Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: A. Blumstein , N. Kitagawa & R. Blumstein (1971): Polymerization of p-Methacryloyloxy Benzoic Acid within Liquid Crystalline Media, Molecular Crystals and Liquid Crystals, 12:3, 215-227

To link to this article: http://dx.doi.org/10.1080/15421407108082774

Molecular Crystals and Liquid Crystals. 1971. Vol. 12, pp. 215–227
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Printed in Great Britain

Polymerization of *p*-Methacryloyloxy Benzoic Acid within Liquid Crystalline Media†

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Received October 2, 1970

Abstract—The possibility of preparing stereospecific polymers from monomers organized in a liquid crystalline medium was investigated. Methacryloyloxybenzoic Acid (I) was polymerized in a smectic and in a nematic mesophase. Cetyloxybenzoic acid (II) was used as the smectogen and heptyloxybenzoic acid (III) as the nematogen. The molar ratios of II and III to I were 1/1 or 1/0.5. All the materials were very carefully purified. The mesophase transition temperatures were determined with the usual techniques. Benzoyl peroxide was the polymerization initiator in the nematic phase and for the polymerization in the smectic state, thin films deposited on freshly cleaved mica plates were subjected to UV radiation.

The tacticity of the polymers was studied by infrared and NMR spectroscopy. The carbonyl region showed two IR absorption bands, one at 1690 and the other at 1740 cm^{-1}, the former predominant in the isotactic and the latter in the syndiotactic polymers. Tacticities were computed from NMR spectra of poly (methyl methacrylate) obtained after acid hydrolysis of poly (methacryloyloxy benzoic acid) followed by methylation with diazomethane.

The increase in the percentage of isotactic component obtained in the nematic and the smectic state is explained on the basis of the steric organization of the monomer in the mesophase.

1. Introduction

The influence of the orientation of monomer molecules on the outcome of polymerization has been studied by a number of authors and the characteristic features of polymerization in preoriented media have been reviewed.$^{(1)}$

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† Presented at the Third International Liquid Crystal Conference in Berlin, August 24–28, 1970.

Inclusion into a liquid crystalline lattice constitutes one of the ways in which monomer molecules can be oriented prior to polymerization. In this study a vinyl monomer, *p*-methacryloyloxybenzoic acid (MBA), which itself is not mesomorphic, has been polymerized by free radical initiation in the nematic and smectic state through its inclusion into the lattice of two mesomorphic solvents, *p*-heptyloxybenzoic acid (HBA) and *p*-cetyloxybenzoic acid (CBA), respectively. MBA had previously been polymerized in CBA by Amerik and coworkers,(2) who compared the kinetics of polymerization of MBA in dimethyl formamide and in CBA.

The purpose of our investigation is to relate the kinetics of polymerization and the stereospecificity of the polymer to the organization of the monomer in the liquid crystalline lattice.

We present here some preliminary results on the stereospecificity of poly (*p*-methacryloyloxy) benzoic acid (PMBA) obtained in a nematic and in a smectic state. The formation of a mesophase within a binary system in which the monomer is nonmesomorphic was ascertained by means of differential thermal analysis (DTA) and polarizing microscopy. In order to avoid polymerization, a model saturated compound, *p*-propionoxybenzoic acid (PBA) was used in the first part of the study of mesophase formation.

2. Experimental

MATERIALS

MBA was synthesized from *p*-hydroxybenzoic acid and methacryloyl chloride by a Shotten–Baumann synthesis.(3) The crude product was recrystallized twice from glacial acetic acid, ethanol and acetone, respectively; m.p. 167–169 °C; yield 48%.

Methyl (*p*-methacryloyloxy) benzoate (MMB) was prepared by diazomethylation of MBA and recrystallized from acetone; m.p. 66–67 °C.

PBA was synthesized from *p*-hydroxybenzoic acid and propionic anhydride.(3) The crude product was recrystallized twice from glacial acetic acid, ethanol and benzene, respectively; m.p. 186–187 °C; yield 61%.

