

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

### Part-VII Copolymerization of Styrene and Methyl Acrylate in the Presence of Some Inorganic Salts

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The thermal copolymerization of styrene and methyl acrylate in the presence of  $\text{CoCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{CdCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{PtCl}_6$  has been investigated. Platinic chloride decreased the rate of copolymerization whereas the rest of the salts accelerate the rate. These salts act as chain transfer agents and do not change the reactivity ratio values of the monomers appreciably.

#### INTRODUCTION

Our earlier papers have established [1-2] that vinyl monomers carrying nitrile or carbonyl group form complexes with the salts soluble in the monomer. The complexation takes place through the nitrile or carbonyl group of the monomer. It has also been reported that allyl alcohol forms complexes too with salts soluble in the monomers, where allylic group is only the prominent site for the complexation [3]. These complexes accelerate or inhibit the rate of copolymerization of vinyl and allyl monomers [4-7]. In this paper we have reported the effects of inorganic salts like zinc chloride, platinic chloride, cobalt chloride, strontium chloride, and cadmium chloride, on the thermal copolymerization of binary mixture of methyl acrylate (MA) and styrene without using any radical initiator.

#### EXPERIMENTAL

##### Material

1. Methyl acrylate (BDH) was first washed with NaOH to remove the inhibitor present in the monomer, and then dried over anhydrous  $\text{CaCl}_2$  and distilled.
2. Styrene (E. Merck) was washed with NaOH for removing the inhibitor, and then washed with water. It was finally dried over  $\text{CaCl}_2$  and distilled.
3. Laboratory grade methanol, acetone, benzene, toluene, and chloroform were purified according to known methods.
4. Extra pure anhydrous  $\text{ZnCl}_2$  of E. Merck, laboratory reagent grade chloroplatinic acid ( $\text{H}_2 \text{PtCl}_6 \cdot \text{H}_2\text{O}$ ) of

BDH, cobalt chloride ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ), strontium chloride ( $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ) of E. Merck, and cadmium chloride ( $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ ) of May and Bakber were used.

##### Copolymerization Procedure

All copolymerization reactions were carried out in sealed tubes. Monomers in different proportions were transferred to the reaction tubes already containing  $2 \times 10^{-5}$  mole of each salt and sealed at constriction. The contents of the reaction tubes were heated for 4 hr. at  $100^\circ$ . After the required heating period a highly viscous liquid was obtained. The solvent precipitant system for copolymerization in the absence of salt was benzene-methanol containing HCl. The product so obtained does not contain any cyclohexane soluble material showing that the cationic polymerization of styrene does not take place. It was then estimated for methoxyl group in the form of ester. Elimination of the salt was confirmed by ash determination. The product is a hard, crystalline, and transparent substance soluble in benzene and toluene. It does not show any sharp melting point but melts into transparent liquid at  $140-200^\circ$ . Above  $350^\circ$  it first converts into brown colour; then an insoluble black material is left behind. I. R. spectra of the product were also recorded.

##### Determination of methoxyl groups [8]

The methoxyl ( $-\text{OCH}_3$ ) group was determined in the form of an ester by treating the copolymer sample with boiling hydroiodic acid using a modified Clark apparatus. By this treatment the  $-\text{OCH}_3$  group was split off and converted into methyl iodide. Methyl iodide so formed was determined iodometrically. The method was standardized by the analysis of poly (methyl acrylate). The accuracy of

\* BCCIFoundation, Labore-11.

the determination was 0.3%.

## RESULTS AND DISCUSSION

The estimation of the prepared sample of poly (MA) gave 35.7%  $-OCH_3$  group while that of the resulting product of all samples contains 10.15-12.5%  $-OCH_3$  group. This difference in the percentage of  $-OCH_3$  group may be due to the attachment of methyl acrylate in the product prepared in the presence or absence of inorganic salts. This suggests that this product is a copolymer. Further, each sample was found soluble in benzene whereas polystyrene and polymethyl acrylate were soluble in benzene and acetone respectively. The solubility of the product in benzene may be another evidence in support of the  $-OCH_3$  group analysis. Infrared spectral studies also support these results. The spectrum of poly (MA) indicates carbonyl band at  $1720\text{ cm}^{-1}$  wave number while the spectra of the product shows carbonyl band at  $1780\text{-}1725\text{ cm}^{-1}$  wave number and  $C=C$  (ar.ring) band at  $1590\text{-}1640\text{ cm}^{-1}$  wave number.

