BULK COPOLYMERIZATION OF ACRYLAMIDE AND CROTONIC ACID

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Bulk copolymerization of acrylamide and crotonic acid has been carried out. The results indicate that both monomers form copolymer in all monomeric ratios. The induction period is 40 minutes. The increasing concentration of acrylamide and benzoyl peroxide and increase in temperature and time enhance the rate of formation of copolymer. Monomer reactivity ratios of acrylamide and crotonic acid are determined experimentally using the rearranged form of copolymer composition equation. Molecular weight of the copolymer samples show that the copolymer of low molecular weight may be prepared at high temperature. All copolymer samples are white crystalline substances that become light brown at 200-210°C and burn when temperature reaches to 270°C.

Key words: UV-radiation, Intrinsic viscosity, Conjugated double bands.

Introduction

A number of monomers have been polymerized in the soil state (Haward 1948). These reactions have usually been carried out with the monomer in its crystalline form below its melting point using atomic radiation as the means of initiation. Some of them proceed by a radical mechanism while others proceed by an ionic mechanism. The crystal lattice structure plays an important role in such polymerizations (Morawetz 1966). In our earlier paper, the bulk copolymerization of acrylamide and maleic anhydride under uv-radiation at a temperature (48°C) below the melting points of monomers without using any solvents was reported (Khan and Farooqi 1995).It was observed that when the binary mixture of acrylamide and maleic anhydride was kept under uv-radiation at a temperature below the m.p. of the reactants, after 20 minutes a fluidy material was obtained which provides vehicle for movement of monomers molecules resulting free radicals for proceeding polymerization reaction. But a mixture of acrylamide and crotonic acid in the presence of benzoyl peroxide at room temperature (27-28°C) begins to convert into fluid (after 15 minutes) which ultimately resulted into a solid material. This paper deals with bulk copolymerization of acrylamide and crotonic acid using benzoyl peroxide as intiator at 25-50°C.

Experimental

Material. Crotonic acid (E.Merck) and acrylamide (BDH) were used without further purification. Benzoyl peroxide of reagent grade was recrystallized in chloroform. Organic solvents were distilled before use.

Process of polymerization. All polymerization reactions were carried out in stoppered glass tubes 12 cm long having 2.5cm internal diameter. A weight amount of crotonic acid,

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acrylamide and benzoyl peroxide were transferred in reaction tubes and flashed with nitrogen. The reaction tubes were kept in water bath maintained at required temperature. After required reaction time the tubes were opened, the product was separated with acetone and dried under vaccum. It was noted that after 15 minutes at 27-28°C, the reactants began to convert into viscous fluid and thus after required reaction time a white solid material was obtained which soluble in water, is 1% NaOH, acetic acid phosphate buffer (pH 8.25) DMSO. It is insoluble in acetone.

I. R. Spectrum. The Spectrum of the product was recorded in KBr as shown in fig. 1. Stretching vibration at 3400-2900 and 1710-1590 cm⁻¹ shows the product to be a copolymer.

Viscometry. Viscosity of dilute solutions of the product samples were measured at 25°C using water as a solvent. Intrinsic viscosity in dl/g was determined from these values.

Elemental analysis. The composition of the product samples was determined, by analysing the samples for nitrogen by kjeldahl's method.

Results and Discussion

The results of the bulk copolymerization of acrylamide and crotonic acid using benzoyl peroxide as initiator are summarized in Tables 1-4. The copolymer was identified by means of elemental analysis, solubility, I.R. spectrum and viscosity of dilute solutions of the product samples. The prepared sample of poly (acrylamide) contains 19.38% nitrogen while the product samples contain 11.05-16.6% N. This variation of percentage of nitrogen suggests that both monomers participated in the reaction. It is also so because both monomers may be polymerised with free radicals initiator and the growing polymer chains of these monomers couple to produce a new prod-

uct. The solubility of the product was also tested in different solvents. Crotonic acid and acrylamide dissolve in alcohol whereas the product does not dissolve in alcohol but it swells in alcohol with solvent uptake 13.18%. The solubility behaviour of the product supports the results of the analysis of nitrogen ensuring that the product is a copolymer. The copolymer also dissolves in phosphate buffer, DMSO, Acetic acid, dilute aqueous solution of NaoH and water. It also swells in different organic solvents with little solvent uptake like DMF (1.57%), THF (10.54%), toluene (5.36%), chloroform (2.47%), n-Hexane (7.58%), Diethyl ether (14.83%), ethyl acetate (5.23%) etc and insoluble in acetone. I.R. spectral studies have also been undertaken which provides a concrete evidence that the

product is a copolymer. In the spectrum (Fig.1) of the product the absorption bands with maxima at about 1440, 1300, 1200, 110, 960, 500 cm^{-1} are characteristics C-c bands whereas the absorption bands at 3400-2900 and 1700-1590 cm^{-1} show stretching vibrations due to amide group of acrylamide whereas the wide absorption bands at 1710-1590 cm^{-1} with two shoulders are due to acid carbonyl of crotonic acid and amide carbonyl of acrylamide.

