS: 344 (parent), 105 (base), 136, 77, 59, 41, 31.

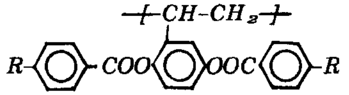
The properties of the monomers synthesized in this work were summarized in Table I where R represents the substituent at the 4-position of the benzoyl moiety as shown by the general formula:



Data used in Table I were taken from microscopic observations which are generally in good agreement with results given by DSC measurements. The DSC traces of the monomers R = H, C_4H_9 and CN given in Figures 2–4 are taken as examples.

SYNTHESIS OF THE POLYMERS

The polymerizations were run in DMF solution at 60°C using AIBN as initiator. Table II collects the molecular weights of the polymers:



RESULTS AND DISCUSSION

The Properties of the Monomers

The thermal properties of the monomers are shown in Table I. Attention is called to the monomer 2,5-di(benzoyloxy)styrene(R = H). This monomer was first syn-

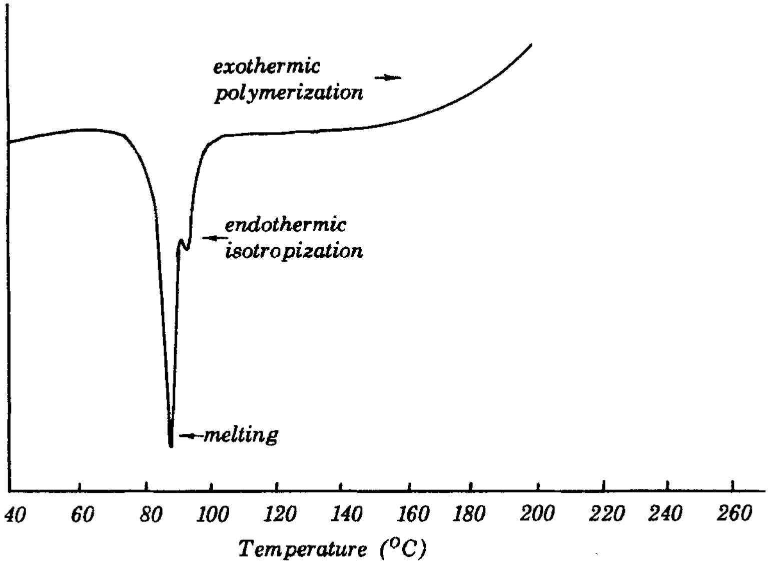


FIGURE 2 DSC of the monomer 2,5-di(benzoyloxy)styrene.

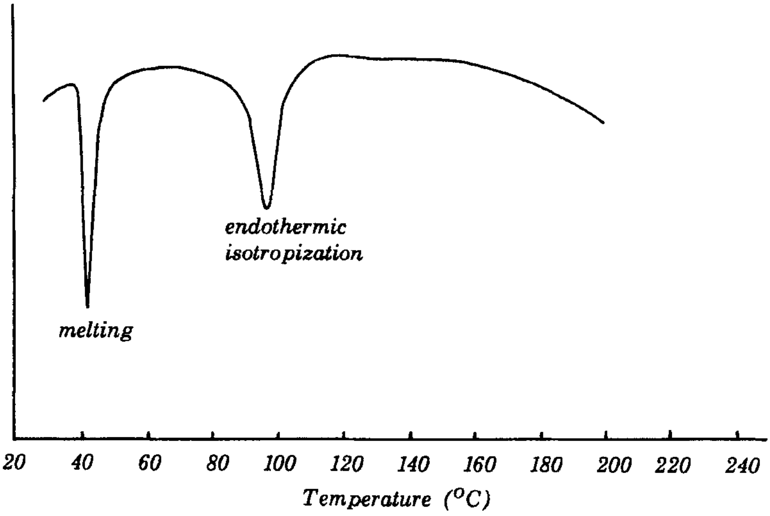


FIGURE 3 DSC of the monomer 2,5-bis[(4-butylbenzoyl)oxy]styrene.

