Technology

BULK SOLID STATE COPOLYMERIZATION OF ACRYLAMIDE WITH PHTHALIC ANHYDRIDE UV-IRRADIATION AT 60±1°C

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Bulk solid state copolymerization of acrylamide (r_1) with phthalic anhydride (r_2) under UV-irradiation was carried out at 60°C a temperature below the m.p. of reactants. It was observed that yield of the products differed for different sets of experiments but the trend remained same. The monomer reactivity ratios $r_1 = 1.4$ and $r_2 = 0$ were determined graphically by using the arranged form of copolymer composition equation. Molecular weights of the products were determined as 3.0×10^5 - 5.5×10^5. All copolymer samples were off white in colour which became light yellow at 140°C.

Key words: Copolymerization, Acrylamide, Phthalic anhydride, UV-irradiation.

Introduction

Bulk solid state copolymerizations of acrylamide with maleic anhydride under UV-irradiation at a temperature below the melting points of the monomers have been previously reported (Khan and Farooqui 1995). Acrylamide forms copolymers with maleic anhydride and cinnamic acid in all monomeric ratios. Molecular weights of the products show that the copolymer prepared under UV-irradiation carry small chains. When the binary mixture of acrylamide and phthalic anhydride is kept under UV-irradiation at 60°C in the absence of initiator, no change occurs. But in the presence of benzoylperoxide under UV-irradiation at 60°C a polymeric solid material is obtained. On increasing the temperature, highly exothermic reaction takes place. The solid polymeric material is changed into liquid and ultimately a hard solid substance insoluble in alcohol is obtained. Phthalic anhydride and acrylamide get dissolve in alcohol. These observations show the formation of a new material and the need of more detailed study. This paper deals with the bulk copolymerization of binary mixture of phthalic anhydride and acrylamide using benzoyl peroxide as initiator under UV-irradiation at 60°C.

Experimental

Materials. Acrylamide (BDH), and phthalic anhydride (E Merck) were used without further purification. All solvents were used after distillation. Reagents grade benzoyl peroxide (BP) was crystallized in chloroform.

Procedure of copolymerization. All copolymerization reactions were made in stoppered glass tubes as reported elsewhere (Khan and Farooqui 1995). Acrylamide, phthalic an-

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hydride and BP were transferred into the reaction tubes and mixed thoroughly with the help of glass rod. The tubes were flushed with nitrogen and then closed at ground neck with stoppers. Finally, reaction tubes were kept under UV-irradiation (Gallenkamp, Peak output at 365 nm, bulb 125 watt 200/250 V 50Hz supplies, Frequency - 50 cycles sec^{-1}) for certain period at 60±1°C. All reactions were accomplished at a temperature below the melting points of acrylamide and phthalic anhydride. After required reaction time, the tubes were opened and the product was separated with methyl alcohol, dried and weighed. It was noted that the yields of the products for the binary mixture of acrylamide and phthalic anhydride in the same ratio did not repeat but trend remained the same. Similar observations were also found in the copolymerization of acrylamide with cinnamic acid. The yield given in the tables is the average of three experiments of each ratio. The products so obtained were completely dissolved in 1% aqueous NaOH and aqueous acetic acid (1:1 ratio). They partially dissolved in water and dispersed in aqueous HCl (1:1 ratio).

The products samples were estimated for nitrogen by Kjeldahl's method. Viscosity of the dilute solutions of the product prepared in 1% NaOH was measured at 30°C using Ostwald type viscometer. IR spectra (Table 1) were recorded on KBr disc using Perkin Elmer spectrometer; IR spectra showed observations at 3400 (s), 3200-2850 (s), 1700 (s), 1560 (w), 1410 (m), 1285 (m), 1130 (w), 1080 (w), 920 (w), 800 (w), 740 (m) cm^{-1}.