The results obtained from the copolymerization of styrene and methyl acrylate in the absence and presence of inorganic salts are given in Tables 1-6. The results indicate the acceleration effect of  $CoCl_2$ ,  $CdCl_2$ ,  $ZnCl_2$  and  $Sr_2Cl_2T_2$  whereas  $PtCl_6$  decreased the rate. Zinc chloride and platinum chloride are soluble in methyl acrylate while the rest of the

salts are insoluble in this monomer. This is why  $CoCl_2$ ,  $CdCl_2$  and  $SrCl_2$  do not form complexes with methyl acrylate while  $PtCl_6$  and  $ZnCl_2$  may form complexes in the 1:1 (MA:salt) molar ratio. The complexation takes place through the carbonyl group of methyl acrylate [2]. These complexes are hygroscopic and soluble in chloroform and acetone. Therefore the acceleration effect of  $ZnCl_2$  was probably due to the formation of a complex with methyl acrylate. The complexation results in a delocalization of  $\pi$ -electrons in the double bond of the complexed monomer and can increase its electron accepting character [4], but in the case of  $PtCl_6$ , the major portion of MA may be converted into a complex and a sufficient amount of methyl acrylate is not left in this system to serve as a solvent and styrene also does not work as a solvent for the complex. Instead of accelerating the reaction it decreases the rate [9-10]. The other probable reason for decrease in the rate may be due to the polymerizability of the complex which is controlled by polar interaction between the monomer and macro radical, suggesting that different inorganic salts have different effects on the rate despite the formation of complex with the monomer [5-7].

Salts like  $CoCl_2$ ,  $CdCl_2$  and  $SrCl_2$  are insoluble in styrene and methyl acrylate and do not form complexes in solution. When a binary mixture of styrene and methyl acrylate is heated in the presence of these salts, the

Table 1. Copolymerization of styrene and methylacrylate (MA) in the absence of inorganic salt at  $100^\circ$  for 4 hr.

S.No.	Monomer in feed		Weight of copolymer g	Analysis $-OCH_3$ %
	Styrene g	MA g		
1.	4.00	1.00	0.258	10.41
2.	3.75	1.25	0.218	11.16
3.	3.50	1.50	0.199	11.64
4.	3.00	2.00	0.150	12.19

Table 2. Copolymerization of styrene and methylacrylate (MA) in the presence of  $CoCl_2$  at  $100^\circ$  for 4 hr.

S.No.	Monomer in feed		Weight of copolymer g	Analysis $-OCH_3$ %
	Styrene g	MA g		
1.	4.00	1.00	0.374	10.70
2.	3.75	1.25	0.350	11.10
3.	3.50	1.50	0.307	11.90
4.	3.00	2.00	0.260	12.20

Table 3. Copolymerization of styrene and methyl acrylate in the presence of  $SrCl_2$  at  $100^\circ$  for 4 hr.

S. No.	Monomer in feed		Weight of copolymer g	Analysis $-OCH_3$ %
	Styrene g	MA g		
1.	4.00	1.00	0.255	10.25
2.	3.75	1.25	0.248	11.05
3.	3.50	1.50	0.198	11.95
4.	3.00	2.00	0.169	12.25

Table 4. Copolymerization of styrene and methyl acrylate (MA) in the presence of zinc chloride at  $100^\circ$  for 4 hr.

S.No.	Monomer in feed		Weight of copolymer g	Analysis $-OCH_3$ %
	Styrene g	MA g		
1.	4.00	1.00	0.492	10.82
2.	3.75	1.25	0.466	11.65
3.	3.50	1.50	0.435	11.92
4.	3.00	2.00	0.353	12.50

initiation reaction takes place by the adsorption of the reacting monomers on the solid surface of inorganic salts [11]. Boundaries between the crystals and cracks and imperfections of the salt probably act as active centres. After adsorption on the solid surface, interaction takes place between the adsorbed species and sorbed species and one from homogeneous phase on the solid surface. The chain carriers are initiated at the surface by opening the double bond of the reactants and carried into the homogeneous phase where the polymer chain propagates. The sorbed layer is very loosely bound to the surface of inorganic salts and can migrate relatively from one surface site to another. The mechanism of such activation is not clear. However it may be concluded that the monomer molecules get activated and initiate the reaction by opening the double bond of the reacting monomers.

