HOMOPOLYMERIZATION OF ALLYL ALCOHOL AND PREPARATION OF COMPLEXES OF ALLYL ALCOHOL WITH SOME INORGANIC SALTS **

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The homopolymerization of allyl alcohol was carried out at 100° in the presence of inorganic salt without using any radical initiator. The monomer homopolymerizes but degree of polymerization is low enough. The complexes of allyl alcohol are also prepared with some inorganic salts like $CuCl_2$, $CoCl_2$ $HgCl_2$, $ZnCl_2$, $NiCl_2$, $SrCl_2$, $MnCl_2$, $PtCl_6$ and $CrCl_3$. Allyl alcohol forms complexes with $PtCl_6$ and $CuCl_2$ in 1:1 (AA/salt) molar ratio whereas rest of the above salts combines in the 1:2 molar ratio These complexes are hygroscopic and viscous material soluble in alcohol and acetone.

INTRODUCTION

In our earlier paper [1], it has been reported that the salts like $ZnCl_2$, $CrCl_3$, $CoCl_2$, $HgCl_2$, $CuCl_2$ and $PtCl_6$ forms complex with AN due to the soluble behaviour of the salts with the monomer. The complexes of acrylonitrile with salt undergo polymerization easier than uncomplexed monomer without using any radical initiator. The accelerating or inhibiting effects of these complexes on the copolymerization of vinyl of allyl monomers has been found.

Allyl monomers may be homopolymerized by a variety of free radicals initiators. Generally the polymerization rate is enough slower than vinyl monomers [2—3]. But allyl monomers copolymerize rapidly with a number of vinyl monomers like styrene, acrylonitrile etc [4, 5]. It is also observed that allyl alcohol may form complexes with the salts soluble in the monomer. This paper deals with the polymerization of allyl alcohol and preparation of complexes of allyl alcohol with inorganic salts like $ZnCl_2$, $CrCl_3$, $CoCl_2$, $HgCl_2$, $CuCl_2$, $PtCl_6$, $CdCl_2$, $SrCl_2$, $NiCl_2$, and $MnCl_2$.

EXPERIMENTAL

1) Allyl alcohol (E. Merck) was dried over sodium sulphate and thus distilled at 97°. The middle third fraction was used. Laboratory grade methanol and acetone were purified by usual methods.

2) All inorganic salts given as under were used without further purification. Extrapure copper chloride ($CuCl_2$ $2H_2O$), cobalt chloride ($CoCl_2$, $6H_2O$), strontium chloride ($SrCl_2$, $6H_2O$), and mangenese chloride ($MnCl_2$, $4H_2O$), of E. Merck: Fine crystals of mercury chloride of E. Merck ($HgCl_2$): Laboratory chemical grade nickel chloride ($NiCl_2$, $6H_2O$) and cadmium chloride ($CdCl_2$ 2. $5H_2O$) of May and Baker, Extrapure anhydrous zinc chloride ($ZnCl_2$) of E. Merck, Laboratory grade chloroplatanic acid ($H_2PtCl_6.H_2O$) of B.D.H. and Analar grade chromium chloride ($CrCl_3.6H_2O$).

Procedure of Homopolymerization of Allyl Alcohol with Salt without using any Radical Initiator. A known quantity of allyl alcohol was transferred to reaction tube containing $4x10^{-4}$ mole percent inorganic salt. The reaction tube was sealed at constriction and than heated at 100° for 10 hours. After required time of heating the tubes were cooled down and than sealed was broken open. No solid substance was separated out. The difference in viscosity of the contents before and after heating was determined at 30° by using ostwald's type viscometer as given in Table 1.

Procedure of Preparation of Complexes. A known amount of salt was dissolved in excess allyl alcohol by heating at 70° for an hour. Excess alcohol was then distilled off. The resulting substance was further kept for 24 hours in vacuum deniccator. The composition of the complexes was determined from the weight of the complex and of inorganic salt initially taken. The detailed results are summarized in Table 2. The weight difference shows that platynic chloride and copper chloride form complexes in the 1:1 (AA/salt) molar ratio. Similarly $ZnCl_2$, $CoCl_2$, $HgCl_2$, $CdCl_2$, $NiCl_2$, $CrCl_3$, $SrCl_2$ and $MnCl_2$ combines with allyl alcohol to form complex in 1:2 molar ratio. The complexes are hygroscopic viscous material soluble in alcohol and methanol.

