

BULK COPOLYMERIZATION OF ACRYLAMIDE AND MALEIC ANHYDRIDE UNDER UV RADIATION

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Bulk copolymerization of acrylamide and maleic anhydride in the presence or absence of benzoyl peroxide was accomplished under UV radiation at a temperature $48 \pm 1^\circ\text{C}$ below the melting points of monomers. The results indicate that the rate of formation of copolymers increases with increasing concentration of acrylamide and benzoyl peroxide enhances the rate of copolymerization appreciably. Monomer reactivity ratios were determined experimentally using the rearranged form of copolymer composition equation. Molecular weight of the product show that the copolymer prepared under uv-irradiation carry small chain ($M_n = 480 - 3555$). All copolymer samples are light yellow solid substances that become light brown at 200°C .

Key words: Viscosity, Jone-Dole parameters, Root equation.

Introduction

The polymerization in solid state has usually been accomplished with the monomers in crystalline state below their melting points, using uv-radiation [1], X-rays [2], high energy electrons [3] and γ -rays [4] as the means of initiation. The most detailed work on the mechanism of solid state polymerization of vinyl monomers reported in the literature has been on salts of acrylic acid and on acrylamide [5]. A free radical mechanism for the acrylamide is supported by the observations that the number of growing polymer chains with the number of free radicals measured by electron spin resonance (esr) spectroscopy [6]. It is observed that when a binary mixture of acrylamide and maleic anhydride is kept under uv-radiation at a temperature below the melting points of reactants after 20 min, the binary mixture becomes viscous fluid and then begins to become solid. It indicates that changes take place as reactants come in liquid form. This paper describes the bulk copolymerization of acrylamide and maleic anhydride under uv-radiation at a temperature ($48 \pm 1^\circ\text{C}$) below the melting points of monomers.

Experimental

Acrylamide (BDH) was recrystallised twice from benzene-acetone mixture. Maleic anhydride (E. Merck) was used without further purification. Reagent grade benzoyl peroxide was twice recrystallised in the chloroform. Solvents were distilled before use.

Procedure of polymerization. All copolymerization reactions were carried out in stoppered glass tubes, 12 cm long and 2 cm internal diameter.

Required quantity of acrylamide, maleic anhydride and

benzoyl peroxide was transferred in reaction tubes and flashed with nitrogen. The reaction tubes thus closed at ground neck with stoppers and kept under uv-radiation for 10 hr at a temperature below the melting point of the monomers ($48 \pm 0^\circ\text{C}$). After the required reaction times the tubes were opened and the product was separated with acetone and dried under vacuum. It was noted that at the early stage of reaction (after 20 min) the binary mixture of monomers become viscous fluids. It is probably either due to interaction between two monomers or temperature at which the reaction accomplished was near below melting point of one of the monomers (52.8°C). During reaction the viscous fluid probably behaves as a homogeneous mixture and the vehicle for movement of monomer's molecules. Further, a set of experiments was performed by keeping the binary mixture of monomer in different monomer ratios under uv-radiation of the temperature below the melting point of monomers. After 20 min the reactions begin to convert into viscous fluid. At this stage the tubes were withdrawn. On dissolving the reactants in acetone the copolymer was found in traces only at 1:1 mole ratios. It shows that weak radicals are formed when the monomers are in crystalline form. The product dissolves in a dilute solution of sodium hydroxide and swells in acetic acid, dimethyl sulfoxide, chloroform, phosphate buffer (pH 8.2). The I.R. spectrum of the product was recorded as 3400-3200 (s), 2500 (w), 1740-1640 (s), 1600 (w), 1440 (w) 1340 (m), 1180 (m), 1100 (w), 970 (w), 860 (w), 640-540 (w) cm^{-1} . This spectrum shows the product to be a copolymer. The viscosity of dilute solutions of products prepared in 0.1% aqueous solution of sodium hydroxide was measured at 30°C using an Ostwald type viscometer. The composition of co-

polymer was determined by analysing the samples for nitrogen. The reaction tubes were irradiated using uv radiation by ultraviolet lamp (with a bulb of 200 watt) of Gallenkamp No.7090.