CBA was synthesized from *p*-hydroxybenzoic acid and cetyl iodide by a variation of the Williamson synthesis.(3) The product was recrystallized twice from glacial acetic acid, methanol, benzene and acetone, respectively; m.p. 99 °C; yield 62%.

HBA from Frinton Laboratories was recrystallized from glacial acetic acid and methanol; m.p. 92 °C.

CHARACTERIZATION OF THE MESOPHASES

The mesophases were studied by a combination of the following methods: observation in a melting point capillary, observation with a polarizing microscope equipped with a Kofler heating stage, recording of DTA diagrams with a Fisher Model 260 Differential Thermanalyzer TM. Traces of hydroquinone were added to the monomer-mesogen mixtures in order to inhibit polymerization.

POLYMERIZATION

The polymerizations were initiated with benzoyl peroxide (1% by weight with respect to monomer) or UV radiation. In the former case, the reactions took place in sealed, evacuated tubes; in the latter, on freshly cleaved mica plates. The reaction mixture was mounted on the plate, quickly melted, cooled to room temperature and placed into quartz flask swept with nitrogen. Sample flask, UV lamp and a thermostated heating plate were enclosed in an insulated box. The temperature of the sample was checked with a platinel thermocouple.

After polymerization, the reaction mixtures were repeatedly extracted with ether containing traces of hydroquinone. The monomer, HBA and CBA are soluble in ether, the polymer is not.

Reference PMBA was prepared in solution in dimethyl formamide at 90 °C with benzoyl peroxide as initiator. Reference polymethyl (*p*-methacryloyloxy) benzoate (PMMB) was prepared in bulk at 75 °C with AIBN as initiator.

HYDROLYSIS AND METHYLATION OF THE POLYMERS

The polymers were hydrolyzed at room temperature with concentrated sulfuric acid for about 200 hours.(4) Infra-red spectra of the resulting polymethacrylic acid showed no trace of residual benzene rings, and the percentage of hydrolysis could be estimated at 95% or better. After hydrolysis polymethacrylic acid was converted to poly(methylmethacrylate) (PMMA) with a solution of diazomethane in ether. Reference polymers were easily methylated, and the percentage of methylation determined from NMR spectra was approximately 95%. For polymers prepared in a mesophase, especially at low degrees of conversion, the methylation had to be repeated several times, but even then a small fraction remained insoluble in chloroform. This was filtered off, the PMMA precipitated in hexane, dried under reduced pressure and dissolved in ethanol free chloroform. The percentage of methylation was approximately 95% for high degrees of conversion to polymer and approximately 60% for low degrees of conversion.

CHARACTERIZATION OF POLYMERS

The polymers were characterized by IR and NMR spectroscopy. Thin films were cast from methanol on salt rock plates and the IR spectra recorded on a Beckmann IR10 spectrophotometer. The NMR spectra were obtained with a Hitachi–Perkin Elmer 60 Mc instrument. The tacticities were determined from spectra of PMMA in chloroform by the usual method of Bovey and Tiers.(5)

2. Results and Discussion

Mixtures of MBA with CBA and HBA display liquid crystalline properties. This was ascertained by DTA, polarizing microscopy and observation of melting points. Because MBA polymerizes at the isotropic transition temperature, a detailed study of mesophase formation was made with a model, nonmonomeric compound, *p*-propionoxybenzoic acid. Figure 1 shows thermograms of several mixtures of PBA–CBA. Pure CBA has a smectic mesophase in the 99–132 °C range. A nematic mesophase, stable over a range of about one degree, was also observed with the polarizing microscope. The existence of a nematic phase for CBA has been both reported and denied in the literature.(6) In the melting point capillary, we have observed the nematic phase at 131.7 °C and the isotropic phase at 132.5 °C. The nematic→isotropic transition was precisely reversible.

