

## EFFECTS OF INORGANIC SALTS ON THE COPOLYMERIZATION OF VINYL AND ALLYL MONOMERS

### Part-IV. Copolymerization of Acrylonitrile and Allyl Alcohol in the Presence of Some Inorganic Salts

S.A.K. Lodhi\* and A. Rasheed Khan

*PCSIR Laboratories, Off University Road, Karachi 39, Pakistan*

(Received December 23, 1981)

The thermal copolymerization of acrylonitrile and allyl alcohol in the presence of some inorganic salts like  $\text{CoCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{PtCl}_6$  and  $\text{NiCl}_2$  without using any radical initiator was investigated. The accelerating effect of these salts was observed. The complexation in the case of acrylonitrile takes place through nitrile group of the monomer whereas in the case of allyl alcohol complex formation occurs on allylic group of the monomer. The inorganic salts act as chain transfer agents and do not appreciably change the reactivity ratios values of the monomers. The copolymerization mechanism is also discussed.

### INTRODUCTION

In our earlier publication, [1] the accelerating effects of  $\text{ZnCl}_2$ ,  $\text{CrCl}_3$ ,  $\text{HgCl}_2$  and  $\text{CdCl}_2$  on the copolymerization of acrylonitrile and allyl alcohol were reported. The acceleration in rate of copolymerization takes place due to the complexation of inorganic salt with the monomers. The accelerating effect of some selected inorganic salts on the copolymerization of acrylonitrile and allyl alcohol was also observed.

This paper deals with the effect of some inorganic salts on the copolymerization of acrylonitrile and allyl alcohol without using any radical initiator. The salts are  $\text{MnCl}_2$ ,  $\text{PtCl}_6$ ,  $\text{NiCl}_2$ ,  $\text{SrCl}_2$  and  $\text{CoCl}_2$ .

### EXPERIMENTAL

#### *Materials*

1. Acrylonitrile (BDH), allyl alcohol (E. Merck), laboratory grade dimethyl formamide, acetone and methanol were purified by following the known procedures. G.R. grade HCl of E. Merck was used without further purification.
2. All inorganic salts given as under were used without further purification.

Extra pure manganese chloride ( $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ )

strontium chloride ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ) and cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ) of E. Merck, laboratory grade chloroplatinic acid ( $\text{H}_2 \cdot \text{PtCl}_6 \cdot \text{H}_2\text{O}$ ) and laboratory grade nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ).

*Method of Copolymerization:* All the copolymerization reactions were performed in sealed tubes. The weighed amount of acrylonitrile, allyl alcohol were added to the reaction tube already containing  $2 \times 10^{-5}$  mole inorganic salt. The reaction tubes were sealed at the constriction and heated at  $100^\circ$  for an hour. A solid material was resulted. Acetone-methanol was the solvent-precipitant system for the copolymerization carried out in the absence of salt whereas for the copolymer prepared in the presence of salt it was acetone-methanol system containing HCl. The copolymer was then investigated by ash determination not to contain salt. All copolymer sample were analysed for nitrogen by Kjeldahl's method. The copolymer samples are white powdery substance and soluble in acetone and DMF. The colour of all samples turns brown at  $155^\circ$  and decomposes at above  $200^\circ$  with the formation of insoluble black material. IR spectra of all samples were also recorded.

Nitrile band in the spectra appears at  $2200-2300 \text{ cm}^{-1}$  wave number and -OH absorption band appears at  $3330-3570 \text{ cm}^{-1}$  wave number.

The number average molecular weight of all copolymer samples was measured at  $25^\circ$  using Ostwald's type visco-

\*Present Address: Department of Chemistry, University of Baluchistan, Quetta, Pakistan.

meter. Dimethyl formamide was used as a solvent.

### RESULTS AND DISCUSSION

The detailed results of the effects of inorganic salts on the copolymerization of AN and AA are summarized in Tables 1-6.

