

Effects of inorganic salts on the copolymerization of vinyl and allyl monomers part-III copolymerization of acrylonitrile and allyl alcohol in the presence of some inorganic salts.

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Summary: The thermal copolymerization of acrylonitrile and allyl alcohol in the presence of complexing agents like HgCl_2 , CrCl_3 , ZnCl_2 and CdCl_2 is investigated. Accelerating effects of complexing agents were observed. The complexation in the case of AN takes place through nitrile group whereas in the case of allyl alcohol the complex formation occurs on allylic group of the monomer. The inorganic salts act as chain transfer agent and do not appreciably change the reactivity ratios values of the monomers. The copolymerization mechanism is also discussed.

Introduction

Attempts have been made in finding out the influence of some inorganic complexing agents like ZnCl_2 , AlCl_3 , AlBr_3 or SnCl_4 on the vinyl polymerization¹⁻⁴. In our earlier papers^{5,6} the effects of some inorganic salts on the copolymerization of styrene and acrylonitrile was determined. The salts which were soluble in acrylonitrile almost form complexes with the monomer and the acceleration effect of the salts was noted due to the complexation through nitrile group of AN with the metal halide.

This paper deals with the effects of some inorganic salts on the copolymerization of AN and allyl alcohol without using a radical initiator. The salts are ZnCl_2 , HgCl_2 , CrCl_3 and CdCl_2 .

Experimental

Material

1. Allyl alcohol (E. Merck), acrylonitrile (BDH) laboratory grade DMF, acetone and methanol were purified according to usual methods. 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 anhydrous Zinc chloride (ZnCl_2) of E. Merck, fine crystals of mercury chloride (HgCl_2) of E Merck, Analar chromium chloride ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) and laboratory grade cadmium chloride ($\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$).

Copolymerization procedure

All reactions were carried out in sealed pyrex tubes. The required amount of acrylonitrile, allyl alcohol and salt (2×10^{-5} mole) was added to the tubes and sealed at the constriction. The reaction tubes were heated at 100°C for an hour. A solid material was obtained. The solvent-precipitant system for the copolymerization in the absence of salt was acetone-methanol and for copolymerization in the presence of salt it was acetone-methanol containing HCl. The copolymer was then investigated by ash determination not to contain salts⁷. All copolymer samples are white powdery substance and found soluble in acetone and DMF. The colour of all samples at 155°C turns brown and decompose above 200°C with the formation of insoluble black material.

The copolymer samples were estimated for nitrogen by using kjeldahl's method. The accuracy of the determination was 0.2%.

The spectrum of copolymer was recorded in KBr pellets. Nitrile absorption band appears at a frequency $2200\text{--}2300 \text{ cm}^{-1}$ whereas OH absorption band was found at a frequency $2375\text{--}3570 \text{ cm}^{-1}$.

Viscosity of copolymer solutions prepared in DMF was measured at $25^\circ\text{C} \pm 0.05^\circ\text{C}$ using Ostwald's type viscometer, following the procedure as given elsewhere⁸.