With the instrument resolution at our disposal, only one peak at 132 °C could be recorded by DTA for pure CBA, but in the case of mixtures, this peak splits into two peaks, delimiting the range of stability of the nematic mesophase. As the amount of PBA in the

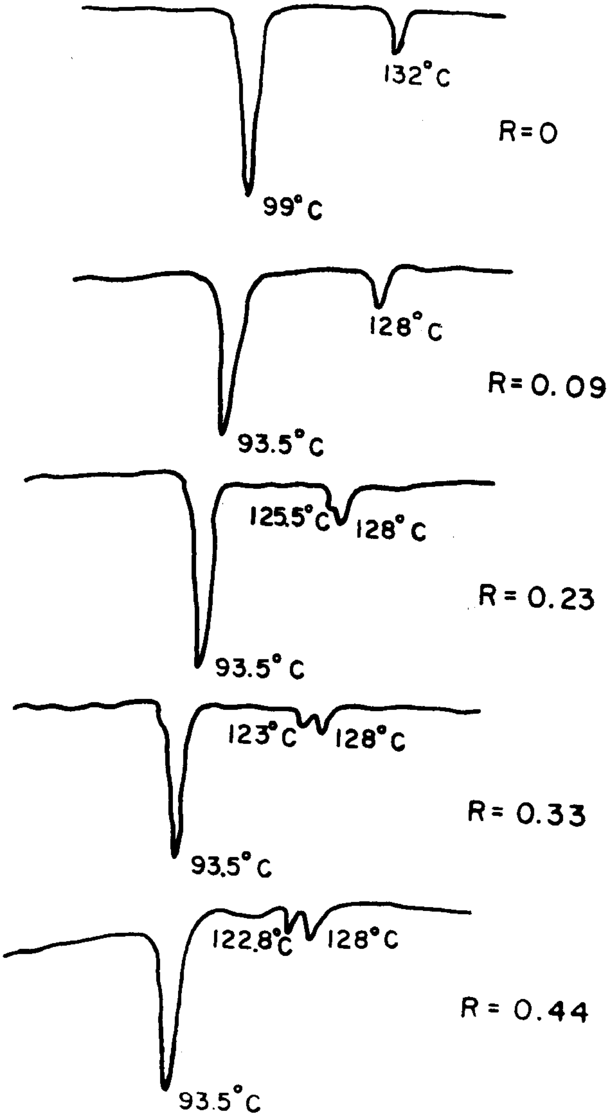

Figure 1. DTA diagrams for the system PBA–CBA (R = Mole fraction of PBA)

mixtures increases, the stability interval of the nematic mesophase appears to increase, but the range of stability of the smectic mesophase decreases. Table 1 shows the interval solid→smectic-smectic→nematic as a function of *R*, the mole fraction of PBA in the mixture.

TABLE 1 Stability Range of the Smectic Mesophase for PBA–CBA Mixtures

R	Stability Range (°C)
zero	99–132
0.03	93.5–128
0.23	93.5–125.5
0.33	93.5–123
0.44	93.5–122.8
0.66	95–121
0.76	93–120

The thermograms obtained with the monomer are similar to the thermograms obtained with PBA, but the transition temperatures and the stability range of the mesophase are lowered by the presence in MBA of the α-methyl group (Fig. 2). Because MBA polymerizes at the isotropic transition temperature, traces of hydroquinone were added to the DTA mixtures.

