

Radiation-Induced Copolymerization of Maleimides and Acenaphthylene in the Solid State

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Synopsis

The γ -ray-induced polymerizations in the binary systems of maleimide-acenaphthylene and *N*-methylmaleimide-acenaphthylene have been studied. The phase diagrams of the two systems show that an eutectic was formed in each system. It has been proven by the solvent extraction and the turbidimetric titration of obtained polymer that copolymer was formed in the eutectic of each system together with homopolymers. The fraction of total homopolymers in the maleimide-acenaphthylene system was nearly the smallest in the monomer mixture of the eutectic composition. The composition of the copolymer, which was isolated by the extractions, was almost independent of the monomer composition. In order to elucidate these results, it was postulated that the copolymerization occurred at grain boundaries between the two components in the eutectic.

INTRODUCTION

It has previously been reported that the radiation-induced copolymerization proceeds even in the solid state—not only in solid solutions^{1,2} but also in eutectic mixtures.^{3,4} The distinctive feature of the solid-state polymerization is that monomer molecules have less mobility in the solid state than in the liquid state. Moreover, the study of copolymerization in the solid state presents some peculiar problems, since the reaction is affected by the restricted mobility of the monomer molecules.

In our laboratory, the γ -ray-induced polymerizations of maleimide and *N*-methylmaleimide in the presence of acenaphthylene were studied below the melting temperature of each eutectic mixture, and the formation of copolymers was observed. The characterization of the copolymers was performed to some extent in order to elucidate the mechanism of the copolymerization in the solid state. The examination of thermal property of the copolymers also will be shown in this article.

EXPERIMENTAL

Preparation and Purification of Materials

Maleimide was synthesized from maleic anhydride by Tawney's method,⁵ and purified by repeated recrystallizations from ethyl acetate and sublima-

tion in vacuo (mp 93.0–93.5°C). *N*-Methylmaleimide was purchased from Aldrich Chemical Co. and purified by recrystallization from ethyl ether and sublimation in vacuo (mp 95.0–96.0°C). Acenaphthylene (Aldrich Chemical Co.) was purified by the following procedure: The picrate was prepared in (1:1) benzene-ethanol and recrystallized from (1:1) toluene-ethanol. Its suspension in benzene was decomposed with aqueous ammonium hydroxide. The benzene solution was washed with water repeatedly and benzene was evaporated. The crystals thus formed were further purified by recrystallization from petroleum ether and sublimation in vacuo (mp 92.5–93.0°C).

Preparation and Irradiation of Samples and Isolation of Polymer

The glass tubes containing two constituents were evacuated and sealed at a pressure of 10^{-4} mm Hg. These samples were melted and then crystallized by cooling with water at room temperature prior to irradiation. Irradiations were performed with a Co^{60} source at a dose rate of 5.9×10^4 r/hr at the temperatures about 20°C below the eutectic points. Polymer was isolated by extracting the residual monomer with methyl alcohol from the partially polymerized sample at room temperature. At first, the extraction was carried out with methyl alcohol containing a small quantity of hydroquinone. However, the addition of hydroquinone did not make a difference in the polymer yield, and the contribution from post-irradiation polymerization seems to be negligible.

Determination of Phase Diagram

Phase diagrams of maleimide-acenaphthylene and *N*-methylmaleimide-acenaphthylene systems were determined with a Perkin-Elmer differential scanning calorimeter, Model DSC-1B.

Determination of Polymer Composition

The determination of polymer composition was carried out by infrared analysis. Calibration curves between polymer composition and D_{1170}/D_{820} or D_{1710}/D_{820} ratio were prepared beforehand by elementary analysis of nitrogen content and measurement of infrared spectra of several copolymers.

Turbidimetric Titration

Turbidity measurements of the polymers in DMF solutions were carried out with a Kotaki turbidimeter at 18°C. Methyl alcohol was used as a precipitant.

Pyrolysis Gas Chromatography

Pyrolysis of the polymers was carried out in a hot tubular reactor and the degradation product was analyzed with a Hitachi Model K-53 gas chromatograph which employs a hydrogen flame ionization detector.