The estimation of prepared sample, of polyacrylonitrile gave 26.2% nitrogen whereas the resulting product contains 21.34-25.58% nitrogen. This difference in percentage of nitrogen may be due to the addition of allyl alcohol in the growing polymer chain of polyacrylonitrile. It suggests that the product prepared in the absence or presence of salt is a copolymer. Further each sample was found soluble in DMF and acetone while polyacrylonitrile is not soluble in acetone. I R spectral studies also support the assumption that the product is a copolymer. The

spectra of polyacrylonitrile and polyallyl alcohol were compared with the spectra of the copolymer prepared in the presence of each salt. The presence of nitrile band at  $2200-2300\text{ cm}^{-1}$  wave number and -OH group absorption band at  $3330-3570$  wave number in I R spectra of copolymer prepared clearly indicates that AN and AA form a copolymer.

Effects of inorganic salt on the copolymerization of AN and AA are condensed in Table 1-6. These results show the acceleration effect of  $\text{MnCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{PtCl}_6$  and  $\text{NiCl}_2$  on the copolymerization of AN and AA. The acceleration in rate may be due to the formation of complexes with either monomers. Amongst the above mentioned inorganic salts  $\text{PtCl}_6$  and  $\text{CoCl}_2$  are soluble in AN and form complex ( $\text{An} \text{---} \text{---} \text{M}^x\text{n}$ ) with salt. The salts like  $\text{SrCl}_2$ ,  $\text{MnCl}_2$  and  $\text{NiCl}_2$  are not soluble in the monomer and do not form complex with the monomer [2-4]. Since in IR spectra

Table 1. Copolymerization of acrylonitrile and allyl alcohol in the absence of salt at  $100^\circ$ .

Expt. No.	Monomer in feed		Weight of copolymer obtained. g	Analysis N%	Rate of polymerization. $R_p \times 10^5$ moles/l/Sec.	
	AN g	AA g			AN	AA
1.	4.75	0.25	0.073	25.46	5.9290	0.2030
2.	4.25	0.75	0.065	23.44	4.9050	0.5710
3.	4.00	1.00	0.061	22.44	4.3880	0.7120
4.	3.75	1.25	0.060	21.70	4.1940	0.8330

Table 2. Copolymerization of acrylonitrile and allyl alcohol in the presence of  $\text{CoCl}_2$  at  $100^\circ$ .

Expt. No.	Monomer in feed		Weight of copolymer obtained. g	Analysis N%	Rate of polymerization $R_p \times 10^5$ moles/l/Sec.	
	AN g	AA g			AN	AA
1.	4.75	0.25	0.057	25.58	4.6100	0.1386
2.	4.25	0.75	0.072	23.25	5.3110	0.6630
3.	4.00	1.00	0.064	22.12	4.5590	0.8050
4.	3.75	1.25	0.060	21.50	4.1830	0.8680

Table 3. Copolymerization of acrylonitrile and allyl alcohol in the presence of  $MnCl_2$  at  $100^\circ$ .

Expt. No.	Monomer in feed		Weight of copolymer obtained. g	Analysis N%	Rate of polymerization $R_p \times 10^5$ moles/l/ sec.	
	AN	AA			AN	AA
	g	g				
1.	4.75	0.25	0.128	25.38	10.3220	0.3850
2.	4.25	0.75	0.114	23.20	8.4490	1.0720
3.	4.00	1.00	0.110	22.10	7.7920	1.3930
4.	3.75	1.25	0.098	21.34	6.7360	1.4650

Table 4. Copolymerization of acrylonitrile and allyl alcohol in the presence of  $NiCl_2$  at  $100^\circ$ .

Expt. No.	Monomer in feed		Weight of copolymer obtained. g	Analysis N%	Rate of polymerization $R_p \times 10^5$ moles/l/Sec.	
	AN	AA			AN	AA
	g	g				
1.	4.75	0.25	0.474	25.18	38.0930	1.7080
2.	4.25	0.75	0.440	23.66	33.2620	3.5390
3.	4.00	1.00	0.414	22.78	30.2290	4.4080
4.	3.75	1.25	0.388	21.83	27.2820	5.2360

Table 5. Copolymerization of acrylonitrile and allyl alcohol in the presence of  $PtCl_6$  at  $100^\circ$ .