Results and Discussion

The data collected from the free radial solid state copolymerization of binary mixture of acrylamide and phthalic anhy-

dride using BP as initiator under UV-irradiation at a temperature (60°C) below the melting point of monomers is summarized in Tables 1-4. The product was characterized to be copolymer by elemental analysis, solubility, IR spectral studies and viscosity of dilute solutions etc. the elemental analysis of the product and the prepared sample of polyacrylamide show that twenty five samples of the product (Table 1) contain 8.46% to 13.9% N whereas the polyacrylamide contains 19.4% nitrogen. This difference in percentage of nitrogen may be due to the attachment of phthalic anhydride units to the growing polymer chain of acrylamide. This suggests that the products are copolymers. The solubility of the products was also examined in different solvents. Acrylamide and phthalic anhydride dissolved in acetone and alcohol whereas the products were insoluble in these solvents. It supports the results of estimation of nitrogen. The spectrum of the products was also recorded (Table 1). It is observed that the spectra of the polymer are much simpler than those of their monomers. The degree of freedom of vibration is restricted in polymer and copolymer, but the general pattern of the spectra of polymer and monomer does not change. As a rule the spectra of polymer and copolymer should show the addition on commutative behavior of their monomers. The spectrum of the products shows less bands than those of acrylamide and phthalic anhydride. The spectra of any product show the absorption bands at 3400, 3200-2850, 1560, 1410, 1285, 1080, 800 and 740 cm^{-1}, characteristic C-C bands whereas the absorption bands at 3400 and 1700 cm^{-1} show stretching vibration indicating the coupling phthalic anhydride and acrylamide. Hence the products so formed are copolymers.

The effects of monomer concentration, time, temperature and initiator concentration on the formation of copolymer are determined and summarized in Tables 1-4. In Fig 1, conversion (mole%) is plotted against monomer (mole%) in feed which shows that in the binary mixture of acrylamide and phthalic anhydride, the rate of formation of growing polymer chain of polyacrylamide increases with increase in concentration of acrylamide but at 76 mole % it drops (43 mole %) and then increases (Fig 1). On the other hand the rate of entering of phthalic anhydride molecular unit in the polymer chain increases with increase in concentration (very little) of phthalic anhydride in feed and becomes steady and then ultimately decreases at 89.3:10.7 mole %. It is also evident from the results (Table 1) that the rate of formation of copolymer increases with increase in concentration of acrylamide and then starts decreasing at 49.295 m mole. It shows the participation of phthalic anhydride in the formation of copolymer.
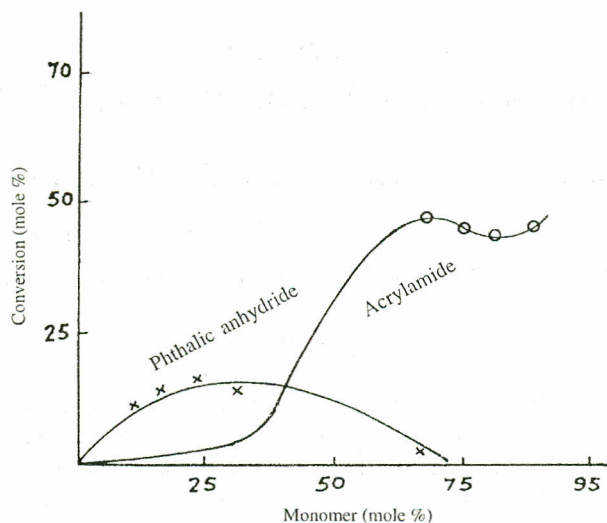

Fig 1. A plot showing % conversion vs monomer (mole %) for bulk solid state copolymerization of acrylamide with phthalic anhydride under UV-irradiation at 60°C in the presence of benzoyl peroxide.