Results and Discussion

The detailed results of the effects of inorganic

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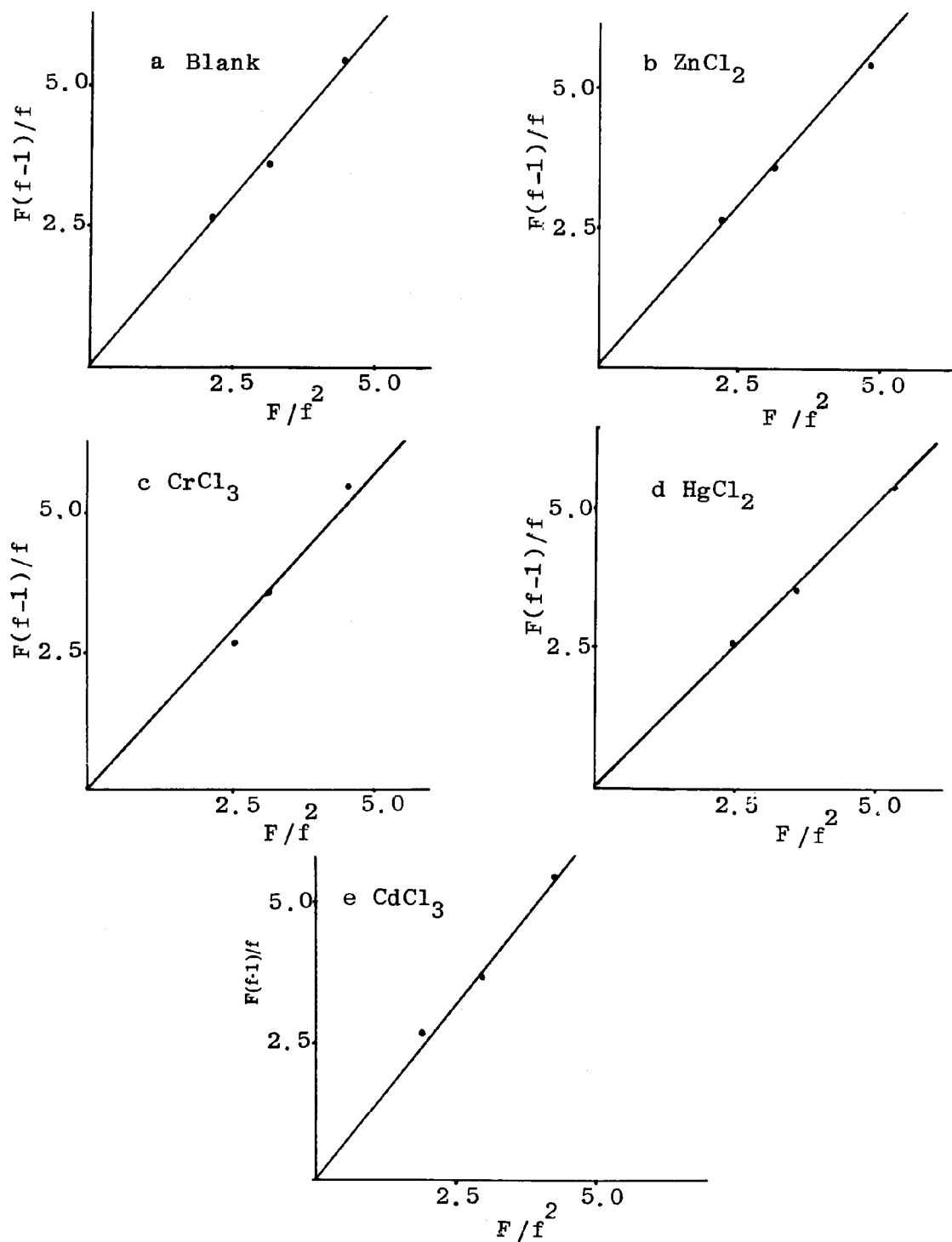


Fig. 1: Plots of $\frac{F}{f(f-1)}$ versus $\frac{F^2}{f}$ according to the mole ratio method to obtain r_1 and r_2 for the copolymerization of acrylonitrile (r_1) and allyl alcohol (r_2) in the absence and presence of salt. (a) Blank (b) ZnCl_2 (c) CrCl_3 (d) HgCl_2 (e) CdCl_2 .

salts on the copolymerization of acrylonitrile and allyl alcohol are given in table I - V.

The results show that the analysis of polyacrylonitrile gave 26.2% nitrogen whereas that of product 21.29 - 25.78% nitrogen. The difference in percentage of nitrogen contents may be due to the attachment of allyl alcohol monomer in the polymer chain of polyacrylonitrile suggesting that the product obtained in the presence or absence of inorganic salts is a copolymer. The I. R. spectra of copolymer was also taken as additional supporting evidence. The spectra of polyacrylonitrile and polyallyl alcohol were compared with the spectra of copolymer prepared in the presence of each salt. The presence of nitrile absorption band at a frequency 2200-2300 cm^{-1} and -OH absorption band frequency 3275 - 3570 cm^{-1} in I.R. spectra of copolymer samples indicates that acrylonitrile and allyl alcohol forms a copolymer.