Expt. No.	Monomer in feed		Weight of copolymer obtained. g	Analysis N%	Rate of polymerization $R_p \times 10^5$ moles/l/Sec.	
	AN	AA			AN	AA
	g	g				
1.	4.75	0.25	0.565	25.42	25.8140	1.6390
2.	4.25	0.75	0.520	24.12	40.1500	3.4910
3.	4.00	1.00	0.490	23.00	36.1200	4.9000
4.	3.75	1.25	0.461	22.40	33.2610	5.4480

Table 6. Copolymerization of acrylonitrile and allyl alcohol in the presence of strontium chloride at 100°.

Expt. No.	Monomer in feed		Weight of copolymer obtained. g	Analysis N%	Rate of polymerization Rp x 10 <sup>5</sup> moles/l/Sec.	
	AN g	AA g			AN	AA
1.	4.75	0.25	0.214	25.38	17.3250	0.6470
2.	4.25	0.75	0.193	24.32	14.9800	1.1950
3.	4.00	1.00	0.183	23.38	13.6770	1.6300
4.	3.75	1.25	0.154	21.38	10.8480	2.0600

nitrile band shifts towards the longer wave number (from 2220 to 2325 cm<sup>-1</sup>), the complexation between AN and salt takes place on the nitrile group of AN in the 1:1 (AN : salt) molar ratio [5-6]. The complexes are highly hygroscopic soluble in polar solvents. Similarly the above mentioned inorganic salts are soluble in allyl alcohol and form complexes with this monomer. Allyl alcohol combines with MnCl<sub>2</sub>, SrCl<sub>2</sub>, CoCl<sub>2</sub> and NiCl<sub>2</sub> in the 1:2 (AA : salt) molar ratio whereas with PtCl<sub>6</sub> it combines in the 1:1 molar ratio and allylic group takes part in complexation. The complexes of allyl alcohol are viscous material soluble in alcohol and acetone as given elsewhere [7]. The complexation of AN and AA with metal halide increase the polarity of the monomer and stabilize the transition state of the reaction resulting increase in the rate [8].

The monomer reactivity ratio values of acrylonitrile (r<sub>1</sub>) and allyl alcohol (r<sub>2</sub>) were determined by the following Fineman and Ross rate equation [9].

$$-\frac{F}{f} \frac{d(f-1)}{df} = r_2 \frac{F_2}{f} - r_2 \dots \dots \dots (1)$$

where f is d[M<sub>1</sub>] / d[M<sub>2</sub>], F is monomer ratio M<sub>1</sub>/M<sub>2</sub>. A plot of  $\frac{F(f-1)}{f}$  against  $\frac{F_2}{f}$  is a straight line whose slope is r<sub>1</sub> and intercept r<sub>2</sub>. This is called mole ratio method. The plot for the copolymerization of acrylonitrile and allyl alcohol in the absence of salt is given in Fig 1. If the monomer concentration are expressed in mole fraction equation (1) may be rearranged [10] as

$$\frac{F_1(1-2F_1)}{(1-f_1)F_1} = r_1 + \frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1} r_2 \dots \dots \dots (2)$$

where f<sub>1</sub> represents the mole fraction of monomer in feed, F<sub>1</sub> the mole fraction of monomer in the increment of

copolymer formed at the start of the copolymerization.