The values of the monomer reactivity ratios of styrene ( $r_1$ ) and methyl acrylate ( $r_2$ ) were determined [3-7] by the Fineman and Ross methods [12], which are shown in Table 7. These values for copolymerization in the absence

of the salt are determined as  $r_1=0.283$  and  $r_2=0.20$ . Similarly the values of  $r_1$  and  $r_2$  for copolymerization in the presence of salts are determined respectively as 0.23-0.283 and 0.20. This shows that addition of salt does not change the values of monomer reactivity ratio values appreciably.

The number average molecular weight ( $\bar{M}_n$ ) was calculated by using the following intrinsic viscosity  $[\eta]$  and molecular weight relationship [13].

$$[\eta] = 0.979 \times 10^{-4} \bar{M}_n^{0.744}$$

The intrinsic viscosity of the copolymer sample prepared in the absence of inorganic salts was determined as 2.39 dl/g. The number average molecular weight  $\bar{M}_n$  of the sample was calculated from this value is 789470. The intrinsic viscosity of the copolymer samples prepared with different inorganic salts was determined in the range 1.6-2.31 dl/g. The number average molecular weight calculated from these values lies in the range 464349-754152 as shown in Table 8. The decrease in molecular weight with

Table 5. Copolymerization of styrene methyl acrylate (MA) in the presence of  $\text{CdCl}_2$  at  $100^\circ$  for 4 hr.

S.No.	Monomer in feed		Weight of copolymer g	Analysis -OCH <sub>3</sub> %
	Styrene g	MA g		
1.	4.00	1.00	0.332	10.55
2.	3.75	1.25	0.321	11.15
3.	3.50	1.50	0.300	11.80
4.	3.00	2.00	0.267	12.45

Table 6. Copolymerization of styrene and methyl acrylate (MA) in the presence of platinum chloride at  $100^\circ$  for 4 hr.

S. No.	Monomer in feed		Weight of copolymer g	Analysis -OCH <sub>3</sub> %
	Styrene g	MA g		
1.	4.00	1.00	0.142	10.15
2.	3.75	1.25	0.125	11.08
3.	3.50	1.50	0.118	11.90
4.	3.00	2.00	0.102	12.05

Table 7. Reactivity ratio values determined by the Fineman and Ross methods for styrene ( $r_1$ ) and methyl acrylate ( $r_2$ ) copolymerization in the presence of different inorganic salts

Salt added	Mole ratio method		Mole fraction method		Average values	
	$r_1$	$r_2$	$r_1$	$r_2$	$r_1$	$r_2$
Blank	0.283±0.02	0.20±0.02	0.275±0.02	0.20±0.02	0.279±0.02	0.20±0.02
Cobalt chloride	0.267±0.02	0.20±0.02	0.250±0.02	0.20±0.02	0.259±0.02	0.20±0.02
Strontium chloride	0.280±0.02	0.20±0.02	0.280±0.02	0.20±0.02	0.280±0.02	0.20±0.02
Zinc chloride	0.23±0.02	0.20±0.02	0.230±0.02	0.20±0.02	0.230±0.02	0.20±0.02
Cadmium chloride	0.270±0.02	0.20±0.02	0.270±0.02	0.20±0.02	0.270±0.02	0.20±0.02
Platinic chloride	0.280±0.02	0.20±0.02	0.273±0.02	0.20±0.02	0.278±0.02	0.20±0.02

the addition of inorganic salt support that chain transfer takes place because to the presence of an inorganic salt.

Table 8. Effect of inorganic salts on intrinsic viscosity  $[\eta]$  and number average molecular weight  $\bar{M}_n$  of the copolymer prepared from styrene methylacrylate system

Name of salt	$[\eta]$ dl/g	$\bar{M}_n$
Blank	2.39	789470
Cobalt chloride	1.60	460349
Strontium chloride	1.66	483700
Zinc chloride	1.85	559544
Cadmium chloride	2.31	754152
Platinic chloride	1.72	507345

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