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Effects of Inorganic salts on the Copolymerization of Vinyl and allyl Monomers Part-II Copolymerization of Styrene and Acrylonitrile in the Presence of some Inorganic salts

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Summary: The thermal copolymerization of styrene and acrylonitrile in the presence of inorganic salts like $SrCl_2$, $CdCl_2$, $MnCl_2$ and $NiCl_2$ was investigated. The decreasing effects of these salts on the rate was observed. The initiation reaction takes place thermally by the adsorption of the reacting monomers on the solid surface of inorganic salts. The addition of salt doesnot appreciably change the reactivity ratio values of the monomer. The lowering of molecular weight suggests that salts behave as a chain transfer agents.

Introduction

In the earlier paper, (1) the effects of some inorganic salts on the copolymerization of styrene and acrylonitrile was reported. The salts were soluble in acrylonitrile and formed complexes with the monomer through nitrile group. The complexation of the monomer with the metal halide increases its electron accepting character and helps in stabalizing the transition state of the reaction. But those salts which are not soluble in the monomers and donot form complexes may decrease or increase the rate of thermal initiated copolymerization. It may be prorably due to absorption and or adsorption of the reacting monomers on the solid surface of the inorganic salts.

This paper deals with the copolymerization of styrene and acrylonitrile in the presence of such salts which are not soluble in either monomer without using any radical initiator. These salts are $SrCl_2$, $MnCl_2$, $CdCl_2$ and $NiCl_2$.

Experimental

Materials:

1. Acrylonitrile (BDH), styrene (E. Merck) and Laboratory grade of methanol, acetone, benzene and DMF were purified according to usual methods.
2. G. R. grade hydrochloric acid of E. Merck was used.
3. All inorganic salts given as under were used without further purification. Strontium chlride ($SrCl_2.2H_2O$) and Manganese chloride ($MnCl_2, 4H_2O$) of E. Merck and laboratory grade cadmium chloride ($CdCl_2.5H_2O$) and nickel chloride ($NiCl_2, 6H_2O$) of May and Baker Co.

Copolymerization Procedure

All copolymerization reactions were carried out in sealed tubes. A known amount of acrylonitrile, stryene and salt ($2x10^{-5}$ moles) were added into the reaction tubes and sealed at the constriction. The tubes were heated at 100°C for 2 hours in thermostatically controlled bath and then the seal was broken open. The copolymer was separated with methanol containing HCl. Finally it was washed with a portion of methanol to remove hydrochloric acid. The copolymer so obtained does not contain cyclohexane soluble material showing that the cationic polymerization of styrene does not take place (2). The copolymer obtained is white crystalline solid substance soluble in acetone, DMF and benzene. It does not show any sharp melting point. At 250°C it turns into brown substance and above 350° the substance decomposes into insoluble black material.

The copolymer samples were analysed for nitrogen by kjeldahl's method. I.R. spectra in KBR pellets were also recorded. Nitrile absorption band shows frequency in the range 2250-2275 cm^{-1} and C=C (ar. rings) absorp-

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tion band appears at 1600-1615 cm^{-1}. The Viscosity of copolymer samples were determined by Ostwald's Viscometer in a thermostatically controlled bath at 25°C.

Results and Discussion

The effects of inorganic salts on the copolymerizaton of styrene and acrylonitrile are shown in table I-V.

The results Show that the analysis of poly-acrylonitrile (PAN) gave 26.2% nitrogen whereas the product give 3.66-7.08% nitrogen. The difference in percentage of nitrogen contents may be due to the addition of styrene in the polymer chain of acrylonitrile suggesting that the product obtained in the presence or absence of salts is a copolymer. This is further supported by the fact that Polystyrene andpoly-acrylonitrile are soluble in benzene and DMF respectivley while the product is also soluble in acetone. The presence of nitrile band at 2250-2275 cm^{-1} and C=C (ar. ing) at 1600-1615 cm^{-1} clearly indicates that the product is a copolymer.