A plot of  $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$  VS  $\frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$

gives a straight line whose slope is r<sub>1</sub> and intercept is r<sub>2</sub>. This is called mole fraction method. The plot for the copolymerization of AN and AA in the absence of salt is shown in Fig. 2. Similarly, by these two plots, the values of r<sub>1</sub> & r<sub>2</sub> for the copolymerization of AN and AA in the presence of salts are determined which are given in Table VII. The reliability of the reactivity ratios values were further checked by using the following equation obtained by rearranging the copolymerization composition equation (2) with appropriate changes [11].

$$F_1 = \frac{\bar{r}_1 f_1^2 + f_1 f_2}{\bar{r}_1 f_1^2 + 2f_1 f_2 + \bar{r}_2 f_2^2} \dots \dots \dots (3)$$

In this equation r<sub>1</sub> & r<sub>2</sub> are the mean of the values obtained

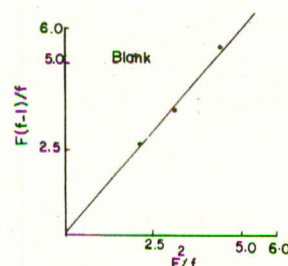


Fig.1. A plot of  $\frac{F}{f(f-1)}$  against  $\frac{F_2}{f}$  according to the mole

ratio method to obtain r<sub>1</sub> and r<sub>2</sub> for the copolymerization of AN and AA in the absence of salt.

Table 7. Reactivity ratio values determined by Finemann and Ross methods for acrylonitrile ( $r_1$ ) and allyl alcohol ( $r_2$ ) copolymerization in the presence of some inorganic salts.

Salt added	Mole ratio method		Mole fraction method		Mean values	
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$
Blank	1.21±0.025	0.05±0.025	1.18±0.025	0.05±0.025	1.195±0.025	0.05±0.025
Cobalt chloride	1.09±0.025	0.05±0.025	1.07±0.025	0.05±0.025	1.080±0.025	0.05±0.025
Strontium chloride	1.73±0.025	0.05±0.025	1.67±0.025	0.05±0.025	1.700±0.025	0.05±0.025
Managanese chloride	1.09±0.025	0.05±0.025	1.07±0.025	0.05±0.025	1.080±0.025	0.05±0.025
Platinic chloride	1.60±0.025	0.05±0.025	1.53±0.025	0.05±0.025	1.565±0.025	0.05±0.025
Nickel chloride	1.10±0.025	0.05±0.025	1.12±0.025	0.05±0.025	1.110±0.025	0.05±0.025

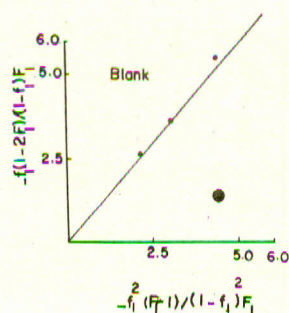


Fig. 2. A plot of  $-F_1(1-2F_1)/(1-f_1)F_1$  versus  $-f_1^2(F_1-1)/(1-f_1)^2F_1$  according to mole fraction method to obtain  $r_1$  and  $r_2$  for the copolymerization of acrylonitrile and allyl alcohol in the absence of salt.

by equation (1) & (2),  $f_1$  and  $f_2$  are found from monomer concentration in feed. The points shown in Fig. 3 by hollow circles are obtained by plotting  $F_1$  determined by equation (3) against corresponding  $f_1$ . Similarly a plot of  $F_1$  using the relation,

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} \dots\dots\dots (4)$$

determined by the chemical analysis of the copolymer formed against  $f_1$  are shown by continuous line in Fig. 3 The calculated values plots are in good agreement with the observed values plots. This points towards the reliability of the measurements<sup>[11]</sup>. The results of reactivity ratio

values show that reactivity ratios values are little influenced by the addition of inorganic salts.

Since  $r_1 > 1$  and  $r_2 < 1$  the copolymerization system is nonazeotropic<sup>[12]</sup>. Also  $r_1$  and  $\frac{1}{r_2}$  are greater than unity both monomers radicals in the copolymerization system prefer the same monomer i.e., acrylonitrile. The copolymer of following type will be formed.