**From Ph. D. thesis

Table 1. Effect of 4×10^{-4} mole percent inorganic salt on polymerization of allyl alcohol for 10 hours heating at 100°, viscosity was determined at 30°.

Salt added	Viscosity of AA before heating in C.S.	Color of solution before heating	Viscosity of AA after heating in C.S.	Colour of solution after heating
Blank	1.4764	Colourless	1.4782	Colourless
Copper chloride	1.5610	Yellowish green	1.5620	Pale yellow
Cobalt chloride	1.4902	Blue	1.5009	Blue
Strontium chloride	1.5048	Colourless	1.5128	Colourless
Mercury chloride	1.5261	Colourless	1.5381	Yellowish
Cadmium chloride	1.5155	Colourless	1.5468	Colourless
Mangenese chloride	1.5408	Colourless	1.5567	Colourless
Zinc chloride	1.5229	Colourless	1.5754	Colourless
Platynic chloride	1.5168	Light brown	1.5221	Browb
Nickel chloride	1.4806	Green	1.4862	Yellowish
Chromium chloride	1.4902	Green	1.5009	Dark green

Table 2. The composition of complexes of allyl alcohol with some inorganic salts.

Name of salt	Amount of salt (moles)	Amount of AA consumed (moles)	Composition of complex AA/salt molar ratio	IR Spectra	Physical properties
$CuCl_2.2H_2O$	2.933×10^{-4}	2.700×10^{-4}	0.920	$-OH$ 3485 cm^{-1} $CH_2=CH-CH_2$ 1740 cm^{-1}	Greenish viscous subsance, soluble in alcohol and acetene.
$CoCl_2.6H_2O$	2.103×10^{-4}	4.640×10^{-4}	2.206	$-OH$ 3485 cm^{-1} $CH_2=CH-CH_2$ 175 cm^{-1}	Bluish viscous substance soluble in alcohol & acetone.
$SrCl_2.6H_2O$	1.876×10^{-4}	3.940×10^{-4}	2.100	$-OH$ 3485 cm^{-1} $CH_2=CH-CH_2$ 1750 cm^{-1}	Colourless viscous substance soluble in alcohol & acetone.
$HgCl_2$	1.842×10^{-4}	3.790×10^{-4}	2.057	$-OH$ 3510 cm^{-1} $CH_2=CH-CH_2$ 1750 cm^{-1}	Brown viscous substance soluble in alcohol & acetone.
$CdCl_2$ 2.5H$_2$O	2.190×10^{-4}	5.165×10^{-4}	2.358	$-OH$ 3570 cm^{-1} $CH_2=CHCH_2$ 1740 cm^{-1}	White viscous substance, soluble in alcohol & acetone.
$MnCl_2$	2.527×10^{-4}	5.165×10^{-4}	2.044	$-OH$ 3425 cm^{-4} $CH_2=CHCH_2$ 1785 cm^{-1}	Light brown viscous substance soluble in alcohol & acetone.
$ZnCl_2$	3.669×10^{-4}	8.520×10^{-4}	2.322	$-OH$ 3415 cm^{-1} $CH_2=CHCH_2$ 1740 cm^{-1}	Brownish viscous substance, soluble in alcohol & acetone
$H_2PtCl_6.H_2O$	1.169×10^{-4}	1.205×10^{-4}	1.031	$-OH$ 3450 cm^{-1} $CH_2=CHCH_2$ 1750 cm^{-1}	Dark brownish substance soluble in alcohol & acetone.
$NiCl_2.6H_2O$	2.104×10^{-4}	4.430×10^{-4}	2.044	$-OH$ 3450 cm^{-1} $CH_2=CHCH_2$ 1750 cm^{-1}	Greenish viscous substance soluble in alcohol and acetone.
$CrCl_3$	1.877×10^{-4}	3.634×10^{-4}	1.936	$-OH$ 3510 cm^{-1} $CH_2=CH_2CH$ 1750 cm^{-1}	Dark brown substance soluble in alcohol & acetone.