In Fig.2 conversion is plotted against acrylamide (mole) in feed which indicates that the rate of formation of copolymer increases with increase in concentration of acrylamide. The result of the estimation of nitrogen also supports these results (Table 1). In another plot (Fig 3), variation of nitrogen

Table 1
Bulk copolymerization of acrylamide and crotonic acid using 0.5% benzoyl peroxide as catalyst at 25°C for 48 h

Sample No.	Acrylamide in feed, mole	Crotonic acid in feed mole	yield g	Elemental analysis %N	Intrinsic viscosity [η] dl/g	Mn̄
1.	0.0141	0.0465	0.84	12.85	0.92	55510
2.	0.0282	0.0349	1.59	13.20	0.88	51885
3.	0.0352	0.0291	2.81	15.13	0.80	44915
4.	0.0422	0.0233	2.50	16.60	0.87	51000

Table 2
Effect of catalyst on the bulk copolymerization of acrylamide (0.0352 mole) and crotonic acid (0.0291 mole) at 28°C for 24 h

Sample No.	Benzoyl peroxide %	yield g	Elemental analysis %N	Intrinsic viscosity [η] dl/g	Mn̄
5.	0.25	1.20	11.05	0.80	44915
6.	0.50	2.08	12.94	0.79	36688
7.	1.00	3.25	12.05	0.70	36688
8.	1.50	3.82	12.25	0.64	32030
9.	2.00	4.24	11.62	0.74	39911

Table 3
Effect of time on the bulk copolymerization of acrylamide (0.0282 mole) and crotonic acid (0.0233 mole) using 1% benzoyl peroxide as catalyst at 30°C

Sample No.	Time (h) %	yield g	Elemental analysis %N	Intrinsic viscosity [η] dl/g	Mn̄
10.	0.50	Traces	-	-	-
11.	0.75	0.0284	11.10	-	-
12.	1.00	0.1012	13.95	-	-
13.	2.00	0.3200	12.33	0.46	19420
14.	3.00	0.9800	13.36	0.53	24070
15.	4.00	1.1236	15.50	0.74	39910
16.	6.00	1.2700	12.66	0.90	53690
17.	24.00	2.9000	12.02	0.62	30525

content in the copolymer against the mole ratio of acrylamide to crotonic acid has been shown. The rate of nitrogen being embedded in the copolymer increasé with the increase in acrylamide concentration. Figs 4 and 5 indicate that rate of formation of copolymer increases with increase in concentration of benzoyl peroxide and increase in temperatures. The rate of formation of free radicals enhances with the increase in temperature. In Fig. 6 conversion is plotted against time which indicates that after an induction period of about 40 minutes, the polymerization begins and rate of formation increases with time.

As the monomers got converted into viscous fluid forming homogenous mixture, the monomer reactivity ratios of acrylamide (r_1) and crotonic acid (r_2) may be determined by the following rearranged form of copolymer composition equation (Mayo and Lewis 1944). The absorption bands at 3400-2900 cm^{-1} are

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

where $[M_1]$ and $[M_2]$ represent the concentration of unreacted monomers in the reaction mixture, $d[M_2]/d[M_1]$ refers to the ratio of the two monomers in the increment of copolymer formed. Data for the feed and copolymer compositions for each experiment with a given feed are substituted into above equation and r_2 is plotted as a function of various assumed values of r_1. Each experiment yields a straight line and the interaction of the lines for different feeds gives the best values of r_1 and r_2. In Fig.6, r_1 values are plotted against r_2 values. The interaction of the different lines of the plot gives $r_1 = 4.4$ and f$r_2 = 0.7$. Since one reactivity ratio is greaer than unity $(r_1 = 4.4)$ and the other is less than unity $(r_2 = 0.7)$, the present copolymer system is nonazeotropic. As both r_1 and 1 $1/r_2$ are greater than unity, both radicals prefer the same monomer i.e., acrylamide. The rate of polymerization of acrylamide increases with increasing concentration of monomer. Estimation of the product shows that % N in the copolymer chain decreases with an increases in the concentration of crotonic acid. All these evidences indicate that acrylamide is more reactive than

