

Effects of Inorganic Salts on the Copolymerization of Vinyl and Allyl Monomers Part – V Copolymerization of Styrene and Allyl Alcohol in the Presence of Some Inorganic Salts

S.A.K. LODHI* AND A. RASHEED KHAN

Polymer Research Division, PCSIR Laboratories Karachi-39, Pakistan.

(Received 31st December, 1981)

Summary: The thermal copolymerization of styrene and allyl alcohol in the presence of salts like SrCl_2 , HgCl_2 , CdCl_2 , ZnCl_2 , PtCl_6 and NiCl_2 without using any radical initiator is investigated. The salts increased the rate of copolymerization. It is due to complex formation of inorganic salts with allyl alcohol which occurs on allylic group of the monomer. The inorganic salts act as chain transfer agent and do not appreciably change the reactivity ratios of the monomers. The copolymerization mechanism is also discussed.

Introduction

In earlier studies^{1,3} we reported different accelerating and inhibiting effects of some inorganic salts on the copolymerization of styrene-AN and AN-allyl alcohol systems without using any radical initiator. It is observed that the salts soluble in vinyl and allyl monomers have capability to form complexes. These complexes carry an electron accepting character resulting decrease or increase in rate of copolymerization. Salts which are not soluble in any monomer of binary mixture may decrease or increase the rate probably by adsorption of the monomer on the solid surface of the inorganic salts. The edges and defects parts of the crystals of the salts are the prominent sites for activating the monomer molecules to initiate the reaction².

In this paper we report the effects of some inorganic salts on the copolymerization of styrene and allyl alcohol without using any radical initiator. The salts are SrCl_2 , HgCl_2 , CdCl_2 , ZnCl_2 , PtCl_6 and NiCl_2 .

Experimental

Materials :

1. Styrene (E.Merck), allyl alcohol (E.Merck), Laboratory chemical grade chloroform, benzene, methanol were purified according to known methods.
2. G.R. grade hydrochloric acid of E.Merck was used.
3. All inorganic salts given as under were used without further purification, Extrapure strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$) of E.Merck, Fine crystals of mercury chloride (HgCl_2) of E.Merck, Laboratory

chemical grade nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) and cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$) of May and Baker, Extrapure anhydrous zinc chloride (ZnCl_2) of E.Merck, and Laboratory reagent grade platinum chloride ($\text{H}_2 \cdot \text{PtCl}_6 \cdot \text{H}_2\text{O}$) of B.D.H.

Copolymerization Procedure :

All reactions were conducted in glass tubes. Required amount of monomers in different proportions as shown in tables I–VII and 2×10^{-5} moles of each inorganic salt were transferred through a long stem funnel into the reaction tubes and cooled. The tubes were sealed at constriction. The reaction tubes were then heated at 100°C for 3 hours in a thermostatically controlled bath. After required reaction time, the contents of the tubes turned into viscous material. Chloroform-methanol was the solvent precipitant system for separating the copolymer prepared in the absence of inorganic salt and for the copolymer prepared in the presence of salt it was chloroform-methanol containing HCl. The copolymer does not contain cyclohexane soluble material showing that cationic polymerization of styrene does not take place⁴. All copolymer samples were white crystalline substances and soluble in chloroform. The copolymer does not show any sharp melting point and begins to melt at 160°C and completely at 180°C . Above 400°C it turns into brown colour and then an insoluble black material is left behind. The copolymer was estimated for hydroxyl ($-\text{OH}$) group.

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

Estimation of Hydroxyl (-OH) group⁵

10-15 mg copolymer sample was introduced in the capillary tube sealed at one end, 3 mm in diameter and 6 cm. in length. After introducing the sample it was weighed. Then 20-25 mg of acetic anhydride was added to capillary tube and reweighed. Four to six drops of water free pyridene was added in the tube. A small glass plunger (1x5 mm) was also added in the tube for stirring purposes. Finally the tube was sealed and set aside for 24 hours. A blank was also run simultaneously. After 24 hours, the tube was placed in 50 ml Erlenmeyer flask covered with 5 ml of distilled water and then broken by means of heavy glass rod. The release of acetic acid was titrated with standard alkali and percentage of -OH group was calculated. The accuracy of the determination was 0.1%.

