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SOLID STATE COPOLYMERIZATION OF ACRYLAMIDE AND CINNAMIC ACID UNDER UV RADIATION

A Rasheed Khan*, Z H Farooqui, Asif Imran and Muhammad Ejaz

PCSIR Laboratories Complex, Off University Road, Karachi-75280 Pakistan

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Solid state copolymerization of acrylamide (r_1) and cinnamic acid (r_2) was accomplished under UV radiation at a temperature 68°C below the melting point of monomers. It is noted that yield of the product does not repeat but trend remains the same. The monomer reactivity ratios were determined to be r_1=1.6 and r_2= 0. Molecular weights of the product samples range between 11205 - 72770. All copolymer samples are off-white solid substances that become light yellow at 140°C.

Key words: Acrylamide, Cinnamic acid, Polymerization, UV radiation.

Introduction

Bulk copolymerization of acrylamide with maleic anhydride (MA) in solid state under UV radiation at a temperature below the melting points of the monomers has already been reported (Khan and Farooqui 1995). Acrylamide forms copolymers with MA in all monomeric ratios. Molecular weight of the product shows that the copolymer under UV-radiation carry small chains. When binary mixture of acrylamide and MA is kept under UV radiation at a temperature below the melting points of these monomers, the reacting mixture becomes viscous fluid and then begins to become solid. But when the mixture of acrylamide and cinnamic acid (CA) is kept under UV radiation below their melting points, the monomeric mixture remains in crystalline form and begins to become solid. It shows that copolymerization takes place in solid form. This paper deals with the solid state copolymerization of acrylamide and CA under UV radiation at a temperature (68°C) below the melting points of monomers.

Materials and Methods

Cinnamic acid (E.Merck) and acrylamide (BDH) were used without further purification. Reagent grade benzoyl peroxide was recrystallised in chloroform. All solvents were used after distillation.

Procedure of copolymerization. Reactions were accomplished in stoppered glass tubes 12 cm long and 2 cm internal diameter. Acrylamide and CA in different ratios and benzoyl peroixde (Table 1-4) were transferred in the reaction tubes, mixed thoroughly and flushed with nitrogen. The reaction tubes were closed at ground neck of the tubes with stopper. Finally these tubes were kept under UV-radiation for specific time at a temperature below the melting point of the monomers (68°C). After the required reaction time, the tubes were opened and the product was separated with acetone, dried under vacuum and weighed. It was observed that yield of the product does not repeat as shown in Table 1. Three sets of experiments are shown in Table 1 labelled as A, B and C. Yields are different from each other but trend is uniform. The product dissolves in 1% aqueous NaOH and aqueous acetic acid (1:1) completely. It partially dissolves in dil HC1 and water and disburse in conc HC1. The IR spectra of the product was recorded at 3400 (s), 3000-2800 (m), 2500 (w), 1680 (s), 1400 (m), 1320 (w), 1280 (m), 1120 (m), 980 (m), 760 (m) cm^{-1}. The spectra showed the product to be a copolymer. The composition of product was determined by analysing for nitrogen. Viscosity of dil solutions of the product samples prepared in 1% NaOH was measured at 33°C using Oswald type viscometer.

Results and Discussion

Tables 1-4 include the data obtained for the bulk solid state copolymerization of acrylamide and cinnamic acid under UV-radiation at a temperature below the melting points (68°C) of the monomers. Elemental analysis, solubility, IR spectral studies, viscosity were used for identification and ensuring the product to be copolymer. The product was estimated for nitrogen. The prepared sample of poly-acrylamide contains 19.4% N whereas the product samples contain 11.0-18.8% nitrogen. The variation in percentage of nitrogen suggests the coupling of cinnamic acid molecules in the growing poly-

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* Author for correspondence

Table 1

Bulk solid state copolymerization of acrylamide and cinnamic acid using 1% benzoyl peroxide as initiator at 68°C for 40 h under UV radiation