RESULTS

Binary phase diagrams for maleimide-acenaphthylene and *N*-methylmaleimide-acenaphthylene systems are shown in Figures 1 and 2. These figures indicate that both systems give eutectic mixtures. Figures 3 and 4 show conversion vs. monomer composition curves. In the maleimide-acenaphthylene system, the rate of γ -ray-induced copolymerization at

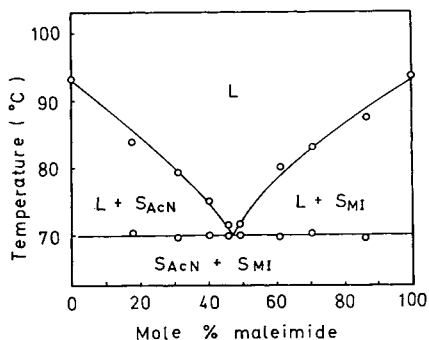


Fig. 1. Phase equilibrium diagram of maleimide-acenaphthylene system.

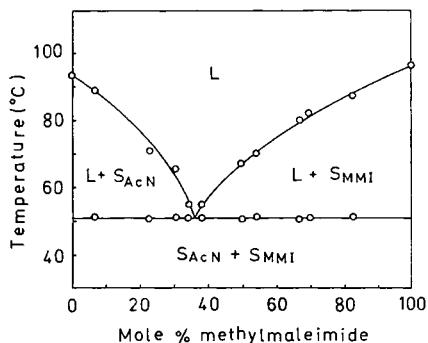


Fig. 2. Phase equilibrium diagram of *N*-methylmaleimide-acenaphthylene system.

90°C in the liquid state decreased with the increasing acenaphthylene mole fraction. This tendency is probably due to the protective effect of the naphthalene ring in acenaphthylene molecule, since the rate of BPO-initiated polymerization in DMF solution was almost independent of the monomer composition. However, the over-all rate of γ -ray-induced polymerization in the solid state increased with the increasing mole fraction of acenaphthylene.

It is apparent that the rate of polymerization of *N*-methylmaleimide in the solid state is relatively large, as is shown in Figure 4.

Typical infrared spectra of the polymers formed in maleimide-acenaphthylene and methylmaleimide-acenaphthylene systems in the solid state are shown in Figures 5 and 6 together with those of polyacenaphthylene.

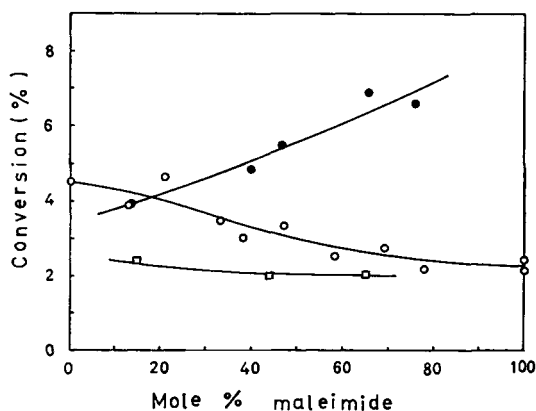


Fig. 3. Effect of monomer composition on polymer yield in maleimide-acenaphthylene system: (●), irradiated in a 5.9×10^4 r/hr source for 5 hr at 90°C in the liquid state; (○), irradiated in a 5.9×10^4 r/hr source for 120 hr at 50°C in the solid state; (□), polymerized with BPO (0.28%) in DMF solution for 14 hr at 50°C .

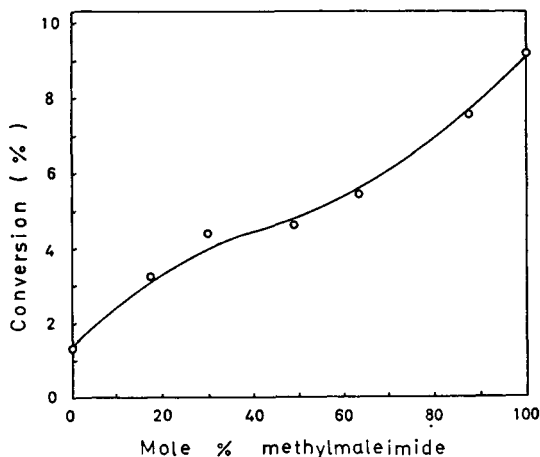


Fig. 4. Effect of monomer composition on polymer yield in *N*-methylmaleimide-acenaphthylene system at 26°C in the solid state: dose rate 5.9×10^4 r/hr, irradiation time 128 hr.