The spectra of the product was recorded. These spectra indicate that -OH absorption band appears at 3076 - 3448 cm^{-1} and C = C (ar.ring) band is at 1600 - 1670 cm^{-1} wave number.

Viscosity of dilute solutions of the product prepared in chloroform was measured at $25^\circ \pm 0.5^\circ \text{C}$ using ostwald's type viscometer.

Results and discussion

The detailed results of the effects of inorganic salts on the copolymerization of styrene and allyl alcohol are summarized in tables I-VII.

The analysis of the product gave 1.02 - 2.55% hydroxyl (-OH) group whereas allyl alcohol contains 29.31% -OH group. The presence of -OH group in the product indicates that allyl alcohol has participated in the reaction and the product obtained in the presence and absence of salt is a copolymer. This is further supported by the fact that polystyrene is soluble in benzene and insoluble in chloroform whereas the product is found soluble in chloroform. The I.R. spectra of copolymer was compared with the spectra of polyallyl alcohol and polystyrene. The spectra of the product indicate that the -OH absorption band appears at 3076 - 3448 cm^{-1} and C = C (ar.ring) band is at 1600 - 1670 cm^{-1} wave number and the product is a copolymer.

Effects of inorganic salts on the copolymerization of styrene and allyl alcohol are summarized in tables I-VII. The results show the acceleration effect of SrCl_2 , HgCl_2 , CdCl_2 , ZnCl_2 , PtCl_6 and NiCl_2 . The acceleration in rate may be due to the formation of complex with

allyl alcohol (AA.Mx_n). Allyl group is only the possible site for the addition of metal salt^{3,6}.

The monomer reactivity ratios values of styrene (r_1) and allyl alcohol (r_2) were determined by Fineman and Ross methods^{7,8}. The behavior of two monomers M_1 and M_2 in free radical type of copolymerization may be described by the following relation,

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

where $[M_1]$ and $[M_2]$ represent the concentrations of styrene and allyl alcohol respectively in the reaction mixture, $d[M_1]/d[M_2]$ refers to the ratio of the two monomers in the increment of copolymer formed. This equation is useful in measuring the factors which govern copolymerization reactions. In the case of Fineman and Ross method the copolymer ratio $d[M_1]/d[M_2]$ in equation (1) is replaced by f and monomer ratio $[M_1]/[M_2]$ by F to obtain the following equation⁷,

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

The slope and the intercept of the plot $\frac{F(f-1)}{f}$ against $\frac{F^2}{f}$ are r_1 and r_2 respectively. This plot for the copolymerization of styrene and allyl alcohol in the absence of salt are shown in fig. 1. This is called mole ratio method. The modified form of equation 2 expressed in mole fraction of monomers is rewritten as,

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

where f_1 denotes the mole fraction of monomer in feed, F_1 the mole fraction of monomer in the increment of copolymer formed at the start of copolymerization reaction. A plot of $\frac{f_1(1-2F_1)}{(1-f_1)F_1}$ versus $\frac{f_1^2(F_1-1)}{(1-f_1)2F_1}$ is a straight line whose slope is r_1 and intercept is r_2 . This is called mole fraction method. The plot for the copolymerization of styrene and allyl alcohol in the absence of salt is shown in fig.2. Similarly the reactivity ratios values for the copolymerization in the presence of salt were determined by drawing the same plots which are condensed in table VIII. The reliability of the values

Table I

Copolymerization of styrene and allyl alcohol in the absence of salt at 100°C.

Expt. No.	Monomer in feed		Weight of copolymer obtained g	Analysis % - OH	Rate of Polymerization Rp x 10 ⁵ moles/l/Sec	
	Styrene g	AA g			Styrene	AA
1.	4.50	0.50	0.180	1.04	2.7701	0.1827
2.	4.25	0.75	0.439	1.56	6.6196	0.6673
3.	4.00	1.00	0.361	2.00	5.3476	0.7022
4.	3.75	1.25	0.340	2.40	4.9438	0.7931

Table II

 Copolymerization of styrene and allyl alcohol in the presence of SrCl₂ at 100°C.