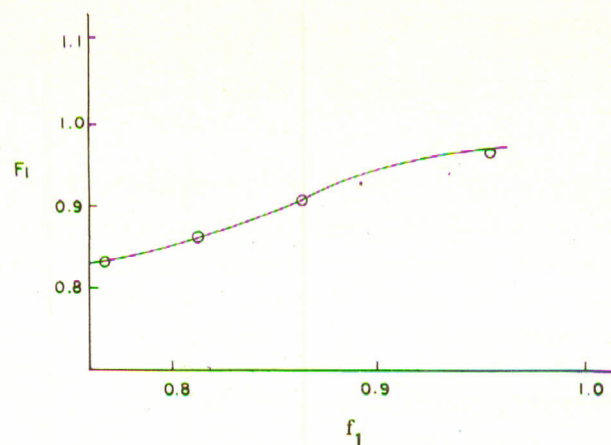
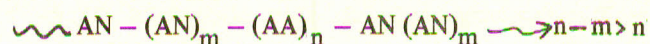


Fig 3. A plot of mole fraction of  $M_1$  in copolymer ( $F_1$ ) against mole fraction of  $M_1$  in feed ( $f_1$ ) for the system acrylonitrile and allyl alcohol. The continuous line shows the calculated values whereas observed values are shown by circles.

The number average molecular weight  $M_n$  was determined by using the following intrinsic viscosity – molecular weight relationship, [13].

$$[\eta] = 3.92 \times 10^{-4} M_n^{-0.75} \quad (5)$$

where  $[\eta]$  is the intrinsic viscosity of the copolymer solution. This is obtained by plotting  $\eta_{sp}/c$  against  $C$ , where  $\eta_{sp}$  is the specific viscosity and  $C$  is the concentration of the solution expressed in percentage. The intrinsic viscosity of the copolymer sample prepared in the absence of salt was found 1.79 dl/g (as shown in Table 8 and Fig 4) which gives the value of  $M_n$  as 75757 and similarly by using the same plot, the intrinsic viscosity of the copolymer samples prepared in the presence of inorganic salt was measured in the range 1.23-1.68 g/l/g. The value of  $M_n$  calculated from these values lies in the range 45737-69614. The decrease in number average molecular weight  $M_n$  with the addition of salt suggests that chain transfer reaction takes place due to the presence of salt as well as allyl alcohol. This behaviour of metal salts with vinyl monomers are also reported elsewhere (1,7, 14).

V.A. Kargin *et al.*, [15] Gaylord [16] and others [1, 17] have proposed the mechanism of copolymerization of vinyl and allyl monomers in the presence of metal salts like  $ZnCl_2$ ,  $HgCl_2$ ,  $CdCl_2$ ,  $CrCl_3$ , etc. The same mechanism may be proposed in the light of present findings since the results obtained are not conflicting. Acryloni-

Table 8. Effect of inorganic salt on the intrinsic viscosity  $[\eta]$  and number average molecular weight  $M_n$  of the copolymer prepared from acrylonitrile-allyl alcohol system.

Name of salt	$[\eta]$ dl/g	$M_n$
Blank	1.79	75757
Cobalt chloride	1.68	69614
Strontium chloride	1.36	52521
Manganese chloride	1.56	63064
Platinic chloride	1.33	50982
Nickel chloride	1.23	45737

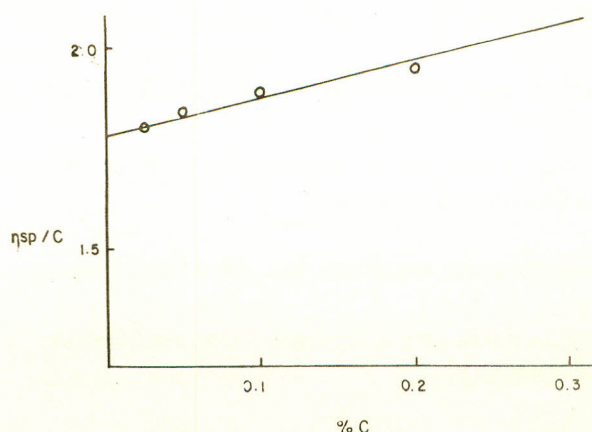
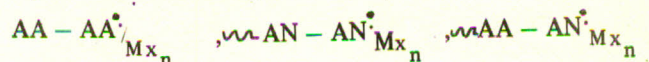
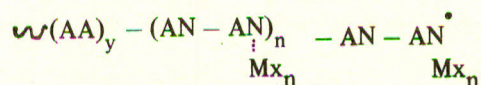