Absorption bands due to C=O group (1710, and 1770) and C—N linkage (1170 or 1120) of maleimides are observable, as well as those due to acenaphthylene (820 and 790) in the spectra of the polymers. It is possible to calculate polymer composition from D_{1170}/D_{820} or D_{1710}/D_{820} ratio as described before.

Composition of the polymers obtained by three different techniques are plotted against the composition of monomer in Figure 7. The composition curve of the polymer formed in the liquid state at 90°C is closely similar to that for the BPO-initiated polymerization in DMF solution at 50°C .

However, these curves are quite different from that for the γ -ray-induced polymerization in the solid state, because the last one contains contribution of the homopolymers of both components.

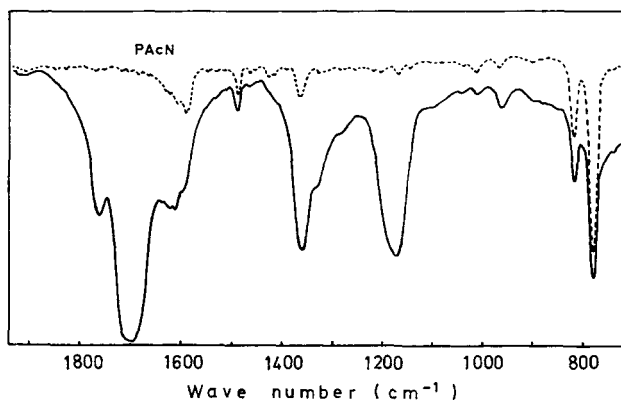


Fig. 5. Infrared spectra of maleimide-acenaphthylene polymer (solid line) and poly-acenaphthylene (broken line) in KBr pellets.

In order to isolate polymaleimide, the polymers formed in maleimide-acenaphthylene system in the solid state were subjected to an extraction with DMF-methyl alcohol mixture containing 84% methyl alcohol, since polymaleimide is practically soluble in this mixture, as will be shown in

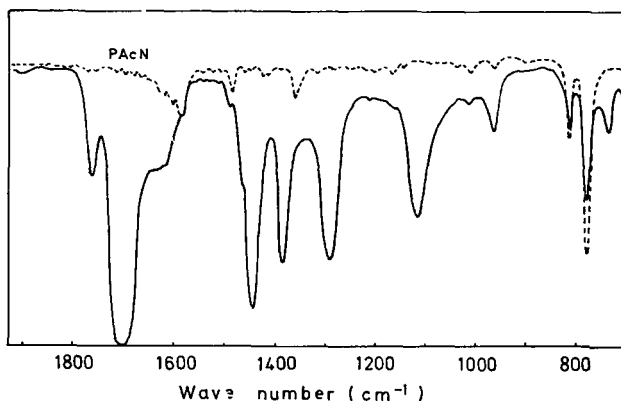


Fig. 6. Infrared spectra of *N*-methylmaleimide-acenaphthylene polymer (solid line) and polyacenaphthylene (broken line) in KBr pellets.

turbidimetry data. No absorption band due to acenaphthylene was found in the infrared spectrum of the extract. The copolymers were also subjected to an extraction with benzene. The infrared spectrum of the extract shows a weak absorption band due to carbonyl group of maleimide com-

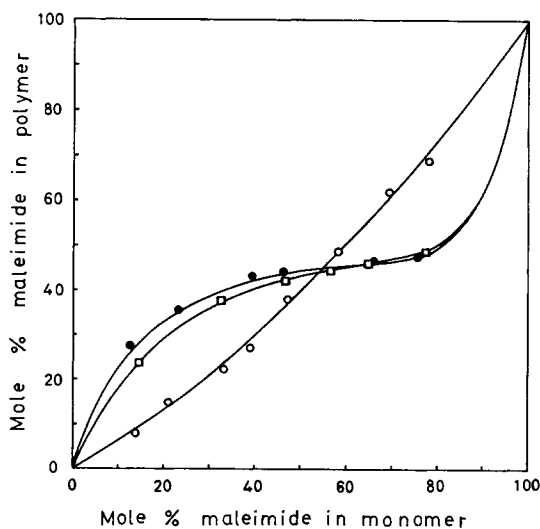


Fig. 7. Composition of polymers formed in maleimide-acenaphthylene system: (●), irradiated in a 5.9×10^4 r/hr source for 5 hr at 90°C in the liquid state; (○), irradiated in a 5.9×10^4 r/hr source for 120 hr at 50°C in the solid state; (□), polymerized with BPO (0.28%) in DMF solution for 7–14 hr at 50°C .

ponent besides those due to polyacenaphthylene. The extraction data are shown in Table I.