Results and Discussion

Table 1 and 2 contain the data collected from bulk copolymerization of acrylamide and maleic anhydride under uv-radiation at a temperature ($48 \pm 1^\circ\text{C}$) below the melting point of monomers. The copolymer was characterised by elemental analysis, solubility, IR spectrum and intrinsic viscosity. The product was estimated for nitrogen. The prepared sample of poly (acrylamide) contains 19.42% N whereas the copolymer samples contain 2.06-11.89% N. This difference in percentage of nitrogen suggests the attachment of maleic anhydride molecules in the growing polymer chain of acrylamide for vice versa. The product samples are soluble in dilute aqueous solution of sodium hydroxide whereas the prepared samples of poly acrylamide and poly maleic anhydride get dissolved in water. Furthermore poly acrylamide dissolves in acetic acid whereas the product does not dissolve in acetic acid but it swells in acetic acid. The solubility behaviour of the product supports the results of the analysis of nitrogen ensuring that the product is a copolymer. The IR spectrum of the product was also recorded which supports the assumption

that the product is a copolymer. In the spectrum of the product the absorption bands with maxima at about 2500, 1440, 1340, 1180, 1100 cm^{-1} are characteristic C-C bands whereas the absorption bands at 3400-3200, 1640-1740 cm^{-1} show stretching vibrations.

In Figs. 1 and 2, % conversion is plotted against mole fraction of acrylamide in feed which show that in the binary mixture of acrylamide and maleic anhydride with or without catalyst the rate of formation increases with increasing concentration of acrylamide. The estimation of nitrogen also supports these results (Table 1). The plot of the variation of nitrogen content in the copolymer against the mole ratio of acrylamide to maleic anhydride for all sets of experiments has been shown in Fig. 3. The rate of nitrogen being embedded in the copolymer increases with the increase in acrylamide concentration. These results further show the presence of benzoyl peroxide enhances the rate of copolymerization appreciably.

TABLE 1. BULK COPOLYMERIZATION OF ACRYLAMIDE AND MALEIC ANHYDRIDE WITH AND WITHOUT CATALYST 1% BENZOYL PEROXIDE UNDER UV-IRRADIATION AT A TEMPERATURE (48°C) BELOW THE MELTING POINT OF MONOMERS FOR 10 Hr.

Expt No.	Acrylamide in feed	Maleic anhydride in feed	Yield (g)		%N	
			with catalyst	without catalyst	with catalyst	without catalyst
1.	0.284	3.528	0.510	0.038	5.34	2.06
2.	0.952	2.744	0.850	0.060	6.85	5.62
3.	1.136	2.342	1.070	0.065	8.85	6.64
4.	1.420	1.960	1.210	0.071	9.95	7.46
5.	1.988	1.176	1.215	0.075	11.89	11.10
6.	2.500	-	0.050	traces	19.40	-
7.	-	2.500	traces	traces	-	-

TABLE 2. INTRINSIC VISCOSITY (η) AND NUMBER AVERAGE MOLECULAR WEIGHT (\bar{M}_n) OF ACRYLAMIDE AND MALEIC ANHYDRIDE COPOLYMERS.

Expt. No.	With catalyst $[\eta]$ dl/g	Without catalyst $[\eta]$ dl/g	With catalyst \bar{M}_n	Without catalyst \bar{M}_n
1.	0.07	-	1120	-
2.	0.08	0.040	1300	480
3.	0.11	0.055	2225	780
4.	0.15	0.060	3555	890

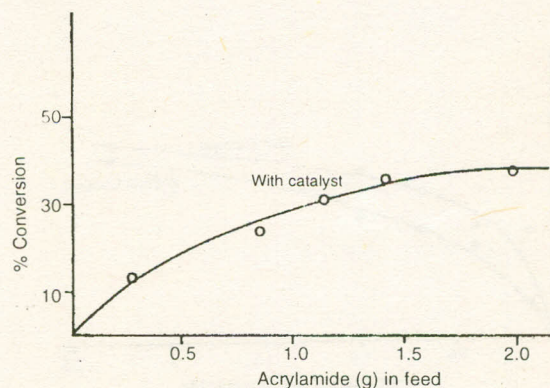


Fig. 1. A plot of % conversion vs mole fraction of acrylamide (in feed) for bulk copolymerization of acrylamide and maleic anhydride with benzoyl peroxide under uv-radiation at a temperature ($48 \pm 1^\circ\text{C}$) below the melting points of both monomers.