S.No.	Acrylamide mole	Cinnamic acid mole	Yield (g)			Elemental analysis % N			[η] dl g^{-1}	M_n
			A	B	C	A	B	C		
1	0.01408	0.02703	0.2000	0.5132	0.3950	11.29	13.5	11.00	-	-
2	0.02817	0.02027	0.3910	1.4436	0.4497	15.34	14.18	13.95	0.32	11205
3	0.03521	0.16892	3.7797	2.4203	2.4200	13.99	13.09	13.88	0.57	26875
4	0.04225	0.01351	0.4497	1.4248	1.4200	14.03	13.03	13.19	0.95	58275
5	0.05634	0.00675	0.2500	0.4380	0.5132	15.32	12.89	17.10	1.10	72770

Table 2

Effect of catalyst on the bulk solid state copolymerization of acrylamide (2.5 g) and cinnamic acid (2.5 g) at 68 °C for 40 h under UV radiation

S.No.	Benzoyl peroxide %	Yield g	Elemental analysis % N
1	0.25	0.2878	11.89
2	0.50	0.5674	12.76
3	1.00	3.7797	13.88
4	1.50	3.8506	13.99

Table 3

Effect of time on the bulk solid state copolymerization of acrylamide (2.5 g) and cinnamic acid (2.5g) using benzoyl peroxide (1%) as initiator at 68°C for 40 h under UV radiation

S.No.	Time h	Yield g	Elemental analysis N%	[η] dl g^{-1}	M_n
1	0.23	-	-	-	-
2	0.25	traces	-	-	-
3	0.50	0.0500	-	-	-
4	1.00	0.0788	-	-	-
5	2.00	0.1041	18.28	-	-
6	5.00	0.3250	14.44	-	-
7	10.00	0.6756	16.78	0.35	12836
8	20.00	1.1734	18.15	0.36	13395
9	30.00	1.6446	17.58	1.00	62985
10	40.00	3.7797	13.88	1.00	62985
11	50:00	3.9050	16.85	0.35	12836
12	60.00	4.0864	15.25	-	-

Table 4

Effect of temperature on the bulk solid state copolymerization of acrylamide (2.5 g) and cinnamic acid (2.5 g) using benzoyl peroxide (1%) at 68°C for 40 h under UV radiation

Sample No.	Temperature	Yield	Elemental analysis
1	35	Traces	-
2	45	0.1000	18.87
3	50	0.1250	18.71
4	55	0.1425	18.63
5	60	0.8498	17.91
6	65	2.6736	17.25
7	68	3.7797	13.88

mer chain of acrylamide or vice versa. The solubility of the product samples was also examined in different solvents. Acrylamide and cinnamic acid are soluble in acetone whereas product does not dissolve in acetone. It supports the results of the analysis of nitrogen ensuring that the product is a copolymer. IR spectrum (Fig 1) of the product was also recorded as described in procedure which supports the assumption that the product is a copolymer. In the spectrum of the polyproduct (expt. 2) the absorption bands with maxima at 2500, 1400, 1320, 1280, 1120, 980, 760 cm^{-1} are characteristic C-C bands whereas the absorption bands at 3400 cm^{-1} and 3000-2800 cm^{-1}show stretching vibrations showing the product to be copolymer.

The effect of monomer concentration, time temperature and catalyst on the conversion of the monomers into copolymer were studied. It was noted that yield of the product did not repeat but trend remained the same. For these reason three sets of experiments labelled as A,B,C were performed (Table 1). In Fig 2, percentage yield is plotted against per-

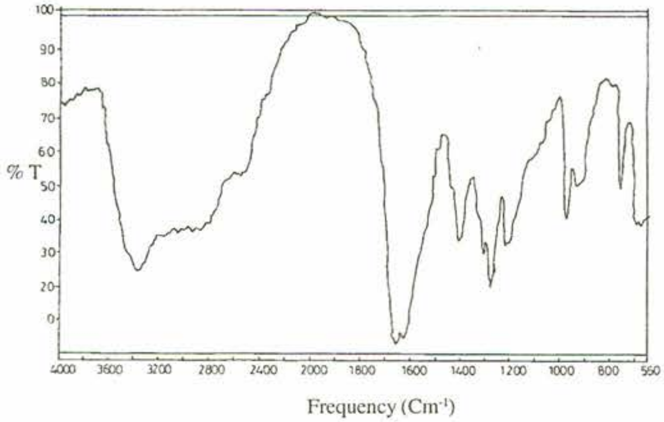

Fig 1. I.R.Spectrum of copolymer (Acrylamide-co-Cinnamic acid).