Effects of inorganic salts on the copolymerization of acrylonitrile and allyl alcohol are described in tables I - V. The results indicate the acceleration effect of ZnCl_2 , CrCl_3 , CdCl_2 and HgCl_2 on the copolymerization of acrylonitrile and allyl alcohol. The acceleration in rate may be due to the formation of complexes with acrylonitrile and allyl alcohol both, since each salt is soluble in both monomers. The complexation between acrylonitrile⁹ and salt may be on the nitrile group in the 1:1 (AN/salt) molar ratio whereas allyl alcohol¹⁰ combines with salt in the 1:2 molar ratio and allylic group takes part in complexation. It was further proved by preparing these complexes separately. The complexes of AN are highly hygroscopic, soluble in polar solvent while the complexes of allyl alcohol are viscous material soluble in alcohol and acetone. These complexes enhance the polarity of the monomers and reaction takes place more easily. Also complexes help in stabilizing the transition state of reaction resulting increase in the rate.

The monomer reactivity ratios of acrylonitrile and allyl alcohol were determined by Fineman and Ross methods⁽¹¹⁻¹²⁾. The behaviour of two monomers M_1 and M_2 in free radical type of copolymerization may be explained by the following equation,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \times \frac{r_1 [M_1] + [M_2]}{r_2 [M_2] + [M_1]} \quad (1)$$

where $[M_1]$ and $[M_2]$ represent concentration of unreacted acrylonitrile and allyl alcohol respectively

in the reaction mixture, $\frac{d[M_1]}{d[M_2]}$ refers to the ratio of

the two monomers in the increment of copolymer formed, r_1 and r_2 are reactivity ratio values of acrylonitrile & allyl alcohol respectively using this equation Fineman and Ross derived the following rate equation to determine r_1 and r_2 ,

$$\frac{F}{f}(f-1) = r_1 \frac{F^2}{f} - r_2 \quad (2)$$

where f is $d[M_1]/d[M_2]$, F is monomer ratio $[M_1]/[M_2]$. A plot of $F(f-1)$ versus $\frac{F^2}{f}$ is a straight line

whose slope is r_1 and intercept r_2 . This is called mole ratio method. The plots are given in figure 1. If the monomer concentration are expressed in mole fraction, equation (2) may be rearranged as,

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = r_2 + \frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1} r_1 \quad (3)$$

Where f_1 represents the mole fraction of monomer in feed, F_1 the mole fraction of monomer in the increment of copolymer at the start of copolymerization. A plot of $f_1(1-2F_1)$ Vs $\frac{f_1^2(F_1-1)}{(1-f_1)^2 F_1}$ gives a straight line whose

slope is r_1 and intercept is r_2 . This is called mole fraction method. The plots are shown in figure 2. The reactivity ratios values determined by these methods are condensed in table VI. The reliability of the values were further checked by using the following equation obtained by rearranging equation (2) & (3) with appropriate changes¹³,

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (4)$$

Where r_1 and r_2 are the mean of the values obtained by mole ratio and mole fraction methods of Fineman and Ross, f_1 and f_2 are found from monomer concentration in feed. The values of F_1 are plotted against f_1 values as shown in figure 3 by hollow circles. Similarly a plot of F_1 using the relation,

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]}$$

determined by the chemical analysis of copolymer formed against f_1 are shown by continuous line in figure 3. In all cases the calculated values plots are in good agreement with the observed values plots. This points towards the reliability of our measurements¹³. The