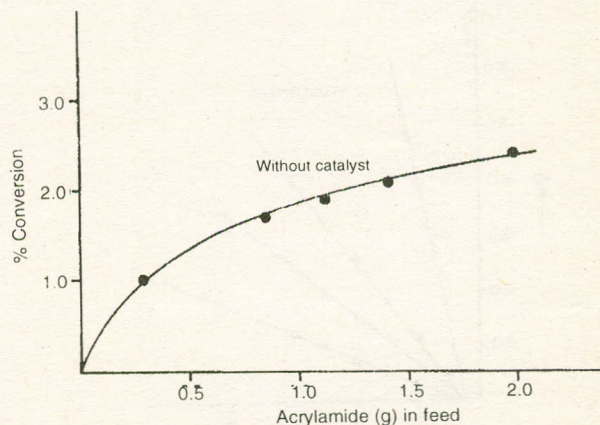


Fig. 2. A plot of % conversion vs mole fraction of acrylamide (in feed) for bulk copolymerization of acrylamide and maleic anhydride without benzoyl peroxide under uv-radiation at a temperature ($48 \pm 1^\circ\text{C}$) below the melting point of both monomers.

The monomer reactivity ratio may be determined by the following rearranged form of copolymer composition equation [7],

$$\gamma_2 = \frac{[M_1]}{[M_2]} \left[\frac{d[M_2]}{d[M_1]} \left\{ 1 + \frac{\gamma_1[M_1]}{[M_2]} \right\} - 1 \right]$$

where $[M_1]$ and $[M_2]$ represent the concentration of unreacted monomers in reaction mixture; $d[M_2]/d[M_1]$ refers to the ratios of two monomers in the increment of copolymer formed; γ_1 and γ_2 are reactivity ratios of monomers. Data for the feed and copolymer compositions for each experiment with a given feed are substituted into equation and γ_2 is plotted as a function of various assumed values of γ_1 . Each experiment yields a straight line and the intersection of the lines for different feeds gives the best values of γ_1 and γ_2 . In Figs.4 and 5, the γ_1 values representing the monomer reactivity ratios of acrylamide have been plotted against the γ_2 values representing those of maleic anhydride. The monomer reactivity ratios in the absence of catalyst calculated from

the plot in Fig.4 are $\gamma_1 = 0.54$ and $\gamma_2 = 0$ whereas monomer reactivity ratios in the presence of benzoyl peroxide calculated from the plot in Fig.5 are $\gamma_1 = 0.55$ and $\gamma_2 = 0$. These values are quite consistent with the values of other maleic anhydride (MA) copolymers such as AN - MA, styrene-MA, methyl acrylate-MA [8]. In the case of monomer pair AN-MA, the reactivity ratios of MA is 0 whereas that of AN is 6. In case of the styrene-MA system the reactivity ratios are 0.01 and 0 respectively while for the system methyl acrylate-MA these are 2.5 and 0 respectively. Since both reactivity ratios are less than unity (γ_1 & $\gamma_2 < 1$) there is a decided tendency to form an alternating copolymer. It is obvious from the reactivity ratio values that acrylamide is more reactive in this binary mixture than maleic anhydride.

When the binary mixture of acrylamide and maleic anhydride in the presence of or absence of benzoyl peroxide are kept under uv-radiation at a temperature below the melting point of any monomer ($48 \pm 1^\circ\text{C}$) the binary mixture of monomers becomes a viscous fluid after 20 min and turns into homogeneous mixture. This change provides a vehicle for the movement of monomer molecules. The monomer molecules absorb a quantum of energy and form free radicals. These radicals will propagate polymer chain. The growing polymer chain of some monomer molecules or different monomer molecules will couple to form a polymer or copolymer. In this polymerization of acrylamide and maleic anhydride the conversion is in traces whereas in the copolymerization of these two monomers it is appreciable (1-2.4%) but very little as shown in Table 1. On the other hand in the presence of benzoyl peroxide, photo dissociation of benzoyl peroxide into phenyl radicals (C_6H_5) as the primary species takes place [9]. These radicals add onto the double bond of monomer molecules to form monomer radicals. Radicals produced by

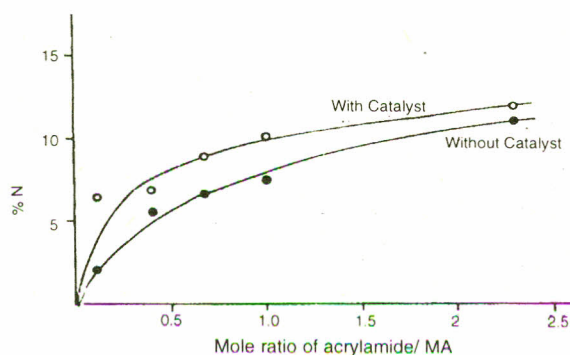


Fig. 3. A plot of % N vs mole ratio of acrylamide MA for the bulk copolymerization of acrylamide and maleic anhydride with or without benzoyl peroxide under uv-radiation at a temperature ($48 \pm 1^\circ\text{C}$) below the melting points of both monomers.