The structure of the monomer-mesogen mesophases is not known. Amerik and coworkers[2] postulated for MBA–CBA mesophases a

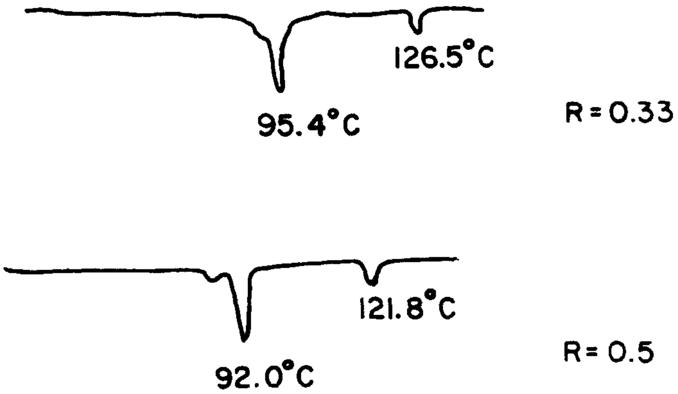

Figure 2. DTA diagrams for the system MBA–CBA (R = Mole fraction of MBA)

model in which the monomer forms strata through dimerization with CBA (Fig. 3). (We assume that the smectic phase of CBA can accomodate the monomer through dissolution.)

In our polymerization experiments, the mole fraction of monomer in the liquid crystal was either 0.5 or 0.33. Table 2 summarizes the DTA data for the systems polymerized:

TABLE 2 Stability Range of the Mesophase of Interest

System	Mole Fraction Monomer	Mesophase of Interest	Range °C
HBA	0	nematic	100–147
CBA	0	smectic	99–132
HBA-MBA	0.5	nematic	89–140
CBA-MBA	0.5	smectic	92–121.8
CBA-MBA	0.33	smectic	95.4–126.5

We report here the results of polymerizations carried out at 98 °C in the smectic state of CBA and at 98 °C in the nematic state of HBA. In the solid state, MBA does not polymerize. Within a given mesophase, the temperature of polymerization does not appear to significantly influence the stereospecificity of the polymer, but no systematic study of this point was made to date. The stereospecificity of the polymers was determined by IR and NMR spectroscopy. Figures 4 and 5 show representative IR and NMR spectra.

Tacticities of PMBA and PMMB could not be studied directly by NMR and the polymers had to be converted to PMMA through hydrolysis and methylation. The relative amounts of isotactic, heterotactic and syndiotactic triads were computed from the α-methyl peaks of PMMA in chloroform. Under the conditions employed in this study, hydrolysis and methylation do not affect the tacticity and the backbone chain length of the polymer.(7)

Figure 4 shows that the conditions of preparation influence the IR spectrum of PMBA, namely the peaks at 1280 and 1380 cm^{-1} and the carbonyl absorption peaks at 1740 and 1690 cm^{-1}.

Table 3 gives the influence of polymerization conditions on the population of isotactic, syndiotactic and heterotactic triads P_i, P_s and P_h determined from NMR spectra. The population of isotactic,