Table 4

Effect of temperature on the bulk copolymerization of acrylamide (0.0282 mole) and crotonic acid (0.0233 mole) using 1% benzoyl peroxide as catalyst for 6 h

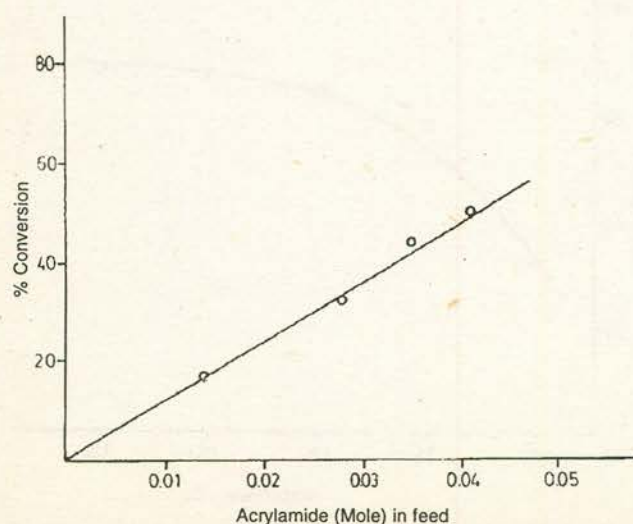| Sample No.	Temperature %	yield g	Elemental analysis %N	Intrinsic viscosity $[\eta]$ dl/g	Mn
18.	30	1.27	12.66	0.62	30526
19.	35	2.33	12.77	0.82	46628
20.	40	2.53	13.15	0.52	23385
21.	45	2.70	13.96	0.28	9154
22.	50	2.72	14.300	0.27	8663

Fig 1. A plot of % conversion vs acrylamide (mole) in feed for bulk copolymerization of acrylamide & crotonic acid using 0.5% benzoyl peroxide as catalyst at 25°C for 48 h.
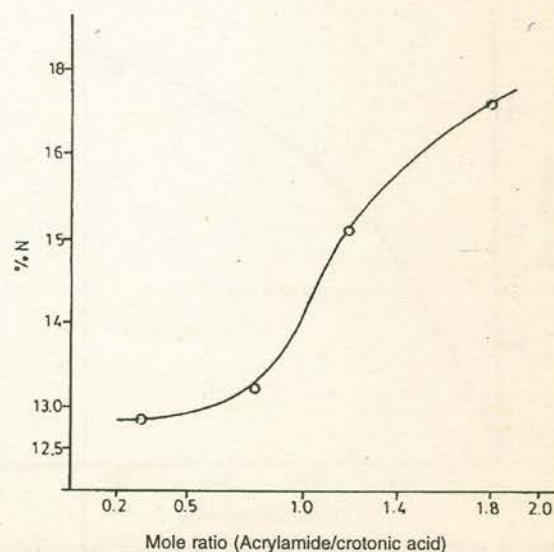

Fig 2. A plot of % N vs mole ratio of acrylamide/crotonic acid for the bulk copolymerization of acrylamide and crotonic acid using 0.5% benzoyl peroxide as catalyst at 25°C for 48 h.

crotonic acid. At the initial stages, homopolymerization of acrylamide takes place and thus acrylamide and crotonic acid are copolymerized. In the case of copolymerization of acrylamide and maleic anhydride (Khan and Farooqui 1995) the reactivity ratio values of maleic anhydride (0) is greater than reactivity value of acrylamide (0.53) wherea the reactivity ratios of acrylamide and crotonic acid as discussed above are respectively 4.4 and 0.7. These values clearly indicate that crotonic acid (0.7) is more reactive thanmaleic anhydride (0) towards acrylamide.