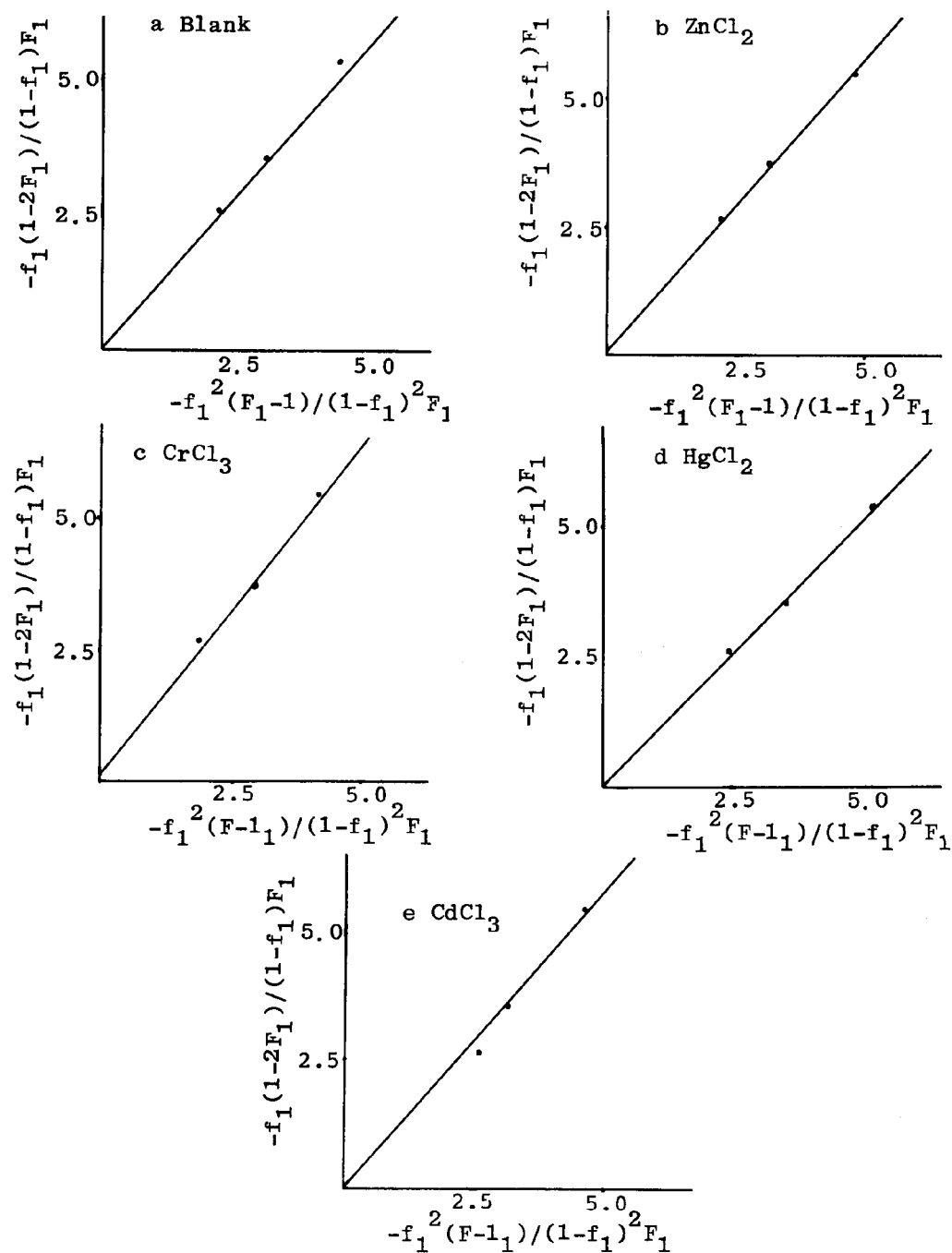


Fig. 2: Plots of $-f_1(1-2F_1)/(1-f_1)F_1$ versus $-\frac{f_1^2(F_1-1)}{(1-f_1)^2F_1}$ according to mole fraction method to obtain r_1 and r_2 for the copolymerization of acrylonitrile and allyl alcohol in the absence and presence of salt (a) Blank (b) $ZnCl_2$ (c) $CdCl_2$ (d) $HgCl_2$ (e) $CrCl_3$.

Table I. Copolymerization of AN & AA in the absence of salt at 100°C

Expt.	Monomer in feed		Weight of copolymer obtained gm	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	0.8710
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 II. Copolymerization of AN and AA in presence of $HgCl_2$ at 100°C

Expt.	Monomer in feed		Weight of copolymer obtained gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/l / sec.	
	AN g	AA g			AN	AA
1.	4.75	0.25	0.400	25.49	32.5240	1.0780
2.	4.25	0.75	0.356	23.00	26.1600	3.5510
3.	4.00	1.00	0.335	21.98	23.6020	4.3520
4.	3.75	1.25	0.315	21.29	21.6340	4.7620

Copolymerization of AN & AA in the presence of $CrCl_3$ at 100°C.

Expt.	Monomer in feed		Weight of copolymer obtained gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/l / sec.	
	AN g	AA g			AN	AA
1.	4.75	0.25	0.410	25.46	33.2980	1.1410
2.	4.25	0.75	0.347	23.65	26.1820	2.815
3.	4.00	1.00	0.351	21.57	24.2330	4.9750
4.	3.75	1.25	0.325	21.80	22.7840	4.4080

Table IV. Copolymerization of AN and AA in the presence of $ZnCl_2$ at 100°C.