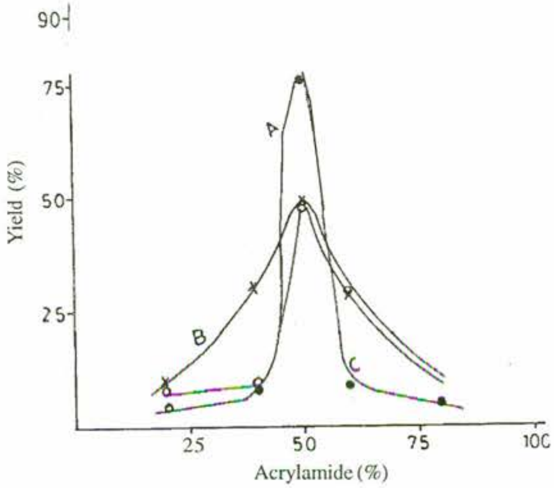

Fig 2. A plot of % yield vs % acrylamide for solid state copolymerization of acrylamide and cinnamic acid.

centage of acrylamide which indicates that rate of formation of copolymer is maximum at 50% acrylamide concentration and then it drops. It might be due to the monomers being in solid state. The movements of monomer molecules under UV radiation did not remain uniform in each set of experiments which affected the formation and coupling of growing polymer chains of monomers. Figure 3 explains the effects of catalyst on the reaction. The rate of polymerization increases with increasing concentration of catalyst. It is due to the presence of large number of free radicals in the vicinity of monomer moleucles at higher concentration of benzoyl peroxide. The plot in Figure 4 shows the effect of temperature on the rate of formation of copolymer. These results indicate that the rate of copolymerization increases with increase in thermal heating (temperature). It shows that not only free radicals are formed due to benzoyl peroxide but radical formation also occurs thermally which enhances the rate of copolymerization. Determination of induction period of any chemical reaction is very significant to understand its kinetics. The results shown in Table 3 indicate that the copolymerization starts after 14-15 minutes and rate of polymerization increases with increase in time. Due to increment in time, maximum number of free radicals are used in the reaction resulting in increase in yield.

The monomer reactivity ratio values of acrylamide (r_1) and cinnamic acid (r_2) were determined by the following rearranged form of copolymer composition equation (Mayo and Lewis 1944).

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

where $[M_1]$ and $[M_2]$ represent the concentrations of acrylamide and cinnamic acid, respectively in the reaction mixture, $\frac{d[M_1]}{d[M_2]}$ refers to the ratio of the two monomers in

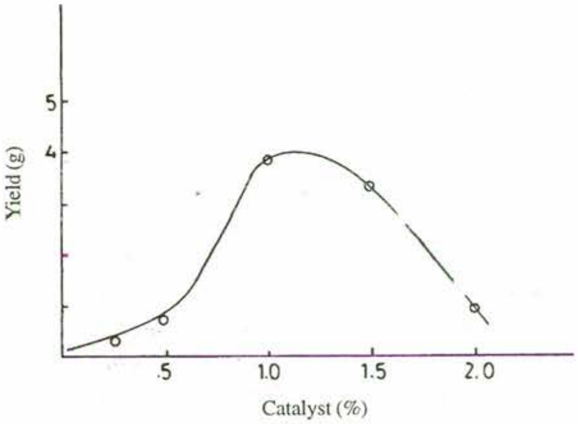

Fig 3. Effect of catalyst on solid state copolymerization of cinnamic acid and acrylamide under UV radiation at 68°C.