Expt. No.	Monomer in feed		Weight of copolymer obtained g	Analysis % - OH	Rate of Polymerization Rp x 10 ⁵ moles/l/Sec	
	Styrene g	AA g			Styrene	AA
1.	4.50	0.50	0.025	1.07	0.3843	0.0261
2.	4.25	0.75	0.445	1.52	6.7198	0.6590
3.	4.00	1.00	0.418	2.00	6.1919	0.8131
4.	3.75	1.25	0.399	2.48	5.7860	0.9589

Table III

 Copolymerization of styrene and allyl alcohol in the presence of HgCl₂ at 100°C.

Expt. No.	Monomer in feed		Weight of copolymer obtained g	Analysis % - OH	Rate of Polymerization Rp x 10 ⁵ moles/l/Sec	
	Styrene g	AA g			Styrene	AA
1.	4.50	0.50	0.556	1.02	8.5625	0.5536
2.	4.25	0.75	0.575	1.50	8.6893	0.5404
3.	4.00	1.00	0.523	2.30	7.6476	1.1677
4.	3.75	1.25	0.464	2.45	6.7362	1.1017

Table IV

Copolymerization of styrene and allyl alcohol in the presence of $ZnCl_2$ at $100^\circ C$.

Expt. No.	Monomer in feed		Weight of copolymer obtained g	Analysis % - OH	Rate of Polymerization $R_p \times 10^5$ moles/l/Sec	
	Styrene g	AA g			Styrene	AA
1.	4.50	0.50	0.250	1.09	3.8404	0.2659
2.	4.25	0.75	0.600	1.55	9.0507	0.9061
3.	4.00	1.00	0.582	2.09	8.5952	1.1789
4.	3.75	1.25	0.542	2.44	7.8713	1.2817

Table V

Copolymerization of styrene and allyl alcohol in the presence of $PtCl_6$ at $100^\circ C$.

Expt. No.	Monomer in feed		Weight of copolymer obtained g	Analysis % - OH	Rate of Polymerization $R_p \times 10^5$ moles/l/Sec	
	Styrene g	AA g			Styrene	AA
1.	4.50	0.50	0.436	1.11	6.6930	0.4724
2.	4.25	0.75	0.471	1.49	7.1202	0.6838
3.	4.00	1.00	0.467	1.40	7.0699	0.6359
4.	3.75	1.25	0.436	2.55	6.3060	1.0775

Table VI.

Copolymerization of styrene and allyl alcohol in the presence of $NiCl_2$ at $100^\circ C$.

Expt. No.	Monomer in feed		Weight of copolymer obtained g	Analysis % - OH	Rate of Polymerization $R_p \times 10^5$ moles/l/Sec	
	Styrene g	AA g			Styrene	AA
1.	4.50	0.50	0.067	1.08	0.7648	0.0706
2.	4.25	0.75	0.248	1.52	3.7749	0.3673
3.	4.00	1.00	0.563	2.28	3.2465	1.2485
4.	3.75	1.25	0.533	2.49	7.7263	1.2862

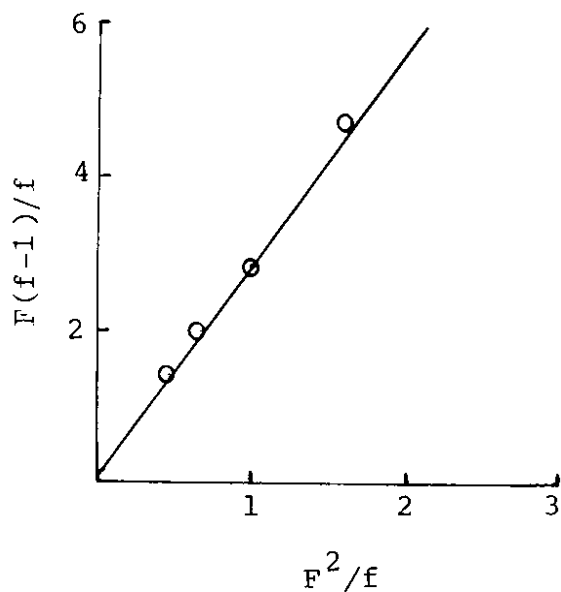


Fig. 1: A Plot of $F/f(f-1)$ against F^2/f according to the mole ratio method to obtain r_1 and r_2 for the copolymerization of styrene and AA in the absence of salt.