thesized in 1952 by Cassidy and coworkers[8] and was named as vinylhydroquinone dibenzoate. According to Cassidy, vinylhydroquinone was benzoylated in pyridine with benzoyl chloride. The product was washed with water, dried and recrystallized from 95% alcohol; yield 78% based on vinylhydroquinone. It was melting at 94°C, and gave 76.3% C and 5.1% H by elemental analysis. As indicated in the experimental section of this report, we obtained the same monomer however with higher purity (found 76.68% C and 4.45% H; cald. 76.74% C and 4.65% H) as judged by the C, H analysis results. In addition, NMR and mass spectroscopy were also

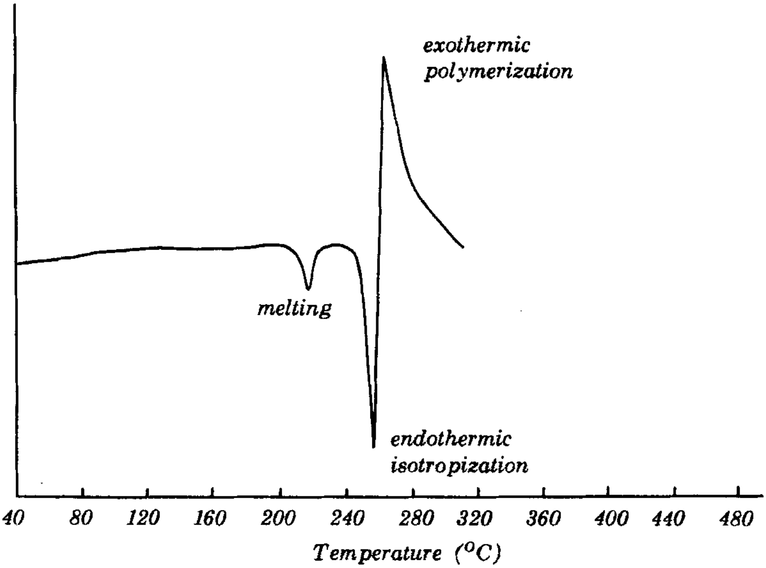


FIGURE 4 DSC of the monomer 2,5-bis[(4-cyanobenzoyl)oxy]styrene.

TABLE II

Molecular weights of the polymers

R	*H*	CH_3	C_2H_5	C_4H_9	*CN*	OCH_3	OC_2H_5	OC_4H_9
$Mn(X10^{-4})$	5.4	7.7	6.8	2.8	*	13	4.5	24
$Mw(X10^{-4})$	10	22	17	8.6		30	9.5	88
Mw/Mn	1.9	2.9	2.5	3.0		2.3	2.1	3.7

• *not soluble in THF and the inherent viscosity was given as 1.1 g/dl in DMF*

used in this restudy to characterize the chemical structure while it was not possible for Cassidy. It was found that higher purity may be obtained by the use of benzoic acid and triphenyl phosphine for the synthesis than by the use of benzoyl chloride.

No liquid crystallinity was reported by Cassidy for 2,5-di(benzoyloxy)styrene (in his time "liquid crystal" was known to very few). We found however this compound gives a DSC trace as shown in Figure 2 with two distinct endothermic peaks at 88 and 95°C. Studies with polarizing microscope showed that the compound does melt at 88 and forms a nematic mesophase which has a clearing temperature of 95°C. Figure 5 is a photomicrograph of this compound taken at 90°C in the cooling circle.

We are not able at the moment to fully understand the ability of this compound to form a liquid crystal phase. It is well known that its non-vinylated homologue, hydroquinone dibenzoate, is not liquid crystal forming with a melting point of 207°C, while most of the 4,4'-disubstituted dibenzoates are liquid crystalline.[9] Nevertheless, hydroquinone dibenzoate is rigid and rod-like, and thus has a potential of liquid crystal forming. The lateral substitution of vinyl group in 2,5-di(benzoyloxy)styrene has significantly lowered the melting temperature from 207°C for the parent hydroquinone dibenzoate down to as low as 88°C, so low that a