Expt.	Monomer in feed		Weight of copolymer obtained gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/l / sec.	
	AN g	AA g			AN	AA
1.	4.75	0.25	0.133	25.78	10.8960	0.2460
2.	4.25	0.75	0.117	23.24	8.6880	1.0850
3.	4.00	1.00	0.109	22.40	7.8260	1.2820
4.	3.75	1.25	0.099	21.60	6.8530	1.3960

Table V. Copolymerization of AN and AA in the presence of CdCl_2 at 100°C .

Expt.	Monomer in feed		Weight of copolymer obtained gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/l / sec.	
	AN g	AA g			AN	AA
1.	4.75	0.25	0.158	25.20	12.7010	0.5590
2.	4.25	0.75	0.137	23.50	10.3070	1.1320
3.	4.00	1.00	0.132	22.61	9.5340	1.4740
4.	3.75	1.25	0.124	22.18	8.8590	1.5530

Table VI. Reactivity ratios values determined by Fineman 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 value	
	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
Mercury chloride.	1.04 ± 0.025	0.05 ± 0.025	1.02 ± 0.025	0.05 ± 0.025	1.030 ± 0.025	0.05 ± 0.025
Chromium 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
Zinc chloride.	1.16 ± 0.025	0.05 ± 0.025	1.14 ± 0.025	0.05 ± 0.025	1.15 ± 0.025	0.05 ± 0.025
Cadmium chloride.	1.28 ± 0.025	0.05 ± 0.025	1.28 ± 0.25	0.05 ± 0.025	1.28 ± 0.025	0.05 ± 0.025

Table 7. Effect of inorganic salt on the intrinsic viscosity $[\eta]$ and number average molecular weight Mn of the copolymer prepared from acrylonitrile-allyl alcohol system.

Name of salt.	$[\eta]$ d l/g	Mn
Blank	1.79	75757
Mercury chloride.	1.51	60384
Chromium chloride.	1.24	46435
Zinc chloride.	1.64	67413
Cadmium chloride.	1.61	65774

results of reactivity ratios show that reactivity ratio values are little influenced by the addition of inorganic salts¹⁴.

Since the monomer reactivity ratios of acrylonitrile is 21.34 times more than that of allyl alcohol, the bulk polymerization of binary mixture gives an initial product which is virtually pure polyacrylonitrile in the very initial stages. This is also supported by the nitrogen percentage in the copolymer showing that even in the presence of allyl alcohol, rate of polymerization of acrylonitrile increases with increase in acrylonitrile concentration alone in the initial stage. The rate of polymerization of acrylonitrile and allyl alcohol as shown in tables I-V provides another evidence that acrylonitrile enters in the copolymer chain more rapidly than allyl alcohol. The specific reactivity (Q_1) of AN is 0.6 while that for allyl alcohol (Q_2) is 0.052 which show that AN is more reactive than allyl alcohol¹⁵. All these evidences suggest that a mixture of AN and AA forms initial product which is almost pure polyacrylonitrile.

The copolymerization system is nonazeotropic since $r_1 > 1$ and $r_2 < 1$. Further more r_1 and $1/r_2$ are greater than unity, both monomers radicals in this system

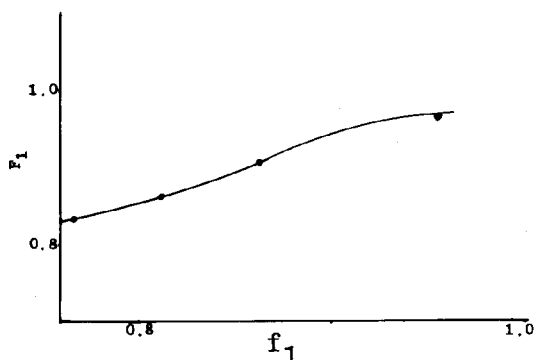


Fig. 3: A plot of mole fraction of M_1 in copolymer (F_1) against mole fraction of M_1 in feed (f_1) for the system acrylonitrile allyl alcohol. The continuous line shows the calculated values whereas observed values are shown by circles.