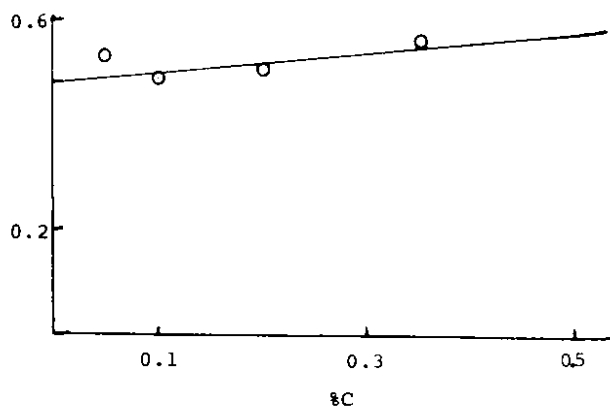


Fig. 3: A plot of mole fraction of M_1 in copolymer (F_1) against mole fraction of M_1 in feed (f_1) for the system styrene and allyl alcohol. The continuous line shows the calculated values whereas observed values are shown by circles.

were further checked by plot shown in fig.3 on the basis of mean values determined by two methods. The observed values plots were found in good agreement with calculated values plots. This suggests that the measurements are reliable⁹. The results also indicate that the reactivity ratios values are little influenced by the addition of inorganic salts¹⁰.

Since the monomer reactivity ratios of styrene is 29–35 times more reactive than that of allyl alcohol, the polymerization of the binary mixture gives an initial product which is virtually pure polystyrene. This is also supported by the $-OH$ group percentage in the copo-

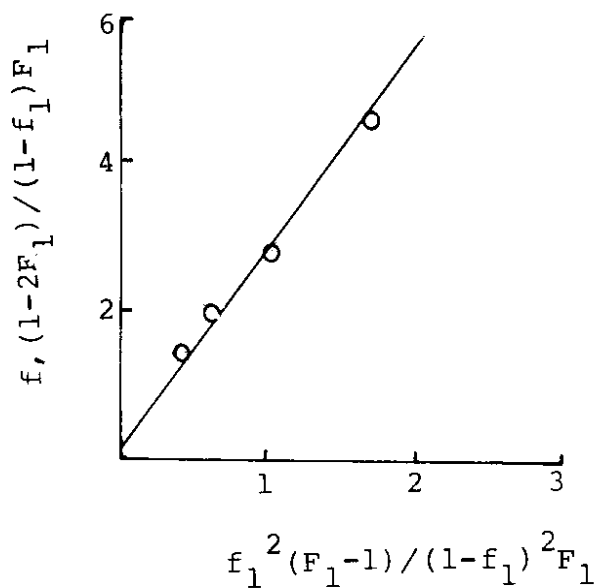


Fig. 2: A plot of $f_1(1-2F_1)/(1-f_1)F_1$ versus $-f_1^2(F_1-1)/(1-f_1)^2F_1$ according to mole fraction method to obtain r_1 and r_2 for the copolymerization of styrene and allyl alcohol in the absence of salt.