When the binary mixture of acrylamide and crotonic acid (1:1) in the presence of benzoyl peroxide is kept at 4°C in an atmosphere of nitrogen, no change occurs. The mixture gets dissolved in acetons indicating that reaction between the monomer does not take place. but when temperature reaches to 27-28°C, the mixture begins to turn into fluid and converts into homogenous mixture. This thermal change provides a vehicle for the movement of reactant molecules. This change may be due to the interaction of monomers and initiator molecules which causes the formation of free radicals thermally. which

propagate polymers chains. The growing polymer chains of monomer molecules couple to form copolymer. Increase in concentration of acrylamide, benzoyl peroxide, temperature and time enhances the rate of propagation of growing polymer chain. The increase in rate due to temperature and initiator indicates that polymerization takes place thermally by free radical mechanism. At the very early stage of reaction (after 50 mintues), traces of polymer are seen (when dissolved in acetone). With the increase of time, propagation of polymer chain becomes rapid. Further due to increase in acrylamide concentration, rate of formation gets increased indicaing that at the early stage of reaction, homopolymerization of acrylamide takes place. This is supported by the elemental analysis of the product.

The number average molecular weight (Mn) of copolymer samples was determined by the following relationship (Colloinson et al 1957).

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

Where [η] is the intrinsic viscosity of copolymer solution pre-

Table 5
Physical parameter of acrylamide-corotonic acid copolymer

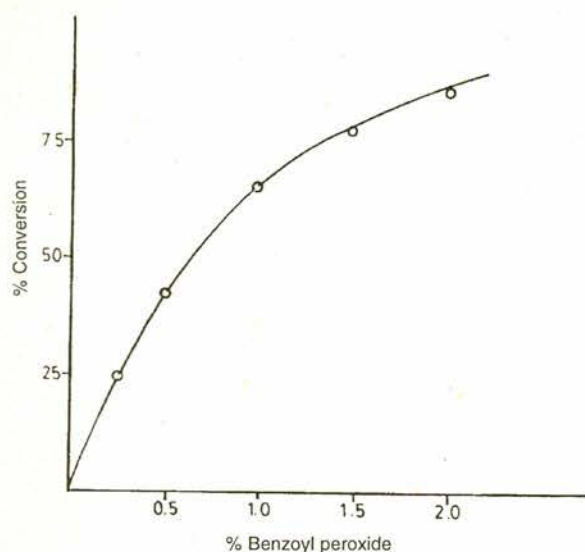| Sample No.	[η] dl/g	Mn̄	Probable number of monomer units in copolymer (Pn)	
			Acrylamide	Crotonic acid
1.	0.92	55510	519	217
2.	0.88	51885	497	193
3.	0.80	44915	493	115
4.	0.87	51000	615	85

Fig 3. Effect of catalyst on the bulk copolymerization of acrylamide (0.0352 mole) and crotonic acid (0.029 mole) at 28°C for 24 h.
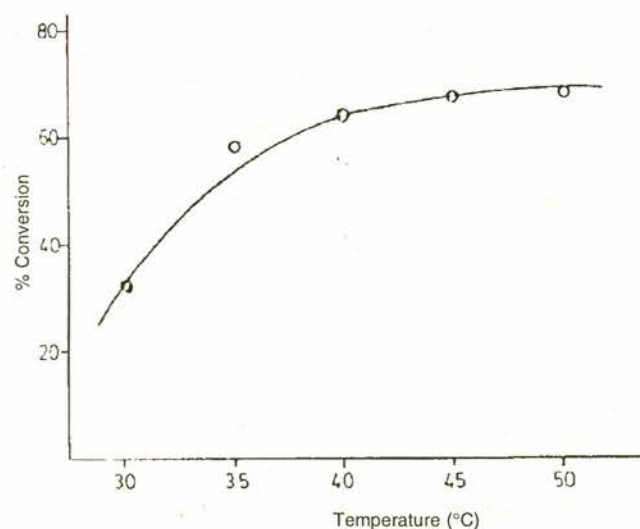

Fig 4. Effect of temperature on the bulk copolymerization of acrylamide (0.0282 mole) and crotonic acid (0.0233 mole) using 1% benzoyl peroixde as catalyst at 30°C.
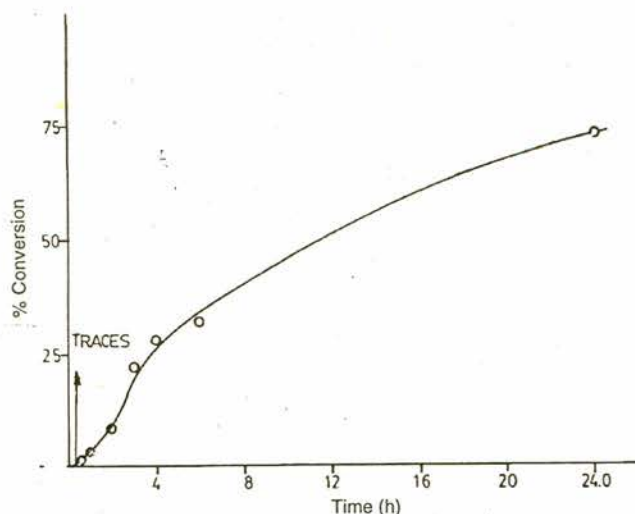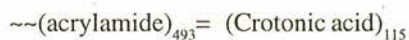
Fig 5 Effect of time on the bulk copolymerization of acrylamide (0.0282 mole) and crotonic acid (0.0233 mole) using 1% benzoyl peroxide as catalyst for 6 h.