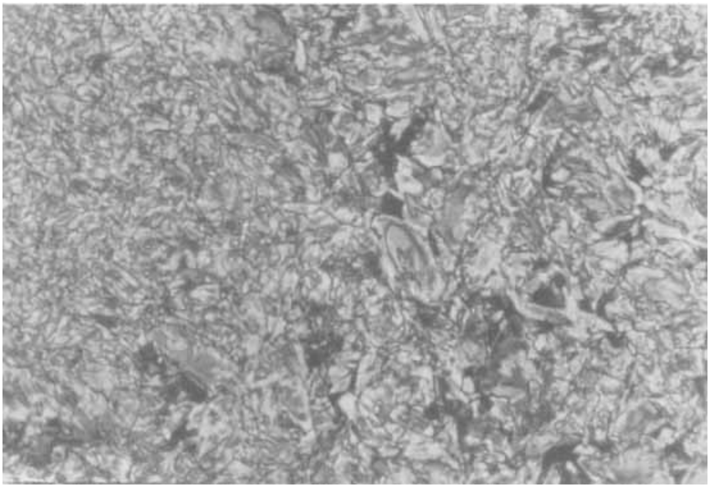


FIGURE 5 Photomicrograph of the monomer 2,5-di(benzoyloxy)styrene, taken at 90°C. See Color Plate VIII.

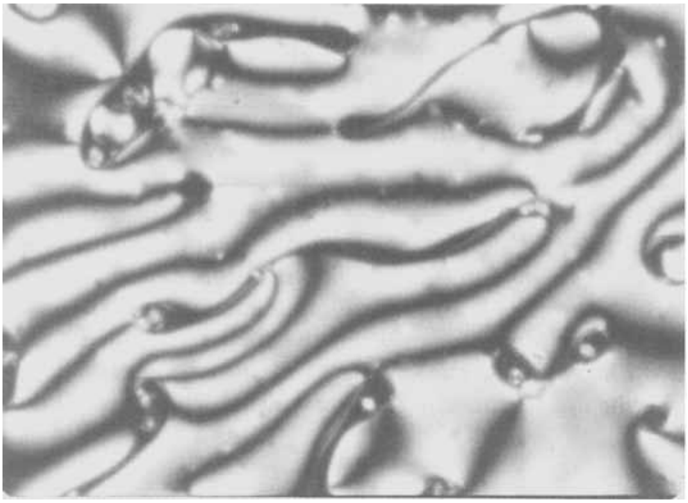


FIGURE 6 Photomicrograph of the monomer 2,5-bis[(4-ethylbenzoyl)oxy]styrene, taken at 95°C. See Color Plate IX.

mesophase is stable in a temperature range a few degrees above melting. In addition, the vinyl group is in conjugation with the central phenyl ring and is highly polarizable, this may also help the stabilization of the mesophase. This finding offers probably the first example of liquid crystal rigid rod-like molecules with lateral but without terminal substitutions.

Other interesting results may be summarized as: 1, the cyano derivative has the highest melting point as compared with the homologues with less polar substituents; 2, all the monomers are thermotropically liquid crystalline; 3, the transition temperatures decrease with lengthening of the alkyl and alkoxy substituents; and 4, the two monomers with 4 carbon atoms in the alkyl or alkoxy substituents both

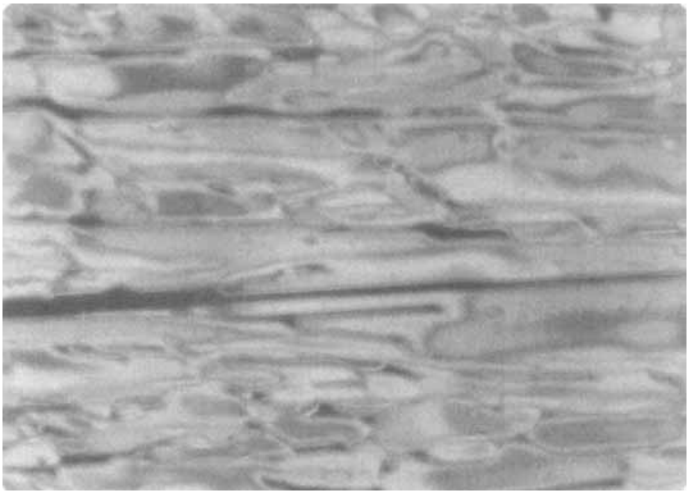


FIGURE 7 The smectic texture of the monomer 2,5-bis[(4-butylbenzoyl)oxy]styrene, photo taken at 74°C. See Color Plate X.