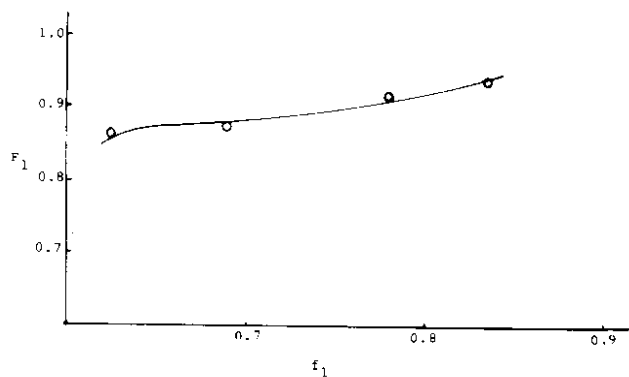


Fig. 4: A plot of Sp/C against C for the determination of intrinsic viscosity of the copolymer prepared in the absence of salt.

lymer chain indicating that even in the presence of allyl alcohol, rate of polymerization of styrene increases with increase in styrene concentration in the initial stages. The rate of polymerization ($R_p \times 10^5$ moles/l/Sec) of styrene and allyl alcohol as shown in table I–VII provide another evidence that styrene monomer enters in the copolymer chain more rapidly than allyl alcohol. The specific reactivity of styrene ($Q_1 = 1$) which is comparatively very large with specific reactivity of allyl alcohol ($Q_2 = 0.052$) suggests that styrene is more reactive than allyl alcohol. Hence polymerization of mixture of styrene and allyl alcohol forms an initial product which is almost pure poly-styrene³.

Table VII.
Copolymerization of styrene and allyl alcohol in the presence of CdCl₂ at 100°C.

Expt. No.	Monomer in feed		Weight of copolymer obtained g	Analysis % - OH	Rate of Polymerization R _p x 10 ⁵ moles/l/Sec	
	Styrene	AA			Styrene	AA
	g	g				
1.	4.50	0.50	0.333	1.06	5.1209	0.3445
2.	4.25	0.75	0.593	1.52	8.9548	0.8782
3.	4.00	1.00	0.558	2.08	8.2417	1.1288
4.	3.75	1.25	0.475	2.43	6.9009	1.1186

Table VIII
Reactivity ratios values determined by Finemann and Ross methods for styrene (r₁) and allyl alcohol (r₂) copolymerization with some inorganic salts

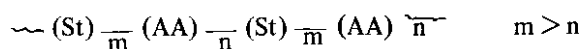
Salt added	Mole ratio method		Mole fraction method		Mean values	
	r ₁	r ₂	r ₁	r ₂	r ₁	r ₂
Blank	2.76±0.04	0.08±0.04	2.78±0.04	0.08±0.04	2.77±0.04	0.08±0.04
Strontium chloride	2.40±0.04	0.08±0.04	2.20±0.04	0.08±0.04	2.30±0.04	0.08±0.04
Mercury chloride	2.76±0.04	0.08±0.04	2.64±0.04	0.08±0.04	2.70±0.04	0.08±0.04
Cadmium chloride	2.80±0.04	0.08±0.04	2.86±0.04	0.08±0.04	2.77±0.04	0.08±0.04
Zinc chloride	2.68±0.04	0.08±0.04	2.60±0.04	0.08±0.04	2.64±0.04	0.08±0.04
Platonic chloride	2.72±0.04	0.08±0.04	2.64±0.04	0.08±0.04	2.68±0.04	0.08±0.04
Nickel chloride	2.60±0.04	0.08±0.04	2.52±0.04	0.08±0.04	2.56±0.04	0.08±0.04

Table IX.

Effects of inorganic salt on the intrinsic viscosity [η] and number average molecular weight \bar{M}_n of the copolymer prepared from styrene - AA system

Name of salt	d1/g	\bar{M}_n
Blank	0.49	97194
Strontium chloride	0.48	94487
Mercury chloride	0.40	73605
Cadmium chloride	0.42	78692
Zinc chloride	0.42	78692
Platonic chloride	0.39	71096
Nickel chloride	0.48	94487

This copolymerization system is nonazeotropic¹¹ since r₁ > 1 and r₂ < 1. In this case, the copolymer consists mostly styrene monomer units at high feed compositions of styrene, essentially a homopolymer of styrene is formed. Further more since both r₁ and 1/r₂ are greater than unity, both monomer radicals in this system prefer the same monomer i.e., styrene. The copolymer of the following type is formed.



The number average molecular weight \bar{M}_n was calculated by using the following relationship¹²,

$$[\eta] = 1.12 \times 10^{-4} \bar{M}_n^{-0.73}$$

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