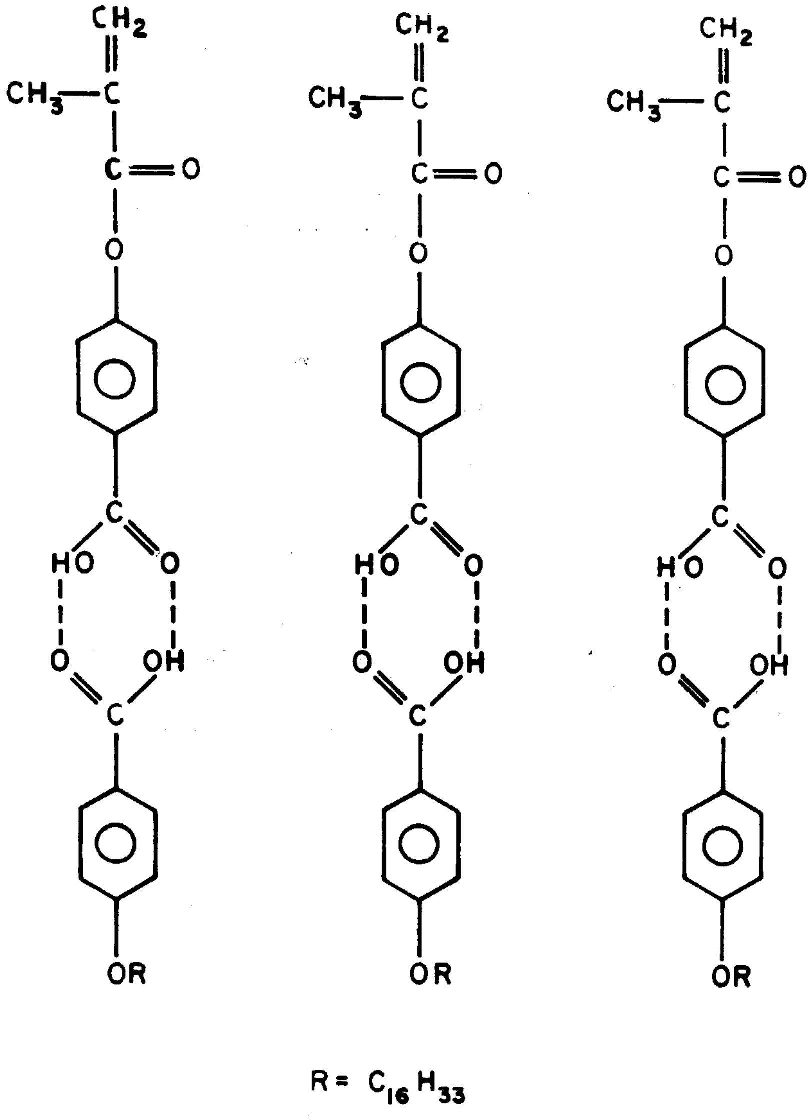

Figure 3. Model of the smectic mesophase of MBA–CBA according to Amerik and coworkers.

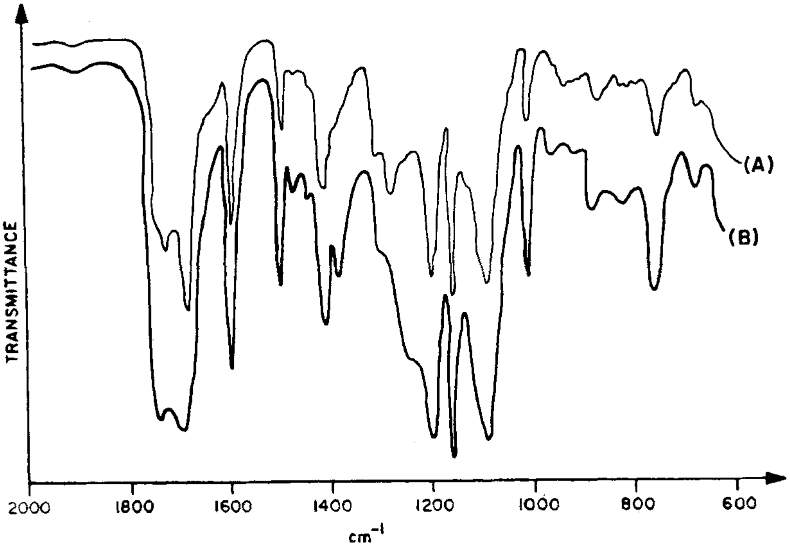

Figure 4. Infra-red spectra of PMBA (A) reference polymer prepared in solution (B) polymer prepared in the smectic state at 110 °C.

TABLE 3 Tacticity as a Function of the Conditions of Polymerization

Polymer	Condition of Preparation	Conversion %	% Triads			% Diads		Average Stereo-sequence Length	
			P_i	P_h	P_s	P(I)	P(S)	μ(I)	μ(S)
PMB ester	bulk	55	21	42	37	0.42	0.58	2.0	2.8
PMBA	solution	50	22	41	37	0.43	0.57	2.0	2.8
PMBA	nematic	7	51	18.5	31	0.60	0.40	6.7	4.3
PMBA	nematic	55	41.5	22	36.4	0.53	0.47	4.8	4.3
PMBA	Nematic	90	30	36	34	0.48	0.52	2.7	2.9
PMBA	smectic	8	50	20	30	0.60	0.40	6.0	4.0
PMBA	smectic	55	43	20	37	0.53	0.47	5.3	4.7
PMBA	smectic	80	27	37	36	0.46	0.54	2.5	2.9