The results summerized in table 1-V show that the addition of inorganic salts like $SrCl_2$, $CdCl_2$, $MnCl_2$ and $NiCl_2$ decreased the rate of copolymerizatiqn. Probably, it is because the salts are insoluble in either monomer and donot form complexes. The effects has been observed in the polymerization of vinyl acetate, vinyl chloride, vinylidene chloride since $ZnCl_2$ is insoluble in these monomers (2-3).

According to the present findings both styrene and acrylonitrile are polymerized separately in the presence of inorganic salt by thermal activation though degree of

Table 1. Copolymerization of styrene and acrylonitrile in the absence of salt.

Expt. No.	Monomer in feed St. gm	AN gm	Weight of copolymer obtained. gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/1/Sec. St.	AN.
1.	4.5	0.50	0.265	3.77	5.4371	1.7762
2.	3.75	1.25	0.345	5.04	6.5527	3.0316
3.	3.25	1.75	0.365	5.99	6.4896	3.7347
4.	3.00	2.00	0.260	6.53	4.6674	3.0077

Table 2. Copolymerization of styrene and acrylonitrile in the presence of strontium chloride.

Expt. No.	Monomer in feed St. gm	AN gm	Weight of copolymer obtained. gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/1/Sec. St.	AN.
1.	4.50	0.50	0.139	3.83	2.8442	0.9465
2.	3.75	1.25	0.288	5.02	5.4748	2.5207
3.	3.25	1.75	0.29	5.12	5.4205	2.5571
4.	3.00	2.00	0.34	5.14	6.5302	3.0959

Table 3. Copolymerization of styrene and acrylonitrile in the presence of cadmium chloride.

Expt. No.	Monomer in feed		Weight of copolymer obtained. gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/l/Sec.	
	St.	AN			St.	AN
1.	4.50	0.50	0.078	3.66	1.6081	0.5078
2.	3.75	1.25	0.298	4.86	5.7071	2.5251
3.	3.25	1.75	0.300	6.90	5.1386	3.5652
4.	3.00	2.00	0.255	6.91	4.4903	3.1215

Table 4. Copolymerization of styrene and acrylonitrile in the presence of manganese chloride.

Expt. No.	Monomer in feed		Weight of copolymer obtained. gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/l/Sec.	
	St.	AN			St.	AN
1.	4.50	0.50	0.170	4.00	3.4523	1.2089
2.	3.75	1.25	0.256	5.03	4.8643	2.2451
3.	3.25	1.75	0.256	6.96	4.3711	3.0688
4.	3.00	2.00	0.183	6.98	3.2108	2.2628

Table 5. Coplolymerization of styrene and acrylonitrile in the presence of nickel chloride.

Expt. No.	Monomer in feed		Weight of copolymer obtained. gm	Analysis N%	Rate of Polymerization $R_p \times 10^5$ moles/l/Sec.	
	St. gm	AN gm			St.	AN
1.	4.50	0.50	0.214	3.84	4.3769	1.4609
2.	2.75	1.25	0.377	5.56	6.9857	3.6546
3.	3.25	1.75	0.341	6.58	5.9365	3.8645
4.	3.00	2.00	0.300	7.08	5.2582	3.7202

polymerization of acrylonitrile is low as compared with styrene. Supposedly styrene or acrylonitrile doesnot act as co-catalyst and hence donot form complex with inorganic salt on the solid surface. During reaction, the monomer comes in contact with inorganic salt and is absorbed by the salt. This monomer molecules then get activated with an ability to initiate the reaction. There are many references found in the literature (4-9) that this type of initiation may take place thermally by the adsorption of the monomer on the solid surface of the salt. The edges and defects parts of the crystals of metal salts are prominent sites, for activating the monomer molecules to initaite the reaction$^{(10)}$. In this type of activation, the polymer grow rapidly. The initial compolymerization reaction of the monomer occurs on the crystal at these defects part of exposed metallic atoms would be found during the initial stages of polymerization reaction. During reaction the reactants first diffuse from homogeneous phase to the solid surface of salt and then get adsorbed making a layer on the available surface. After adsorption of the one or both monomers, the interaction between adsorbed species or sorbed species and one from homogeneous phase takes place. The monomer molecules are probably activated by this process. Hence the radicals are formed and polymer chain begins to grow rapidly. The mechanism of such activation is still not clear. However it may be said that the chain carriers are initiated at the surface by opening the double bond of the monomer and carried out into the reacting mixture where the polymer chain begins to propagate and ultimately the growing polymer gets deposited in the form of thick layer onthe solid surface of crystals of inerganic salts resulting decrease in rate of copolymerization. The decrease in rate is due to small available surface of the crystals at these temperatures.