Turbidimetric titration of the polymers was carried out, since the extraction with benzene was suspected to remove the copolymers which contained a small amount of maleimide component and, therefore, it is requisite to check the presence of pure polyacenaphthylene. Polymaleimide fraction was eliminated beforehand from the samples by extraction. As is shown in Figure 8, turbidity curves *A*, *B*, *C*, and *D* consist of two components. Polyacenaphthylene precipitates at lower concentration of precipitant (broken line). The lower parts of the curves *A*, *B*, *C*, and *D* coincide with

TABLE I
Extraction of Acenaphthylene-maleimide Polymers with Organic Solvents

Mole % maleimide in monomer	Weight % maleimide in polymer mixture as a whole	Benzene soluble fraction (weight %)	DMF-methanol soluble fraction (weight %)	Insoluble fraction (weight %)	Mole % maleimide in insoluble fraction
13.0	5.48	81.5	0	18.5	39.7
20.9	10.10	71.5	1.3	27.2	42.9
33.1	15.42	59.2	4.9	35.9	39.4
47.0	27.96	27.6	14.3	58.1	32.5
58.0	37.74	14.2	23.1	62.7	32.3
69.1	50.94	21.0	39.5	39.5	39.0
78.0	58.37	18.9	48.8	32.3	39.7

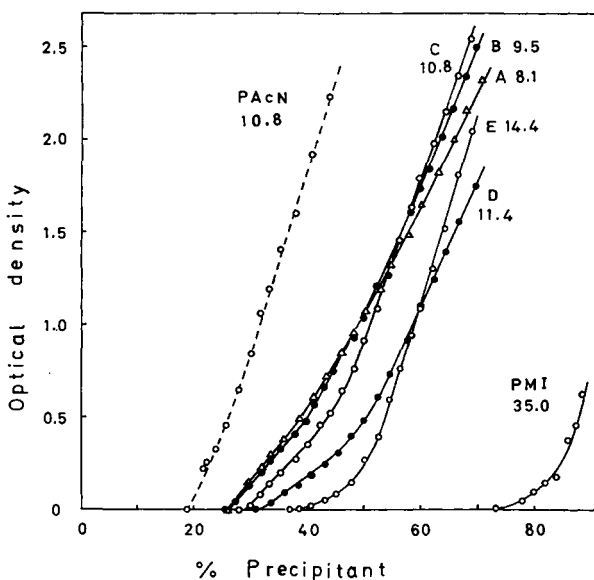


Fig. 8. Turbidimetric titration curves of polyacenaphthylene, maleimide-acenaphthylene polymers and polymaleimide: initial concentration of samples in mg/100 ml indicated by numbers in figure; Samples A, B, C, D, and E = polymers obtained in maleimide-acenaphthylene system in the solid state, polymaleimide was eliminated beforehand by extraction with DMF-methyl alcohol (16:84); initial monomer compositions in the sample preparation: A = 13.0, B = 20.9, C = 33.1, D = 38.5, and E = 47.0 mole % maleimide.

turbidity curves for polyacenaphthylene of various concentrations. The upper parts of the curves were identified to be turbidity curves for copolymer, since the precipitation point of polymaleimide is higher than 75% precipitant concentration. The curve *E* represents the turbidity for the poly-

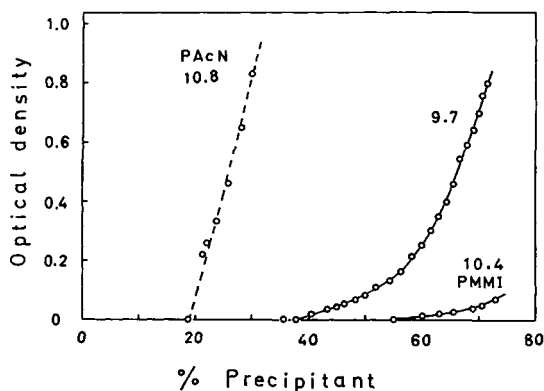


Fig. 9. Turbidimetric titration curves of polyacenaphthylene, *N*-methylmaleimide-acenaphthylene polymer and poly(*N*-methylmaleimide): initial concentration of samples in mg/100 ml indicated by numbers in figure; initial monomer composition in the sample preparation = 26.2 mole % *N*-methylmaleimide.

mer obtained in the eutectic mixture. The results of turbidimetric titration and extraction with DMF-methyl alcohol mixture show that the sum of the homopolymers is the smallest approximately at the eutectic composition.