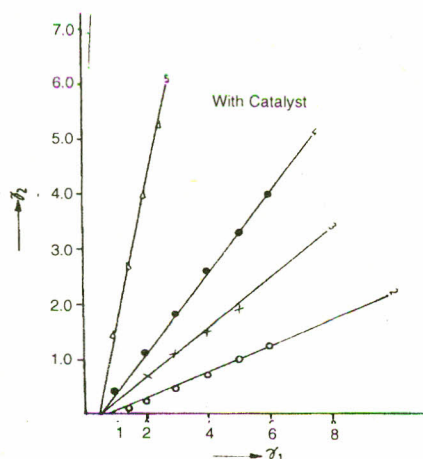


Fig. 4. Mayo and Lewis plot of γ_2 (maleic anhydride) and γ_1 (acrylamide) for the bulk copolymerization of acrylamide and maleic anhydride with catalyst under uv-radiation.

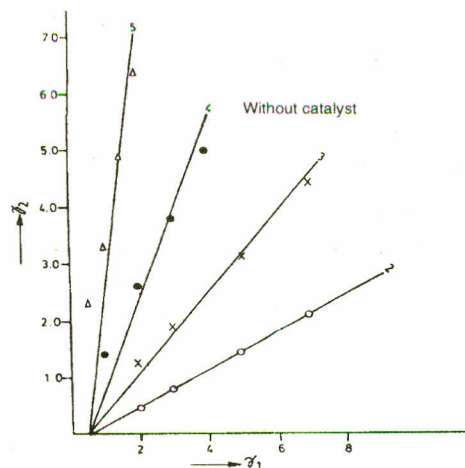


Fig. 5. Mayo and Lewis plot of γ_2 (maleic anhydride) and γ_1 (acrylamide) for the bulk copolymerization of acrylamide and maleic anhydride without catalyst under uv-radiation.

benzoyl peroxide increased the rate of propagation in homopolymerization of acrylamide and copolymerization of acrylamide and maleic anhydride (Table 1). The increase of rate due to benzoyl peroxide also shows that copolymerization takes place by free radical mechanism. Furthermore, many imperfections at the early stage of reaction will be formed which will act as additional centre of initiation [2, 10].

The viscosity of copolymer solutions in 0.1% aqueous solution of NaOH was measured at 30°C. The number average molecular weight (\overline{M}_n) was determined by using the following relationship of intrinsic viscosity (η) and \overline{M}_n [11].

$$[\eta] = 6.8 \times 10^{-4} \overline{M}_n^{0.66}$$

Intrinsic viscosity is obtained by plotting η_{sp}/c against C whereas η_{sp} is specific viscosity and C is the concentration of the solution expressed in dl/g. The intrinsic viscosity of copolymer samples prepared in the presence of benzoyl peroxide was found to be 0.07-0.15 dl/g which gives the molecular weight as 1120-3555 whereas the intrinsic viscosity of copolymer samples prepared in the absence of benzoyl peroxide comes in the range 0.04-0.06 dl/g resulting molecular weight as 480-890. This difference in intrinsic viscosity and \overline{M}_n shows that the monomer combine in different ratios to form copolymers. Furthermore, the copolymer prepared by uv-irradiation carry small chain.

All the copolymer samples are light yellow solid substances which may be powdered on crushing. It dissolves in dilute aqueous solution of NaOH and swells appreciably in acetic acid, DMSO, chloroform, phosphate buffer (pH 8.2). It also swells in toluene, THF and DMF comparatively with small solvent uptake of 5.8, 13 and 7% respectively. When the copolymer sample (expt no. 4) was heated for 4 hr at 100-150°C in air, it appeared to retain its original colour but lost about 13% weight. On further heating the same sample at 200°C becomes light brown and loses a weight 0.6%;

when the temperature reaches to 300°C the copolymer decomposes into a dark brown substance. The decomposed product was mostly insoluble in aqueous solution of sodium hydroxide. The change in colour and insolubility of decomposed product in its solvent might be rather due to intermolecular and intramolecular rearrangement of amide group in the copolymer chain. The colouration [12] of copolymer by heat or radiation is usually attributed to the formation of a long chain conjugated double bonds.

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