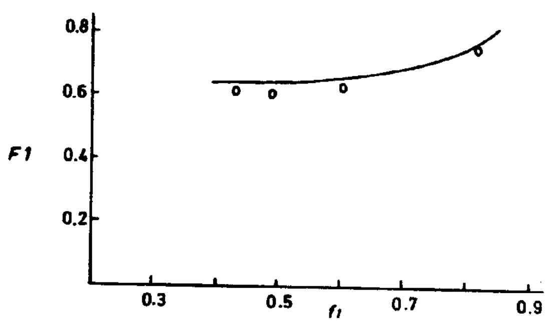

Figure No. 1: A plot of mole faction of M_1 in copolymer (E_1) against mole fraction of M_1 in feed (f_1) for the system styrene-acrylonitrile. Coninous line represents calculated values plot whereas circles show observed values plot.

The monomer reactivity ratios of styrene (r_1) and acrylonitrile (r_2) were detemined graphically by mole ratio and mole fraction methods$^{(11-12)}$. The values of r_1 and r_2 obtaine9 are summerized in table VI. The reliability of the values were further checked by plot shown in fig. 1 on the basis of mean of the values determined by two methods. The observed values plots were found in good agreement with the calculated values plots.

The number average molecular weight (Mn) was calculated by using the following relationship (13)

$$\eta_{sp} = 3.92 \times 10^{-4} \text{ Mn } 0.75$$

Table 5. Reactivity ratios determined by Finemann & Ross methods for styrene (r_1) and AN (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	0.58±0.20	0.08±0.02	0.60± 0.02	0.08±0.02	0.59 ±0.02	0.08±0.02
Strontiun chloride.	0.49±0.02	0.08±0.02	0.48±0.02	0.08±0.02	0.485±0.02	0.08±0.02
Cadmium chloride.	0.57±0.02	0.08±0.02	0.55±0.02	0.08±0.02	0.56 ±0.02	0.08±0.02
Manganese chloride.	0.42±0.02	0.08±0.02	0.41±0.02	0.08±0.02	0.415±0.02	0.08±0.02
Nickel chloride.	0.42±0.02	0.08±0.02	0.39±0.02	0.08±0.02	0.405±0.02	0.08±0.02

Where η_{sp} is the intrinsic viscosity of the polymer solution prepared in DMF. The intrinsic viscosity is obtained by poltting η_{sp}/C against C. Here η_{sp} is the specific viscosity and C is the concentration of solution. The intrinsic viscosity of the copolymer samples prepared in the presence of salt ranges from 2.38 to 2.76 dl/g. The number average molecular weight Mn calculated from these values obtained in the range 110761 to 134947 as given in table VII. The intrinsic viscosity of the copolymer sample prepared in the absence of salt was found 2.77 dl/g which gives the value of Mn as 135600. The lowering of molecular weight due to the addition of salt suggests that the inorganic salts act as chain transfer agent (2).

Table 7; Effect of Inorganic Salts on Intrinsic Viscosity [η] and number average molecular weight Mn of the Copolymer prepared from styrene – acrylonitrile.

Name of salt.	[η] dl/g.	Mn
Blank	2.77	135600
Strontium Chloride.	2.38	110761
Cadmium Chloride.	2.75	134296
Manganese Chloride.	2.70	131050
Nickel Chloride.	2.76	134947

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