From the above results we could assume that benzene removes mainly polyacenaphthylene from the polymer mixture, if we neglect a small amount of contamination which is shown by the presence of C=O absorption band in the infrared spectrum of the extract, because the C=O absorption band in polymaleimide is very strong as is seen in Figure 5 and the possible contamination was considered to be less than a few per cent.

The last column of Table I shows the percentage of maleimide based on moles in the insoluble fraction, that is, in the copolymer, calculated from the extraction data. The particular feature is that the maleimide occupies 32 to 43% of the copolymer independently of the monomer composition. The result is considered to be natural, since the eutectic mixtures from which the copolymer is originated should have the same composition irrespectively

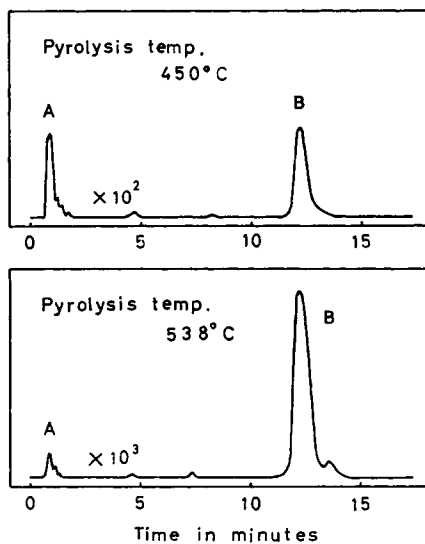


Fig. 10. Pyrolysis gas chromatograms of maleimide-acenaphthylene polymer: sample quantity: top 0.935 mg, bottom 0.905 mg column: 20% SE-30 on Chromosorb W, 2 m column temp. 160°C, carrier gas N_2 , flow rate 21 ml/min; attenuation scale indicated by numbers in figure.

of the initial monomer composition. Another important aspect observable from Table I is that at the eutectic composition of monomers the copolymer is really the main product of γ -ray irradiation, but the homopolymers are also formed considerably.

The turbidity curve for the polymer formed in *N*-methylmaleimide-acenaphthylene system is also shown in Figure 9. It seems probable that the copolymer is relatively rich in the *N*-methylmaleimide component.

Typical pyrolysis gas chromatograms of acenaphthylene-maleimide copolymer is shown in Figure 10. The peak A is mainly related to the maleimide component, while the peak B is attributed to acenaphthylene. Figure 11 shows the recovery of acenaphthylene monomer by the thermal

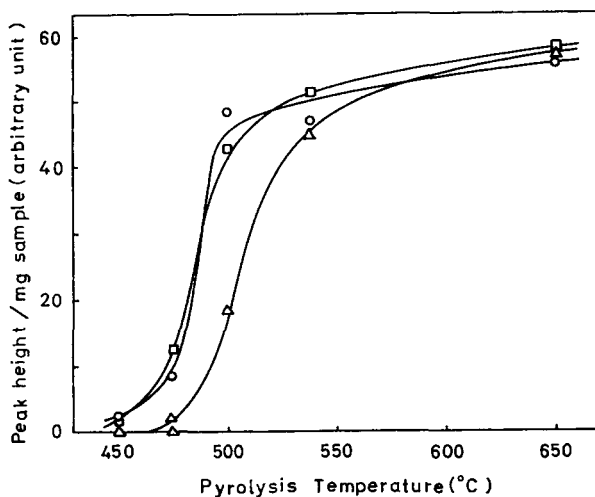


Fig. 11. Effect of pyrolysis temperature on recovery of acenaphthylene from maleimide-acenaphthylene polymers (peak B): (O), polymer obtained in maleimide-acenaphthylene system at 50°C in the eutectic, maleimide component in polymer = 28.0% (wt); (Δ) polymer obtained in maleimide-acenaphthylene system at 90°C in the liquid state, maleimide component in polymer = 27.0% (wt); (□), a mixture of polymaleimide and polyacenaphthylene, both polymerized at 50°C in the solid state, polymaleimide in the mixture = 28.6% (wt).

decomposition of copolymers and a mixture of homopolymers. The decomposition temperature of the polymer mixture and of the polymer obtained in the binary eutectic were about 25°C lower than that of the polymer obtained in the liquid state.