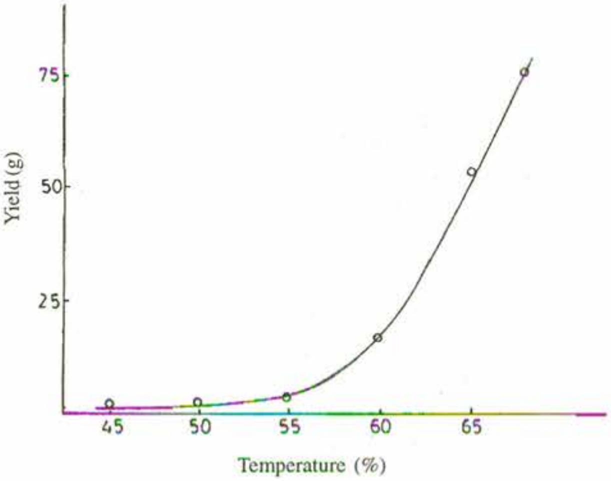

Fig 4. Effect of temperature on the solid state copolymerization of acrylamide and cinnamic acid under UV radiation at 68°C.

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 intersection or meeting of the lines at one point for different feed gives the best values of r_1 and r_2. For this purpose from three yields shown in Table 1, only yields labelled as 'C' are used for the determination of reactivity ratios. Figure 5 shows r_1 - r_2 plot for determining reactivity ratios. The values of monomer reactivity ratios r_1 and r_2 obtained from this plot are: $r_1 = 1.6$ and $r_2 = 0$. Since one reactivity r_1 is greater than unity and other r_2 is less than unity, the copolymer system of acrylamide and cinnamic acid is nonazeotropic as both r_1 and r_2 are greater than unity (Bamford *et al* 1958; Mullik and Khan 1970) both radicals prefer the same monomers i.e., acrylamide. Acrylamide is 1.6 times as reactive as cinnamic acid towards the polyacrylamide radicals but cinnamic acid radicals prefer to adding acrylamide monomer by a factor of infinity. Hence, polymerization of a mixture of similar amounts of acrylamide and cinnamic acid gives an initial product which is virtually pure polyacrylamide. When most of the acrylamide monomer are consumed, the coupling of growing polymer chains of both monomer radicals take places forming copolymer. It is clear that copolymerization of these monomers gives a mixture of homopolymer and copolymer. When cinnamic acid is kept under UV-radiation for 40 h, a product insoluble in acetone is not obtained. It shows that cinnamic acid does not homopolymerize readily but copolymerizes with acrylamide. Many such examples are found in the literature e.g., copolymerization of acrylonitrile with crotonic acid or tetra-chloroethylene (Mullik and Khan 1970; Lodhi and Khan 1971) and copolymerization of acrylamide and maleic anhydride (Khan and Farooqui 1995). The reactivity ratios of crotonic acid, tetrachloroethylene and maleic anhydride are zero. These monomers do not readily homopolymerize but help in copolymerization. The monomer reactivity ratios of acrylamide to maleic anhydride is 0.55 whereas reactivity ratios of crotonic acid and tetrachloroethylene to acrylonitrile are respectively 14 and 456.

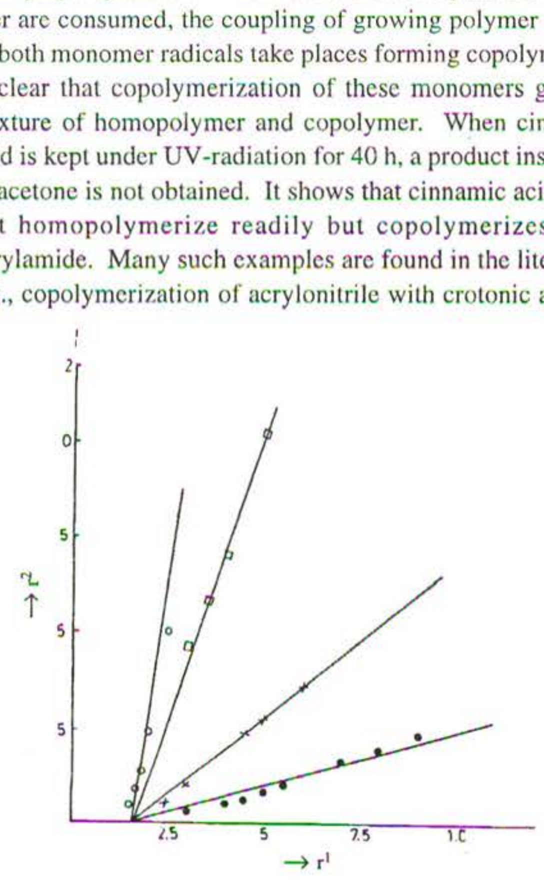

Fig 5. Mayo and Lewis plot for the solid state copolymerization of acrylamide (r_1) and cinnamic acid (r_2) under U V radiation at 68°C.