In the experimental part, it is noted that the conversion of reactants does not repeat. It might be due to the monomers being in solid state. The movement of monomer molecules under UV-irradiation does not remain uniform and becomes low which affect the formation and coupling of growing polymer chain. In brief, when the binary mixture of acrylamide and phthalic anhydride in the presence of BP were kept under UV-irradiation (a bulb of 125 watt) at a temperature below the melting point of any reactant, radicals are formed in two ways, one is the decomposition of BP into free radicals which hit the double bond of monomers molecules to form monomer radicals. Lattice defects and crystal boundaries (imperfections) is the other source which produces monomer radicals. Beside these many imperfections will be formed in the vicinity of the growing polymer chain and these may act as additional centre of initiation so that reaction will develop autocatalytically. Radicals produced by initiator increased the rate of propagation in homopolymerization of acrylamide and copolymerization of acrylamide and phthalic anhydride. On the other hand phthalic anhydride does not homopolymerize but helps in terminating growing polymer chain of polyacrylamide and considerable units of phtalic anhydride enter in the growing polymer chain of acrylamide as indicated from Table 1 (d[M$_2$]). Furthermore, with the decrement of phthalic anhydride in feed, molecular weight also gets decreased from 5.5 x 10^{-5} to 3 x 10^{-5}. It shows that coupling of phthalic anhydride unit molecules take place with growing polymer chain of polyacrylamide. It is also supported from elemental analysis and reactivity ratios of these monomers, but the kinetics is not clear. However a possible structure may be as follows:
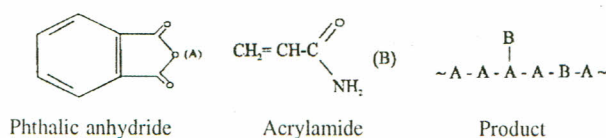
Phthalic anhydride   Acrylamide   Product

Table 2 includes the results of effect of concentration of initiator on the rate of formation of copolymer. The rate of formation of copolymer increases with the increase in concentration of BP. Percentage of nitrogen also indicated that with increase in concentration of BP, the rate of entering of both the monomers unit in polymer chain increased as indicated from the variation in % yield of product (Table 3). It is due to the presence of large number of free radicals in the vicinity of both the monomers molecules at higher concentration of initiator. Table 3 includes the results of effect of time on the rate of copolymer formation. Polymerization starts after 12 min but at this stage a very small amount of product is obtained which is soluble in water and acetic acid. It shows that only acrylamide is polymerized. The binary mixture of

Table 1

Comparative statement of IR spectra of acrylamide, phthalic anhydride and product, strong (s), medium (m) and weak (w)

Acrylamide cm^{-1} wave number	Phthalic anhydride cm^{-1} wave number	Product cm^{-1} wave number
3335-3125(s)	3300(s)	3400(s)
1670(s)	1710(s)	3200(s)
1430(m)	1600(w)	1700(s)
1330(w)	1470(m)	1560(w)
1125(m)	1350(m)	1410(m)
980(w)	1250(m)	1130(w)
720(w)	1162(m)	1080(w)
	1110(w)	920(w)
--	--	800(w)
--	--	740(m)

acrylamide and phthalic anhydride under UV-irradiation for 13-15 min gives a product which is soluble in 1% NaOH indicating the interaction of the two monomers. Hence induction period is probably 13-14 min. The results indicate that rate of polymerization increases with the increase in time. Due to increment in time, most of the free radicals are utilized in the formation of polymer.

The results of the effects of the temperature on conversion (Table 4) show that when temperature rises, conversion enhances. It is also observed that just above 60°C, highly exothermic reaction takes place, the reactants first melt and become liquid and then the whole mass converts into hard solid material. Nitrogen analysis of these samples products also show that the rate of entering of acrylamide monomer unit in the growing polymer chain increases with rise in temperature whereas the rate of entering of phthalic anhydride monomer unit does not change. It may be concluded that not only free radicals are formed due to decomposition of BP but radical formation also takes place thermally which enhances the rate of entering of monomer units in the copolymer chain. Furthermore, at the initial stage of reaction homopolymerization of acrylamide also takes place and a mixture of homopolymer and copolymer is obtained, this is evident from the variation % N in products samples.

Monomer reactivity ratios of acrylamide (r_1) and phthalic anhydride (r_2) are determined by using the following rearranged form of copolymer composition equation (Mayo and Lewis 1994).

$$r_2 = \frac{[M_1]}{[M_2]} \left[\frac{d[M_2]}{d[M_1]} \left(1 + \frac{r_1 [M_1]}{[M_2]} - 1 \right) \right]$$

where $[M_1]$ and $[M_2]$ are the concentrations of the unreacted monomers in the binary reaction mixture, $d[M_2]/d[M_1]$

Table 2

Bulk solid state copolymerization of acrylamide (M_1) with phthalic anhydride (M_2) using 1% benzoyl peroxide as initiator at 60 ± 1°C under UV-irradiation

