

Radiation-induced solid-state copolymerization in binary acrylamide–maleic anhydride systems

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γ -Ray-initiated copolymerization of acrylamide and maleic anhydride was studied in the solid state at 25°C. The polymeric product was found to be free of the homopolymers. The mole fraction of acrylamide in the monomer mixture was varied from 0.33 to 0.91. The copolymerization reached a 'limiting conversion' the value of which was dependent on the composition of the monomer feed. The mole fraction of maleic anhydride in the copolymers did not exceed 0.50 and the compositions of copolymers obtained from acrylamide-rich mixtures were virtually the same as those from the monomer feed compositions. The alternating tendency of maleic anhydride was evidenced by the variation of the copolymer compositions and the consumption rates of the individual monomers.

(Keywords: copolymerization; acrylamide–maleic anhydride systems; solid state)

INTRODUCTION

Radiation-induced solid-state copolymerizations of various vinyl and cyclic monomers were studied and the results published in several papers and review articles^{1,2}. Binary systems involved eutectic mixtures, solid solutions, glassy states, and other molecular complexes. Copolymerization of maleic anhydride (MAH) with acrylamide (AM) in the solid state was first studied by Zurakowska-Orszagh and Wojno³. They reported the eutectic point of the MAH–AM system as 0.67 mole fraction of MAH and 43°C. The absence of homopolymerization and radiolysis of MAH below the eutectic temperature were shown and the effect of cooling rate on conversion was studied by the same authors³. The effects of temperature and physical state of the system on polymer yield and copolymer composition have also been investigated⁴. It was observed that two-phase systems had maximum polymerization conversions above the eutectic composition. The copolymerization took place in the liquid phase and homopolymerization of AM occurred in the solid phase. A marked inhibitory effect of MAH on the polymerization of AM was observed in both solution and liquid melt at 70°C. On the other hand, an acceleration in the polymerization was seen at 47°C in a two-component system containing a liquid and a solid⁴.

In the present study, the relationship of the composition of the monomer mixtures, kinetic behaviour, and the compositions of polymer obtained in the binary AM–MAH system are described.

EXPERIMENTAL

Materials

AM and MAH were recrystallized three times from chloroform.

Preparation of monomer mixtures

The monomer mixtures were prepared in glass ampoules by weighing various compositions, then sealed at a reduced pressure of 10^{-4} mm Hg. The samples were warmed to the liquid state and then shock-cooled by immersing into an ice-salt bath at -15°C .

Irradiation

'In-source' polymerization was performed with a ^{60}Co radiation source at a dose rate of 1.74 kGy h^{-1} . The temperature of the radiation chamber was 25°C .

Isolation of polymer

The samples were placed into a large volume of a 1:1 mixture of methanol–water, which is a solvent for both monomers and AM homopolymer. The insoluble copolymer was then filtered and dried in a vacuum oven to constant weight at room temperature. The addition of a large excess of methanol to the filtrate showed the absence of AM homopolymer.

Composition of polymers

Determination of the composition of the polymer obtained was by elemental analysis using the micro-Kjeldahl method.

Eight samples were analysed by using a Hewlett Packard Model 185 C–H–N Analyzer. A good agreement was obtained between the results of the micro-Kjeldahl method and the C–H–N analysis.

RESULTS AND DISCUSSION

γ -Ray-initiated copolymerization of AM with MAH was carried out in the solid state at 25°C . Polymer yields, based on the total mass of comonomers, for different monomer feeds are shown in *Figure 1* as a function of irradiation time. It must be emphasized that polymeric

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products contained no homopolyacrylamide. Irradiated mixtures containing polymeric product and comonomers were extracted with 1:1 methanol-water which is a known selective solvent for this system³. Homopolyacrylamide could be precipitated out upon addition of large excess (more than 1:10) of methanol.

It is apparent from the per cent conversion *versus* irradiation time plots given in *Figure 1* that the conversion reaches a 'limiting' value in the presence of MAH. The 'limiting conversion' decreases as the MAH content of the mixture increases. AM is known to polymerize completely in the radiation-induced solid-state polymerization systems^{5,6}. The decrease in the slopes of conversion *versus* time plots and in the values of the limiting conversion with the increasing mole fraction of MAH clearly indicates the retarding effect of MAH on the polymerization of AM.