In brief when binary mixture (in solid state) of acrylamide and cinnamic acid with benzoyl peroxide is kept under UV-radiation, radicals are formed in two ways. One is the decomposition of benzoyl peroxide into free radicals by ultraviolet radiation; these radicals hit the double bonds of monomer molecules to form monomer radicals. Lattice defects and crystal boundries (imperfections) is the other source which produces 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 so that reaction will develop automatically (Bamford *et al* 1963). Radicals produced by benzoyl peroxide, increased the rate of propagation in homopolymerization of monomers and copolymerization of binary mixture.

Average molecular weight Mn of copolymer sample was calculated by using the following intrinsic viscosity [η] and molecular weight relationship (Collonson *et al* 1957)

$$[\eta] = 6.8 \times 10^{-4} M_n^{0.66}$$

The intrinsic viscosity of dilute solutions of copolymer samples prepared in 1% NaOH was determined by plotting ηsp/C vs C, where ηsp is the specific viscosity and C is the concentration of the solution expressed in percentage. Viscosity was measured at 33°C. The intrinsic viscosity of the copolymer samples (Tables 1 & 3) was found to be in the range of 0.32 - 1.1 $dl^{-1}g$ which gives the molecular weight as 11205-72770. This difference in intrinsic viscosity and Mn shows that monomers combine in different ratios to form copolymer. It is also evident from the molecular weights that copolymers prepared by UV-radiation carry comparatively small chains.

The copolymer samples mentioned in Tables 1-4 are off-white in colour and are easily soluble in 1% aqueous NaOH and aqueous acetic acid (1:1) as described earlier. After heating for 2 h at 68°-100°C in air, the copolymer samples retained their original colour (off-white) but had lost 11.5% weight. On further heating a sample at 130° C for 1 h, still retained the colour with loss in weight as 1.7%. When temperature reached to 140°C, the copolymer began to change the colour into light yellow with a loss in weight of 6%. Finally the product was found to decompose into reddish brown substance at 215°C with loss in weight of 5.6%. The decomposed product (140 - 145°C) became insoluble in 1% NaOH. The change in colour and insolubility of decomposed product in its solvent might be probably due to intermolecular and intramolecular rearrangements of amide groups in the copolymer chain. The colouration of copolymer by heat is usually attributed to the formation of a long chain conjugated double bonds (Jellinek 1962)

References

Bamford C H, Borb W G, Jenkins A D and Onyon P M 1958 *The Kinetics of Vinyl Polymerization by Radical Mechanisms.* Butter Worths & Co, London p 104.

Bamford C H, Eastmond G C, Ward J C 1963 Studies in polymerization. XIV. The solid state polymerization of acrylic and methacrylic acids. *Proc Roy Soc London* **A 271** 357

Collonson E, Dainton F S, Menanghton G S 1957 Effect of acrylamide on the X-& γ-rays yields of H_2 O_2 from aerated water. *Trans Faraday Soc* **54** 489.

Jellinek H H G 1962 *Macromole Chem IUPAC.* Butterworths & Co, London, pp 419.

Khan A R, Farooqui Z H 1995 Bulk copolymerization of acrylamide and maleic anhydride under UV radiation. *Pak J Sci Ind Res* **38** 288.

Lodhi S A K, Khan A R 1971 Copolymerization of acrylonitrile and determination of their reactivity ratios. *Pak J Sci Ind Res* **14** 467.

Mayo F R, Lewis F M 1944 Copolymerization. I. A basis for comparing the behaviour of monomer in copolymerization. *J Am Chem Soc* **66** 1594.

Mullik S U, Khan A R 1970 Copolymerization. Part III. Copolymerization of acrylonitrile and tetrachloroethylene. *Pak J Sci Ind Res* **12** 186.