TABLE III

Glass transition of the polymers

R	H	CH_3	C_2H_5	C_4H_9	CN	OCH_3	OC_2H_5	OC_4H_9
Tg	170	172	160	130	200	160	130	80

show a smectic phase. Figure 6 shows a typical nematic texture of the monomer R = C_2H_5. As shown in Table I, the liquid crystal phase of this monomer is monotropic, which forms only in the cooling course from above melting and not during heating. Figure 6 was taken when the melt was cooled to 95°C. In comparison, Figure 7 shows a smectic texture of the monomer R = C_4H_9 as taken at 74°C. These results are predictable if, for example, Reference 10 is consulted.

LIQUID CRYSTALLINITY OF THE POLYMERS

The primary characterization has revealed that all these polymers are non-crystalline but are liquid crystal forming. The glass transition temperatures of these polymers were collected in Table III. Like other polymer systems of the laterally attached (side-on) side chain type of Hessel and Finkelmann[11] and of Gray *et al.*,[12] the mesophase is nematic. However for our polymers, no clearing temperature was observed below 300°C. Above this temperature the samples suffer slow decomposition and makes the Ti determination difficult. The rigid mesogenic units are attached via no spacers to molecular main chain in our system while flexible spacers were used in both that of Hessel and of Gray. This molecular structural difference may have resulted in the difference in mesophase thermal stability of the polymers.

Among the polymers, the unsubstituted homologue poly-2,5-di(benzoyloxy)styrene was first synthesized (and named as polyvinylhydroquinone dibenzoate) 40 years ago by Cassidy and coworkers[8] and was described as a white fluffy material with a molecular weight of 52,000. In this restudy the same polymer was synthesized with very similar molecular weight as shown in Table II (R = H; Mn = 54,000, Mw = 100,000), which is now found to be liquid crystalline. The white powder sample showed only a glass transition in its DSC curve, and no birefringence was observed on polarizing microscope. In the course of heating, however, the sample started to become birefringent at about 160°C and became highly birefringent at 200°C. It became a viscous melt at about 260°C. The melt birefringence was observed even at 350°C but slowly disappeared at such a high temperature because of decomposition. A TGA test of this sample at a heating rate of 20 degrees per minute suggested a 5% weight loss at 370°C. Figure 8 shows the nematic texture of this polymer observed at 280°C.

The banded texture of this series of polymers was also observed. The first description of banded texture of MJLCPs is given in Reference 7. Figure 9 shows this characteristic morphology of the unsubstituted homologue which was formed after shear at 280°C and was taken at room temperature. The shear direction was perpendicular to the direction of the bands. (The two dark parallel lines, with short dark strokes on, were formed during the cooling, these dark lines and strokes will disappear if the sample is heated again to above its glass transition and a neat banded area is obtained. Note that the direction of the short strokes is the same as the shear direction.) According to References 6 and 7, the banded texture is not only a further proof of liquid crystal state but also a suggestion of molecular chain rigidity.