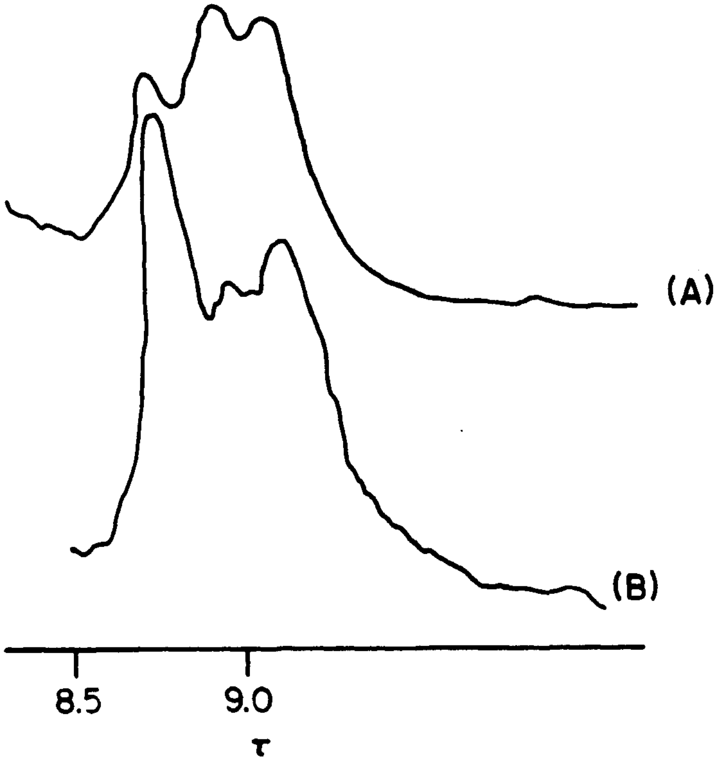

Figure 5. NMR spectrum of the α-methyl peak of PMMA in chloroform (A) PMMA obtained from reference PMBA prepared in solution (B) PMMA obtained from nematic phase, 55% conversion.

syndiotactic diad placements $P(I)$, $P(S)$, the average stereosequence length $\mu(I)$ and $\mu(S)$, can be calculated from Coleman and Fox equations$^{(8)}$:

$$P(I) = P_i + \tfrac{1}{2}P_h \qquad P(S) = 1 - P(I)$$

$$\mu(I) = \frac{2P(I)}{P_h} \qquad \mu(S) = \frac{2P(S)}{P_h}$$

Table 3 shows the considerable influence of the conversion to polymer on the stereospecificity. As the degree of conversion increases, the percentage of isotactic triads decreases significantly and the percentage of heterotactic triads increases, approaching that observed in the reference polymer prepared in solution. Increasing amounts of heterotactic triads indicate decreasing length of the stereoregular sequences in the polymer and increasing randomness of polymerization. It is probable that the growing polymer chains break down the anisotropic organization of the liquid crystal and the stereospecificity decreases as polymerization progresses. Tsuruta and coworkers(7) have studied the tacticity of seventeen different polymethacrylic esters, after hydrolysis and diazomethylation. In their work the percentage of hydrolysis varied from 39 to 95.8% and the percentage of esterification was 65% and above. According to these authors the percentage of methylation does not affect the stereospecificity. We must however keep in mind the possibility that incompleteness of methylation may introduce some error on our values of P_i, P_s and P_h. This point is presently being investigated.

For polymerization in the smectic mesophase, in which translation of the monomer molecules is severely restricted, we had predicted a mechanism illustrated in Fig. 6.

