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SHORT COMMUNICATIONS

RADIATION INDUCED COPOLYMERIZATION OF TRIOXANE AND MALEIC ANHYDRIDE

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ABSTRACT

Irradiation of mixtures of trioxane and maleic anhydride in various proportions leads to the formation of copolymers at 40°C and 60°C in the liquid state. Copolymers are crystalline with melting points of 170-172°C. Maleic anhydride has an inhibitory effect on radiation induced polymerization in this binary system.

INTRODUCTION

Radiation induced solid state polymerization is well known for ring compounds such as trioxane (1,2), derivatives of oxetanes (3,4) and hexamethylcyclotrisiloxane (5). Trioxane gives crystalline polymers in solid state polymerization. The yields and melting points of polymers depend on the purity and crystal size of trioxane (2). Larger crystals give higher yields and polymers with distinctly higher melting points.

The polymerization of the cyclic ether alone is difficult in the liquid phase. It was stated that radiation induced polymerization of trioxane in a solvent-nonsolvent mixture at 55°C led to the formation of fibrous high molecular weight polyoxymethylene in high yields, if 10-20% maleic anhydride (MAH) was added to the mixture (6).

This report covers our investigations on the radiation induced copolymerization of trioxane and MAH in the molten state and on the structure of the polymeric products.

EXPERIMENTAL

Trioxane was recrystallized from chloroform and dried in vacuo (m.pt. 64°C). MAH was recrystallized twice from diethyl ether and chloroform (m.pt. 54°C).

Mixtures of trioxane and MAH in various proportions were prepared in tubes which were carefully degassed on a high vacuum system. The mixtures in sealed tubes were then melted and shock-cooled in a bath at -15°C. The melting-freezing cycle was performed five times for each sample. Irradiation was performed using gamma rays from a cobalt-60 source. The dose rate was 1.44 kGy/h. Unpolymerized monomers and homopolymer were removed by washing the mixture with methanol and then with cyclohexane.

RESULTS AND DISCUSSION

Trioxane and MAH form a eutectic mixture containing 55 mole% MAH; the eutectic temperature is 9°C (7). To ensure the solid state, the irradiation temperature was first chosen as 0°C. At that temperature, no polymeric product could be obtained, in agreement with a report (8).

The irradiation of a trioxane-MAH mixture containing 0.67 mole fraction of trioxane at 40°C gave polymer. The mixture is liquid at 40°C. It was observed that polymerization proceeds with the precipitation of polymeric product. An IR spectrum of the product showed the incorporation of MAH. The absorption bands between 2900-3000 cm^{-1}, corresponding to C-H stretching of CH_2 groups and those between 1730-1860 cm^{-1}, corresponding to the carbonyl stretching of anhydride groups, match the absorption bands in the same regions of IR spectra of trioxane and MAH homopolymers (9,10). The quantitative evaluation of the IR spectrum using these absorption bands indicated that the copolymer obtained after 103 hours of irradiation at 40°C contained 12 mole% MAH.

The irradiation of mixtures at 40°C in the presence of air gave polymers in higher yields than under high vacuum. Figure 1a shows the change of yield with irradiation time.
The copolymerization of trioxane and MAH in the melt at 60°C was also studied. The yield vs. irradiation time plots for mixtures with trioxane mole fractions of 0.67, 0.80 and 0.86 are shown in Figure 1b. Yields based on the total amount of the monomer mixture become lower as the MAH content of the mixture increases. The inhibitory effect of MAH on trioxane polymerization can also be seen from Table 1. The results of copolymerization at 60°C for 67 hours for mixtures with mole fractions of trioxane ranging from 0.33 to 0.91 are summarized in this Table; the inhibitory effect of MAH is apparent.