RESULTS AND DISCUSSION

The copolymerization of allyl alcohol in the presence of inorganic salts without using any radical initiator are described in Table 1.
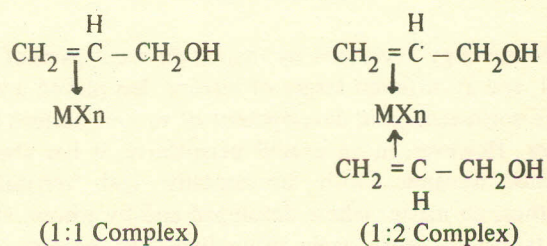
On heating allyl alcohol in the presence of metal halides, no solid substance was separated out. The difference in viscosity of the contents before and after heating shows that some polymer is indeed formed although the degree of polymerization appeared to be very low. The difference in viscosity before and after heating the monomer with salt also shows that the rate of polymerization of allyl alcohol is maximum with $ZnCl_2$ whereas minimum with copper chloride. IR spectra of the viscous material obtained after evaporating unreacted allyl alcohol show OH absorption band at a frequency 3335 cm^{-1} supporting the formation of poly-allyl alcohol. The detailed results are shown in Table 1. Similarly Kargin *et al.* [6] also supporte that the polymerization during preparation of polyally alcohol by radical initiator is increased by the presence of $CaCl_2$, $MgCl_2$, LiCl, $ZnBr_2$, HCl and H_3PO_4 in the monomer. Addition of $CaCl_2$ also increased the molecular weight from 1000 to 500000 of polyallyl alcohol.

Polak *et al.* [7] prepared high molecular weight poly-allyl alcohol by radical polymerization of the monomers in the presence of inorganic acids or their salts and group I and group II metals. It is now suggested that allyl alcohol in the presence or absence of salt without using any radical initiator may form free radicals under thermal activation. Besides these chain transfer with monomer is more important in allyl polymerization because of the ability of the allyl radical to be stablized by resonance, this stabilitization provides the driving force for the abstraction of hydrogen atom. Gaylard *et al.* [8] 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. Hence allyl alcohol may produce free radicals and homopolymerizes, though degree is very low but considerable.

$$\sim\!\!\sim A\dot{A} + AA \longrightarrow AA-A\dot{A} \sim\!\!\sim$$

It is a tendency of vinyl and allyl monomers that they form complexes with inorganic salts if the salts are soluble in the monomer. The salts underdiscusssion are soluble in allyl alcohol and therefore may form complexes with each salt. The detailed results are given in Table 2. The IR spectral studies of these complexes show that —OH absorption band shifts [9, 10] from 3335 cm^{-1} to 3570 cm^{-1} frequency, whereas allyl band shifts from 1700 to 1785 cm^{-1}. There is no possibility of complexation on —OH group of the monomer. Allyl group [11] is only the possible place for the addition of metal salt. Further the weight difference (Table 2) show that $PtCl_6$ and $CuCl_2$ form complexes in the 1:1 molar ratio whereas $ZnCl_2$, $CoCl_2$, $HgCl_2$ $CrCl_3$, $CdCl_2$, $NiCl_2$, $SrCl_2$ and $MnCl_2$ combines with allyl alcohol in the 1:2 (AA/salt) molar ratio to form complexes. All these complexes are viscous material soluble in alcohol and acetone etc. These results suggest that allyl alcohol may form complexes with each salt mentioned above in different molar ratios and allylic group takes part in complexation. The formation of these complexes enhances the polarity of allyl alcohol and hence reaction takes place more easily. These complexes defintely stablizes the transition state of reaction and results an increase in rate of polymerization [12]. The complexation may be due to delocalization of electrons in the double bond of complexed monomers. The possible structures of these complexes may be suggested as under.

$$
\begin{array}{cc}
\overset{H}{\underset{\downarrow}{CH_2 = C - CH_2OH}} & \overset{H}{\underset{\downarrow}{CH_2 = C - CH_2OH}} \\
MXn & MXn \\
 & \uparrow \\
 & CH_2 = C - CH_2OH \\
 & H \\
(1:1\ Complex) & (1:2\ Complex)
\end{array}
$$

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