Fig 6. Mayo & lewis plot of r_2 (crotonic acid) and r_1 (acrylamide) for the bulk copolymerization of acrylamide & crotonic acid using 0.5% benzoyl peroxide as catalyst at 25°C for 48 h.

pared in water and is obtained by plotting $n_{sp/c}$ against C. Here $n_{sp/c}$ is the specific viscosity and C is the concentration of polymer solution experessed in dl/g. The intrinsic viscosity of 22 copolymer samples is found to be 0.27-0. 92 dl/g which gives molecular weight as 8663-55509. From these results, it may be concluded that at high temperature, the copolymer of comparatively lower molecular weight may be obtained (Table 4). Table 1 indicates that with increase in acrylamide concentration, of nitrogen contents i.e. acrylamide is increasing but molecular weight gets decreased. Keeping in view, the elemental analysis and composition of monomers in copolymer, degree of polymerization of acrylamide and crotonic acid has been calculated. At a feed of 54.7 mole % acrylamide and 45.3 mole % crotonic acid, the copolymer of the following type may be prepared.

$$\sim\sim(\text{acrylamide})_{493} = (\text{Crotonic acid})_{115}$$

As the system is nonazeotropic, the number of repeating units of acrylamide are more than that of crotonic acid. It is also because r1 and 1 l/r$_2$ are both greater than unity.

All copolymer samples are white crystalline substances. When the copolymer sample (expt. No.2) was heated for 1½ hr at 65-100°C in air, it appeared to retain its original colour but it lost about 8% weight. On further heating the same sample at 110-180°C it converted into light yellow with a loss inweight of 12%. At 200-210°C, the same sample softened and changed into light brown. When temperature reaches to 270°C, the sample burnt. The decomposed product (180-200°C) became
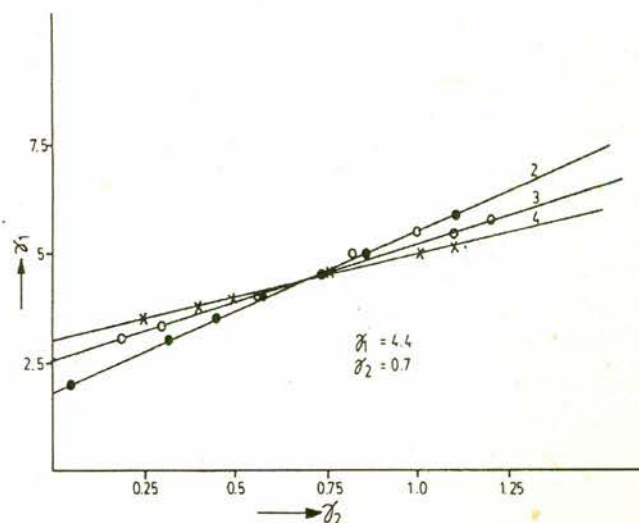
insoluble in its solvents. This change was probably due to intermolecular & intramolecular rearrangements of amide group in the copolymer chain (Khan and Farooq 1998). The colouration of copolymer by heat or radiation is usually attributed to the formation of long chain conjugated double bonds (Jellinek 1962; Mullik and Khan 1970).

Conclusion

The polymerization of scrylamide and crotonic acid in solid state is free radical in nature but quite different from ordinary liquid state solution. When the binary mixture of crotonic acid and acrylamide is mixed with benzoyl peroxide at room temperature, after 15 min. the mixture begins to convert into fluid and ultimately a thick fluid is obtained resulting a solid material. The initiation seems to occur preferentially at crystal imperfections and converts into solid solution. Propagation may continue thus at the polymer - monomer interface being controlled in part by local strains and defects in the crystal and may be the polymer already present. At high temperature the copolymer of low molecular weight may be prepared.

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