The compositions of copolymers were found to depend mainly on the composition of monomer feed for the systems in which the mole fraction of MAH is less than 0.5. For such mixtures, the compositions of copolymers were virtually the same as the composition of the monomer feed. On the contrary, the MAH-rich monomer feeds

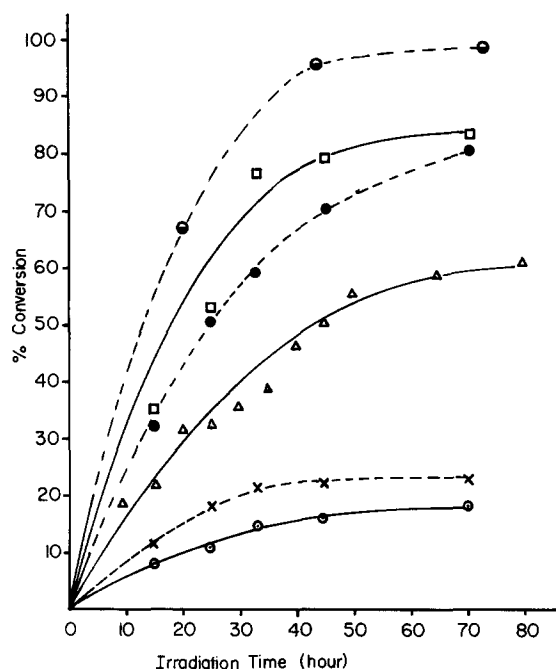


Figure 1 Conversion *versus* irradiation time plot for the solid-state copolymerization of acrylamide and maleic anhydride (temperature 25°C, irradiation dose 1.74 kGy h⁻¹). Mole fraction of AM: (○) 0.20, (×) 0.33, (△) 0.50, (●) 0.67, (□) 0.80 and (◐) 0.91

produced copolymers containing nearly 0.6 mole fraction of AM. This behaviour can be interpreted as MAH not having a tendency towards homopropagation. A similar behaviour was reported for the copolymerization of AM and MAH in the liquid state. The copolymerization reactivity ratios were given as 0.75 for AM and 0.00 for MAH⁴. The AM content of copolymers for all monomer feeds slightly decreased with the irradiation time. The compositions of copolymers at the limiting conversion are given in *Table 1*.

Conversions of the individual monomers were calculated from the yields and compositions using the ratios of polymerized amounts of monomers to their initial amounts. It was observed that the conversions of both AM and MAH reached limiting values. The limiting values for AM and MAH polymerization are also shown in *Table 1*. The conversion of MAH to copolymer was almost complete for the monomer feeds containing less than 50 mol% MAH. None of the copolymers contained more than 50 mol% MAH. It is known that MAH shows very little tendency towards radical homopolymerization^{7,8}. However, it readily reacts with various monomers to give alternating copolymers⁹. The alternating structure of the copolymer was also observed in the radiation-induced copolymerization of MAH and phenanthrene for a fairly wide range of monomer composition¹⁰.

Initial rates of consumption of AM and MAH were estimated from the conversions of individual monomers and are given in *Table 1*. The initial rate of consumption of AM decreases as the MAH content in the monomer mixture increases. This suggests that MAH has an inhibitory effect on the AM polymerization. The initial consumption rate of AM in the mixture containing 0.91 mole fraction of AM was found to be 3.3% h⁻¹. The initial rate of polymerization of AM in the solid state was reported as 12.8% h⁻¹ for which the radiation dose rate and the temperature were very close to those in the present study¹¹. This comparison supports our conclusion of the inhibitory effect of MAH.

The alternating character of the polymerization dictates that the cross-propagation reaction is the dominant reaction in the system. Accordingly, the consumption rate of MAH must exhibit a parallel trend to that of AM. This can also be seen in *Table 1*.

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Table 1 Limiting conversions, copolymer compositions, limiting values of conversion of individual monomers and initial consumption rates of monomers in the solid-state copolymerization of acrylamide and maleic anhydride

Mole fraction of AM in monomer mixture	Limiting conversion (%)	Mole fraction of AM in copolymer	Limiting value of conversion of individual monomers (%)		Initial consumption rate of monomers (% h ⁻¹)	
			AM	MAH	AM	MAH
0.20	19	0.57	60	12	1.6	0.3
0.33	24	0.60	46	14	1.5	0.5
0.50	60	0.52	65	58	1.9	1.0
0.67	82	0.61	73	94	2.1	2.1
0.80	84	0.74	77	~100	2.4	2.7
0.91	99	0.89	96	~100	3.3	4.6

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