S. No.	Monomers in feed		Copolymer obtained %	Elemental analysis % N	Monomer in polymer		[η]	Mn x 10^{-5}
	Acrylamide [M$_1$]m mole	Phthalic anhydride [M$_2$] m mole			Acrylamide d[M$_1$]m mole	Phthalic anhydride [M$_2$]m mole		
1.	14.10	27.30	3.2	9.67	1.10	0.55	--	--
2.	28.17	20.27	45.0	11.33	18.22	6.47	4.2	5.5
3.	35.21	16.89	53.8	12.71	24.42	6.46	3.4	4.0
4.	42.25	13.51	63.6	13.90	31.60	6.34	3.3	3.8
5.	49.30	10.13	57.1	10.62	21.62	8.85	3.2	3.7
6.	56.34	6.76	34.6	13.6	16.76	3.65	2.8	3.0

represents the ratio of the two monomers in the increment of the copolymer formed. Data for the feed and copolymer composition for each experiment with a given feed is substituted in above equation. The r_2 values are plotted as a function of various assumed values of r_1. Each experiment gives a straight line and the interaction of these lines for different feeds gives the best values of r_1 and r_2. In Fig 2, r_2 is plotted against r_1 for four experiments shown in Table 1. The values of monomer reactivity ratios obtained from this plot are r_1=1.4 and r_2=0. Since one reactivity ratio is greater than unity (r_1=1.4) and other less than unity (r_2=0), the copolymerization system of acrylamide and phthalic anhydride is nonazeotrapic (Bamford *et al* 1958). Acrylamide is more reactive than the phthalic anhydride towards both propagating species. The product will contain large proportions of the more reactive monomer in random placement. Hence polymerization of acrylamide with phthalic anhydride gives initial product which is virtually pure
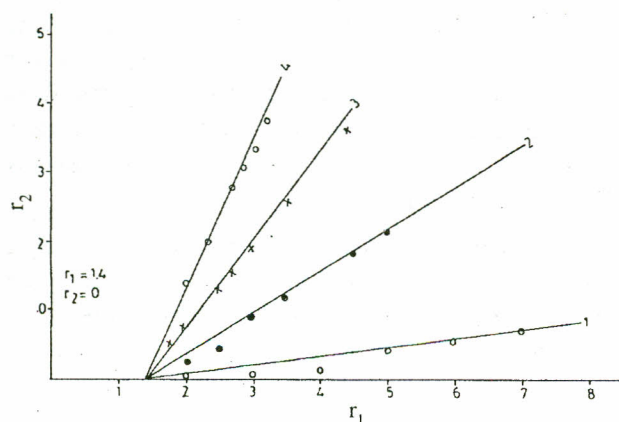
polyacrylamide. When most of the acrylamide monomer is consumed, the coupling of growing polymer chains of both acrylamide and phthalic anhydride takes place to form copolymer. Similar behaviour is observed in the solid state copolymerization of acrylamide with maleic anhydride (Khan and Farooqui 1995) and cinnamic acid. Similar other examples are also found in the literature like copolymerization of acrylonitrile with crotonic acid (Lodhi and Khan 1971) or tetrachloroethylene (Mullik and Khan 1970). The reactivity ratios of cinnamic acid, crotonic acid and tetrachloroethylene are zero. These monomers do not homopolymerize but help in copolymerization. The reactivity ratio of acrylamide towards maelic anhydride is 0.55 and towards cinnamic acid is 1.6 whereas reactivity ratios of crotonic acid and tetrachloroethylene towards acrylonitrile are 14 and 456 respectively.

When the binary mixture of the monomers is kept under UV-irradiation at 60°C, probably the imperfections in the monomer crystals or lattice cause the formation of activated centres on the monomers molecules. The monomer molecules

Fig 2. Mayo and Lewis plot of r_1 (acrylamide) and r_2 (phtalic anhydride) for bulk solid state copolymerization of acrylamide with phthalic anhydride under UV-irradiation at 60±1°C in the presence of benzoylperoxide.