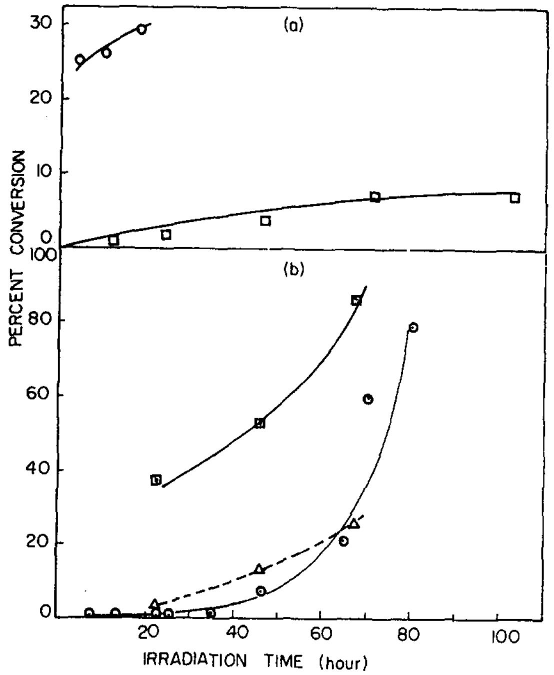

Figure 1. Radiation induced copolymerization of MAH with trioxane. Dose rate = 1.44 kGy/h.
(a) at 40°C, mole fraction of trioxane = 0.67.
○ in the presence of air
□ under high vacuum.
(b) at 60°C under vacuum. Mole fractions of trioxane ○ 0.67; △ 0.80; □ 0.86.

Table 1. Variation of polymer yield and copolymer composition with composition of initial trioxane - maleic anhydride mixture. Irradiation at 60°C for 67 hours to give a total dose of 94.40 kGy.

mole fraction of trioxane in the initial mixture	% yield based on total amount of mixture	mole fraction of maleic anhydride in copolymer
0.33	0.11	not determined
0.50	16.0	not determined
0.67	20.9	0.08 ± 0.02
0.75	29.6	not determined
0.80	25.4	0.20 ± 0.06
0.86	86.0	0.16 ± 0.05
0.91	92.3	0.10 ± 0.03

The compositions of four samples were determined by elemental analysis. The compositions were calculated from both C and H contents and the mean values are shown in Table 1. Results of elemental analyses and IR spectroscopy suggest that MAH is incorporated into the copolymer in relatively small proportions.

The most interesting feature of the synthesis is the crystallinity of the copolymers. Figure 2 shows the photographs of crystals of copolymers taken using a polarizing microscope. Both ring- and radial-type spherulites were observed. The type of spherulite formation seemed to to depend on the rate of supercooling; at low rate, ring-type spherulites formation was observed whereas radial—type resulted from fast supercooling.

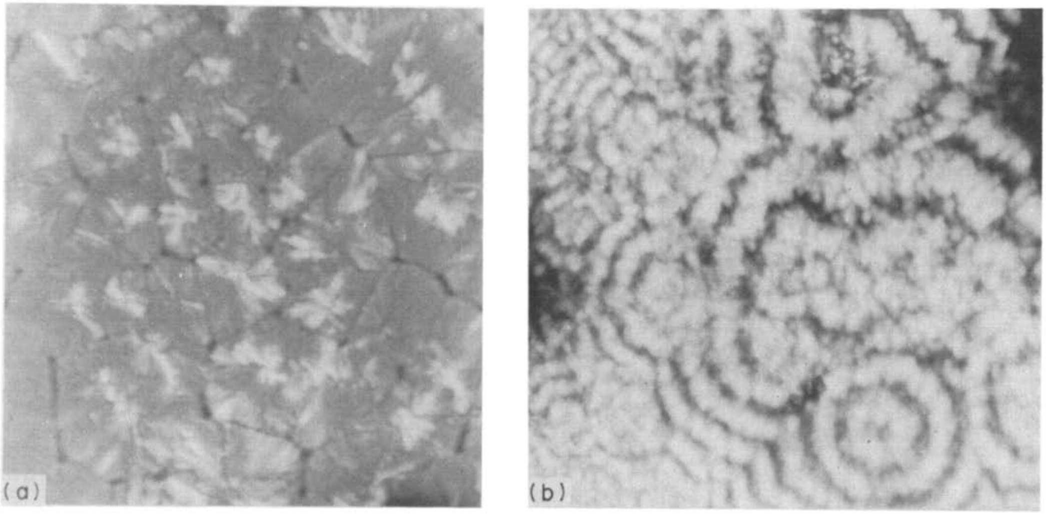

Figure 2. (a) Radial and (b) ring-type spherulites of MAH-trioxane copolymer obtained from a trioxane-MAH mixture containing 0.67 mole fraction of trioxane. (Magnified x100 by a polarizing microscope).

X-ray diffraction studies clearly demonstrated that the crystal structure of copolymers is distinctly different from those for the monomers and polyoxymethylene. Diffractograms vary with monomer composition and irradiation time.

The melting points of copolymers were found as 170-172°C using a hot stage microscope. This value is significantly lower than the reported melting point of about 200°C for oxymethylene homopolymers (11). The copolymers are partially soluble, to about 10%, in hot cyclohexane. They can be dissolved in paraffin at temperatures above 120°C. Melting point, solubility and X-ray diffraction results support the conclusion drawn from IR spectroscopy and elemental analysis studies.

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