DISCUSSION

It has been proven that the copolymerizations occurred in the binary systems of maleimide-acenaphthylene and *N*-methylmaleimide-acenaphthylene below their eutectic temperatures, and that the homopolymers were formed considerably together with the copolymer. The results of the turbidimetric titration and the extraction suggest that the homopolymers and the copolymer were formed in separate phases, i.e., the homopolymers were formed mainly in crystals of acenaphthylene or maleimide, and the copolymer was formed only in the eutectic mixture, as the formation of total homopolymer is considered to be the smallest at the eutectic composition of monomer. This is the main reason why the over-all composition of the polymer formed in the solid state is quite different from that in the liquid state in Figure 7. The effect of monomer composition on the over-

all rate of polymerization in the solid state should be considered from this viewpoint.

Shimizu et al. assumed "a liquid like state" at the boundary of two monomer crystals in the study of the radiation-induced solid-state copolymerization of maleic anhydride and acenaphthylene.³ In the binary system of maleimide and acenaphthylene, however, the copolymerization does not seem to proceed in the liquid like state by the following reasons, i.e., (1) the rate of polymerization at the eutectic composition is comparable with those of pure solid monomers. (2) The polymerization was carried out 20 degrees below the eutectic temperature. (3) The molecular weight (\bar{M}_n) of the polymer mixture formed in the eutectic, which was determined with a Hitachi-Perkin-Elmer vapor pressure osmometer Model 115 in a THF solution, was about 5,000. This is smaller than that of polyacenaphthylene formed in the solid state ($\bar{M}_n = 30,000$). It is known that the molecular weight of polyacenaphthylene or polymaleimide formed in the liquid state is much higher than that formed in the solid state.

It is most probable that the homopolymerization of maleimide or acenaphthylene proceeds by the two-phase mechanism which was proposed by G. Adler,⁷ since both monomers form amorphous polymers.^{8,9} In accordance with this mechanism, polymerization occurs with a nucleation process in which free radicals initiate polymerization at sites of crystal defects, and proceeds at the interface between a crystalline monomer region and an amorphous polymer region. Monomer molecules reach growing radicals by diffusion through the interface.

An interaction between two components is essential for the formation of copolymer. The fact that crystals in binary eutectics are usually much smaller than those of each component is favorable to the formation of copolymer in the eutectic. The solid-state copolymerization of maleimides and acenaphthylene is pictured as follows; in the eutectic, polymerization is initiated preferentially near grain boundaries between two components, and both monomers participate in the propagation reaction, which leads to the copolymerization. As is well known, the grain boundary is a kind of crystal defect and also a high-diffusivity path¹⁰ for the constituents.

Above discussions would also be applied to the *N*-methylmaleimide-acenaphthylene system, because the over-all feature in this system looks similar to that of the maleimide-acenaphthylene system.

Pyrolysis gas chromatograms show that one of the parent monomer, acenaphthylene, was recovered from the copolymers, and that the yield got closer to a limiting value rapidly as the pyrolysis temperature was raised to 500–540°C. In Figure 11, the curve for the polymer obtained in the eutectic is almost similar to that for the mixture of homopolymers. On the other hand, height of peak *A* increased gradually, as the pyrolysis temperature was raised to 650°C. The peak would be attributed to a low molecular weight compound produced mainly by further decomposition of maleimide unit.

The result on the decomposition temperature of the three samples, which

is seen in Figure 11, may be explained by assuming that the polymer formed in the binary eutectic has block-type sequences of monomer units. However, it seems that the decomposition temperature is also affected by the molecular weight of the samples.

As far as the present data are concerned, we cannot reach a definite conclusion as to the microstructure of the copolymer obtained. The results on pyrolysis gas chromatography and the constancy of the copolymer composition (Table I) would support the formation of block-type copolymer. Further investigations concerning the microstructure of the copolymer formed in the solid state is desirable.

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Received July 18, 1968

Revised April 22, 1969