The acid group of the monomer is attached to a neighboring molecule through hydrogen bonding (not represented); one side of the active center in the growing polymer chain is hindered by the bulky pendant side-groups. Consequently, polymerization can occur only in either of the two conformations represented in Fig. 6. An isotactic triad results in both cases. A syndiotactic placement would be incompatible with the smectic structure.

We had, therefore, expected that for a given degree of conversion, the polymers prepared in the smectic state would be considerably more isotactic than the " nematic " polymers.

Table 3 shows that the stereospecificity of " smectic " and " nematic " polymers is basically the same. It is possible that the heat of polymerization is less efficiently dissipated in the smectic than in the nematic state. In the immediate vicinity of the growing chain this could cause a breakdown in the molecular organization postulated for the smectic state.

We hope that the results of experiments currently under way will help us to understand the relation between monomer organization in the mesophase and stereospecificity of the polymer.

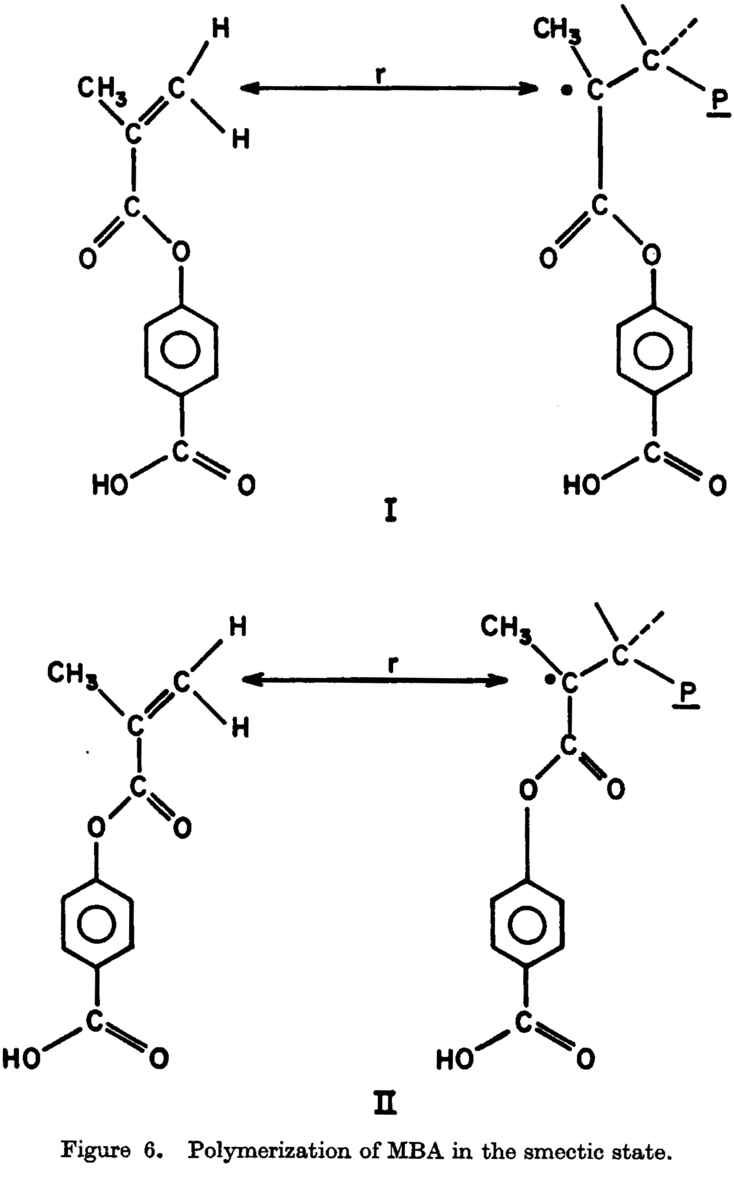

Figure 6. Polymerization of MBA in the smectic state.

Acknowledgement

Thanks are expressed to Owens–Illinois Technical Center for the support of this work.

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