Table 3
Effect of Initiator on the bulk solid state copolymerization of acrylamide (35.2112m mole) with phthalic anhydride (16.8918m mole) at 60°C for 2 h under UV-irradiation

S. No.	Benzoyl peroxide %	Yield analysis	Elemental %N
7.	0.25	2.2	1.00
8.	0.50	4.6	10.04
9.	1.00	11.8	10.25
10.	1.50	20.5	10.60
11.	2.00	26.2	10.98
12.	2.25	33.0	11.27
13.	2.50	53.2	13.60

Table 4
Effect of time on the bulk solid state copolymerization of acrylamide (35.2112m mole) with phthalic anhydride (16.8918m mole) using 1% benzoyl peroxide at 60°C for 2 h under UV-irradiation

S. No.	Time (min)	Yield	Elemental analysis %N
14.	15	2.50	10.20
15.	30	4.00	10.80
16.	60	7.40	6.97
17.	120	11.80	11.50
18.	180	53.80	12.71
19.	240	91.40	8.48

Table 5
Effect of temperature on the bulk solid state copolymerization of acrylamide (35.2112 m mole) with phthalic anhydride (16.8918 m mole) using 1% benzoyl peroxide for 3h under UV-irradiation

S. No.	Temperature °C	Yield	Elemental analysis %N
20	40	5.7	6.02
21	45	6.9	8.46
22	50	8.0	10.25
23	55	9.0	11.62
24	57	10.2	12.18
25	60	53.8	12.71

in the vicinity of imperfections absorb a quantum of energy with a second monomer molecules to form a diradical (Encyclopedia 1967). The radicals so formed will propagate the polymer chain by striking the double bond of the monomer molecules situated in their vicinity. The growing polymer chain of same monomer molecules or different monomer molecules will couple to form a long chain polymer or copolymer. In the polymerization of acrylamide the conversion is obtained in traces and phthalic anhydride does not homopolymerize whereas binary mixture of acrylamide and phthalic anhydride under UV-irradiation gives about 2% yield. On the other hand in the presence of BP radicals are formed in two ways. One is the decomposition of BP into free radicals by ultraviolet radiation. Lattice defects and crystal imperfections are the other sources which produce monomer radicals. Beside this many imperfections will be formed in the vicinity of the growing polymer chain and these may act as additional centre of initiation as that reaction will develop autocatalytically. Radicals produced by BP increased the rate of propagation in homopolymerization of acrylamide and copolymerization as well (Bamford *et al* 1963).

The number average molecular weight $\overline{M}_n$ of the products was determined by the following intrinsic viscosity [η] and molecular weight relationship (Colloinson *et al* 1957).

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

Viscosity of dilute solutions were measured in 1% aqueous NaOH at 30°C by using Ostwalds type viscometer. The intrinsic viscosity of products samples was found to be 2.8-4.3 dl g^{-1} which gives the molecular weights as 3.0×10^5 -5.5×10^5. The molecular weight increased with the increase in concentration of phthalic anhydride molecules in feed (Table 1). This shows the entering of the phthalic anhydride molecules in the growing polymer chain of acrylamide. Phthalic anhydride forms copolymer with acrylamide of higher molecular weight (3.0×10^5 - 5.5×10^5) as compared with maleic anhydride (4.8×10^2 -3.6×10^2) and cinnamic acid (1.1×10^4 -7.3×10^4). This also supports the coupling of phthalic anhydride molecular unit in the growing polymer chain of acrylamide.

All copolymers mentioned in Tables 1-4 are off white in colour. When kept in 100°C in air for 1.5 h, the product (sample no. 2) retains its original colour with a loss in weight about 12.4%. When further kept at 140°C for ! h the copolymer begins to convert into light yellow with a loss in weight about 11%. At 170°C the copolymer begins to convert into material of dark yellow colour and after one hour about 6.6% loss in weight is observed. Finally the product sample was found to decompose into reddish brown colour at 200°C. The decomposed product becomes insoluble in 1% NaOH. The change in colour and insolubility of decomposed product in its solvent might be probably due to the crosslinking of degraded product and the intermolecular and intramolecular rearrangements of amide group in the copolymer chain. Moreover in the presence of air, the copolymer might have undergone chain scission and oxidation reactions (Jellinek 1962). Furthermore, the colouration of copolymer into reddish brown by heat is usually attributed to the formation of a long chain conjugated double bond.

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