Gray and co-workers had an excellent account for the novel properties of polysiloxanes with laterally attached side chains with the help of the MJLCP model and the W-W theoretical treatment.[12] We would also like to call attention to two unusual properties: The formation of banded texture of MJLCPs and the very high

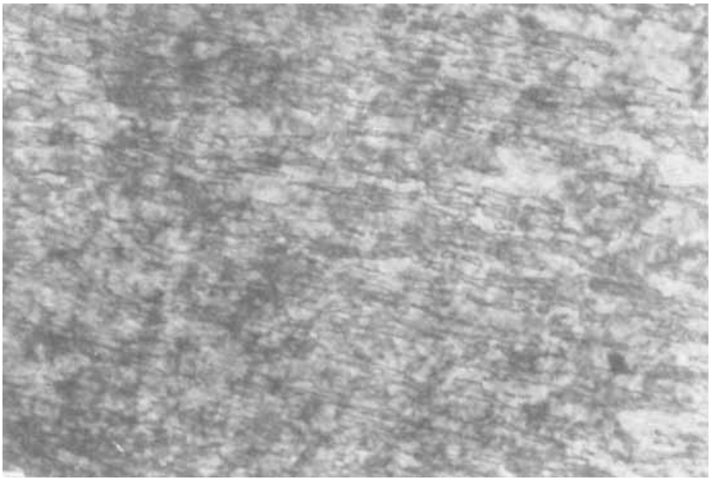


FIGURE 8 The photomicrograph of the unsubstituted polymer, poly-2,5-di(benzoyloxy)styrene, taken at 280°C showing a nematic texture. See Color Plate XI.

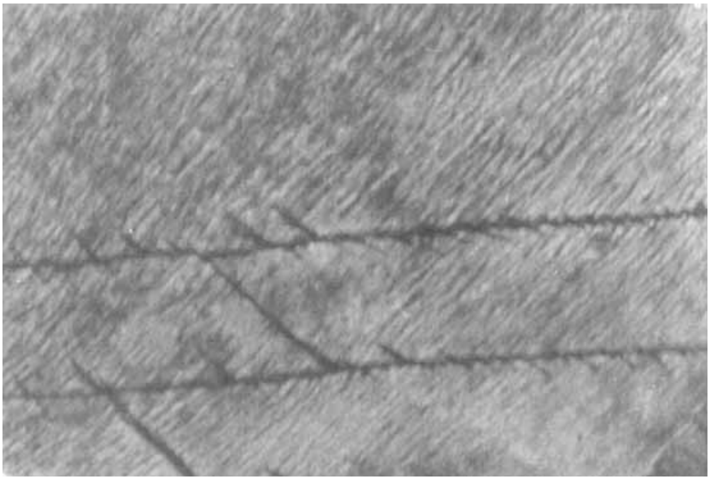


FIGURE 9 Banded texture of poly-2,5-di(benzoyloxy)styrene. See Color Plate XII.

thermal stability of the liquid crystal phase of MJLCPs. The formation of banded texture implies that MJLCPs, though of side chain type, have similar properties as that of main chain liquid crystal polymers. On the other hand, though hydroquinne dibenzoate is not liquid crystalline, poly-2,5-di(benzoyloxy)styrene, a polyethylene with hydroquinone dibenzoate moiety as side groups laterally attached via a single bond to every two chain carbon atoms, is truly liquid crystalline. Besides, its liquid crystal phase is also very stable with a clearing temperature higher than 300°C, much higher than the melting point (207°C) of hydroquinone dibenzoate. The clearing temperatures of the 4-substituted homologous polymers are also higher than that of the corresponding 4-substituted homologous hydroquinone dibenzoates, for example, that of poly-2,5-bis[(4-methylbenzoyl)oxy]styrene ($R = CH_3$, $Ti > 300°C$) is higher than that of hydroquinone ditoluoate ($R = CH_3$, $Ti = 236°C$). We have the feeling that for this series of MJLCPs, with mesogenic units laterally attached via no spacers to main chains, the mesophase is formed by polymer chains as a whole and not only by the mesogenic units as for most conventional (end-on) side chain polymers of which main chains usually take random coil conformation as described by the oblate NI phase proposed by Wang and Warner.[13] For MJLCPs discussed in this report, main chains are expected to take extended conformation and behave as main chain liquid crystal polymers. The unusual properties of these MJLCPs, especially the formation of a stable liquid crystal phase of the unsubstituted poly-2,5-di(benzoyloxy)styrene, are otherwise very difficult to understand.

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