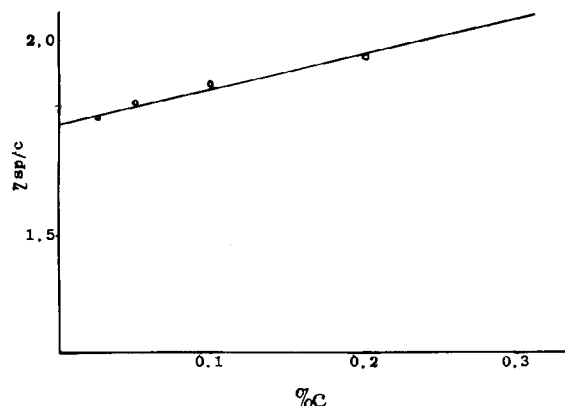
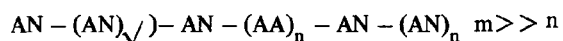


Fig. 4: A plot of η_{sp}/c against C for the determination of intrinsic viscosity of the copolymer prepared in the absence of salt.

prefer the same monomer i.e., acrylonitrile. The copolymer of the following type will be formed¹⁶.



The number average molecular weight M_n was calculated by using the following relation¹⁷.

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

Where $[\eta]$ is the intrinsic viscosity of the copolymer solution obtained by plotting η_{sp}/C against C . Here η_{sp} is the specific viscosity and C is the concentration of copolymer solution prepared in DMF. The intrinsic viscosity of the copolymer samples prepared in the absence of salt was found 1.79 dl/g (as shown in table

VII and fig. 4) which gives the values as 75757 and similarly the intrinsic viscosity of the copolymer samples prepared in the presence of inorganic salt was measured in the range 1.24 – 1.68 dl/g. The value of M_n calculated from these values lies in the range 46435 – 67413 as summarized in table VII. The decrease in number average molecular weight M_n with the addition of salt suggests that chain transfer takes place due to the presence of inorganic salts as well as allyl alcohol. This behaviour of metal halide with vinyl monomers was also noted by many other workers^{1,7}.

The mechanism of copolymerization of AN and AA in the presence of salt is proposed as follows. Acrylonitrile 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. These free radicals initiate the copolymerization reaction. This is supported by the nitrogen analysis, solubility, nitrile and – OH absorption bands in the I.R. spectra of the product and provides clear evidences that free radicals are formed by thermal activation of monomer molecules to initiate the copolymerization reaction. It is proposed that the initiation step of the copolymerization of acrylonitrile and allyl alcohol might be the thermal initiation. The formation of free radicals by thermal activation may be caused by hydrogen transfer between acrylonitrile and allyl alcohol^{4,18}.

Acrylonitrile and allyl alcohol when heated in the presence of salts both monomers form complex with such salts which are soluble in the monomers. In the presence of metal halide (Mx_n) acrylonitrile forms complex with nitrile group since there is not only a triple bonding between C and N but two non bonding electrons are also available on nitrogen. Acrylonitrile forms complex with nitrile group due to delocalization of electrons in the double bond of complexes monomers discussed elsewhere¹⁰. The complexation of acrylonitrile with metal halide increases its electron accepting character. The uncomplexed acrylonitrile will donate electrons to form molecular complex. In the case of 1:1 molecular complex the uncomplexed acrylonitrile will behave as a donor to form 1:1 molecular complex by a one electron transfer¹⁹⁻²⁰.

Allyl alcohol may form complex more easily on the double bond of allylic group since in I.R. spectra the allyl absorption band shifts from lower to high frequency 1700-1790. The complexation may be due to delocalization of the electrons in the double bond of complexed monomers.

Chain transfer with monomer is more important in allyl polymerization because of the ability of allylic radical to be stabilized by resonance, this stabilization provides the driving force for the abstraction of hydrogen atom. Gaylord and Kujawa²¹ has pointed out that although chain transfer is quite usual for allylic polymerization, allylic radicals do have the capability of adding monomer and thus of continuing the chain reaction ($AA - AA AA'$). This tendency is termed as effective chain transfer. Therefore allyl alcohol may produce free radicals and homopolymerize, although degree is very low. The allyl alcohol probably acts as an electron donor towards its complex ($AA.Mx_n$) and polymerizes giving complexed radicals. The coupling of complex radicals of both allyl alcohol and acrylonitrile takes place to yield copolymer.

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