Fig.4. A plot of  $\eta_{sp}/c$  against  $C$  for the determination of intrinsic viscosity of the copolymer prepared in the absence of salt.

trile and allyl alcohol when heated in the absence of salt, the initiating free radicals containing unshared electrons results from thermal activation of AN and AA molecules. The formation of free radicals by thermal activation may be caused by hydrogen transfer between AN and allyl alcohol [8,18]. These free radicals ( $\sim AN^\bullet$ ,  $\sim AA^\bullet$ ) initiate the copolymerization reaction. Acrylonitrile and allyl alcohol when heated in the presence of salts, both monomers form complexes with such salts which are soluble in the monomers. The complexation of AN with metal halide ( $AN \xrightarrow{\quad} Mx_n$ ) occurs on nitrile group whereas in the case of allyl alcohol it occurs on the double bond of allylic group ( $AA \xrightarrow{\quad} Mx_n$ ) of the monomer due to delocalization of electrons [4,7]. The complex formation increase the electron accepting character of the monomers and reaction takes place more easily. Also the transition state of reaction gets stabilized [8]. Both acrylonitrile and allyl alcohol form complex radicals,



The coupling of complex radicals of both allyl alcohol and acrylonitrile takes place to yield copolymer,



#### REFERENCES

1. S.A.K. Lodhi and A. Rasheed Khan, J. Chem. Soc. Pak. (1981) (in press).
2. M. Imoto, T. Otsu and T. Harada, Makromole. Chem.,

- 65, 180 (1963).
3. F.A. Bovey, *J. Polym. Sci.*, **47**, 480 (1966).
  4. S.A.K. Lodhi and A. Rasheed Khan, *Revue Roum. de Chimie* (1981) (in press).
  5. G.N. Shrauzer, *Am. Chem. Soc.*, **81**, 5310 (1959).
  6. S.F.A. Kettle and I. E. Orgel, *Chem. and., Ind No.* **2**, 49 (1960).
  7. S.A.K. Lodhi and A. Rasheed Khan, *Pakistan J. Sci. Ind. Res.* **24**, (1981).
  8. Shigeru Yabumoto, K. Ishii and K. Arita, *J. Polym. Sci., Part-A-1*, **7**, 1577 (1969).
  9. Fineman and S.D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).
  10. P. J. Flory, *Principial of Polymer Chemistry* (Cornell University Press, New York, 1953) p. 185.
  11. S.A.K. Lodhi and A. Rasheed Khan, *Pakistan J. Sci. Ind. Res.*, **13**, 358 (1970).
  12. C.H. Bamferd, W.G. Barb, A.D. Jenkins and P.F. Onyon, "*The Kinetics of Vinyl Polymerization of Radical Mechanism*" (Butter-worths Scientific Publication, London, 1958). p. 157.
  13. P. F. Onyon *J. Polym. Sci.*, **22**, 13 (1956).
  14. S.A.K. Lodhi and A. Rasheed Khan, *Revue Roum de Chimie* 1980 (Under publication).
  15. V.P. Kulikova, V.A. Kabanov, L.S. Polak and V.A. Kargin, *J. Polym. Sci.*, **23**, 147 (1967).
  16. N.G. Gaylord and A. Takahashi, *J. Polym. Sci., Letters* **6**, 743 (1968).
  17. *Encyclopedia of Polymer Science and Technology* (Inter Science Publication, New York, 1967), Vol. 5 p. 173.
  18. M. Imoto and Kajshiro, *Kobanski Kagaka Kyotei, Asakura Tokyo* (1965), p. 43.