

## Copolymerization of Acrylonitrile & Ethyl Methacrylate in Presence of Zinc Chloride

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The kinetics of copolymerization of acrylonitrile (AN) with ethyl methacrylate (EMA) in DMF solution in the presence of zinc chloride have been investigated. It is observed that the rate of the reaction as well as the molecular weight of the obtained polymers increase with increasing concentration of  $ZnCl_2$ . The intrinsic viscosities of the resultant polyacrylonitrile, polyethyl methacrylate and their copolymers increase with the addition of  $ZnCl_2$  in the system. The relative rate of the reaction increases as the concentration of AN is increased in the monomer feed. The results are explained on the basis of interactions of  $ZnCl_2$  with the monomers and the obtained radicals during polymerization.

THE rate of polymerization of polar vinyl monomers such as acrylonitrile and methyl methacrylate (MMA) has been shown<sup>1-7</sup> to increase in the presence of Lewis acids such as  $ZnCl_2$ ,  $AlBr_3$  etc. These salts also affect the composition and structure of the resultant copolymers. This property of the Lewis acids has been exploited in the production of polymers of required properties. This also helps in differentiating between two groups of reacting co-monomers. In the first group, the two monomers can form complexes with Lewis acids, for example, via the oxygen atom of the carbonyl group as in the copolymerization of MMA with methyl acrylate (MA) or butyl acrylate (BA). In the second group, one of the two monomers can form a complex with these complexing agents but the other one cannot, e.g. copolymerization of MMA with styrene, 2,6-dichlorostyrene or *p*-chlorostyrene<sup>6</sup>.

The present work reports the effect of  $ZnCl_2$  on the copolymerization behaviour of acrylonitrile and ethyl methacrylate in solution medium. For the kinetic investigation homo- and copolymerization of acrylonitrile and ethyl methacrylate at different concentrations of zinc chloride have been studied.

The reactions in question are considered to be multicomponent systems, i.e. between free acrylonitrile, free ethyl methacrylate and acrylonitrile, ethyl methacrylate complexed with zinc chloride etc.

### Materials and Methods

Acrylonitrile (BDH) was distilled under nitrogen and the fraction distilling at  $76.5-77.5^\circ$  was used. Ethyl methacrylate (Koch-Light) was washed several times with 5% aq. sodium hydroxide followed by distilled water, dried and fractionated under nitrogen, b.p.  $117.5^\circ$ . Azobisisobutyronitrile (ABIN) was purified by recrystallizing the commercial grade sample

from ethyl alcohol, m.p.  $104^\circ$ . Anhydrous zinc chloride was heated at  $150^\circ$  for several hours *in vacuo* before use.

**Polymerization** — The rate of the polymerization was determined using dilatometric method. Acrylonitrile or/and ethyl methacrylate in the required molar ratios were mixed and known amounts of dimethylformamide and azobisisobutyronitrile added. To this mixture a calculated amount of  $ZnCl_2$  was also added. The mixture was then introduced into a dilatometer, flushed with nitrogen, sealed and then immersed in a thermostat at  $60 \pm 0.1^\circ$ . The decrease in the volume during initial polymerization was measured as a function of time. After a given time, the dilatometer was emptied by suction to isolate the polymer. The obtained polymer was purified using the following solvent-precipitant systems: acetone-water for polyethylmethacrylate and acrylonitrile-ethyl methacrylate copolymer and dimethylformamide-water systems for polyacrylonitrile. The polymer was then dried at  $60^\circ$  *in vacuo*.

Viscosities of the obtained polymers were measured in acetone at  $30 \pm 0.1^\circ$ , using Ubbelohde-type viscometer. The viscosity of polyacrylonitrile was measured in dimethylformamide at  $30 \pm 0.1^\circ$ .

IR spectra of acrylonitrile or ethyl methacrylate in the absence and presence of  $ZnCl_2$  were measured by the Nygel method using SP 200 G grating spectrophotometer (Germany).

### Results and Discussion

The homo- and co-polymerizations of acrylonitrile (AN) and ethyl methacrylate (EMA) in the presence of  $ZnCl_2$  were initiated by azobisisobutyronitrile (ABIN) at  $60^\circ$  in the presence of dimethylformamide (DMF) as a solvent. In such investigation bulk polymerization of AN was avoided, since exothermic reaction occurred and it was difficult to regulate the temperature of the reaction medium.

Fig. 1 shows the relation between the relative rate of acrylonitrile polymerization and intrinsic viscosities of the resultant polyacrylonitrile as a

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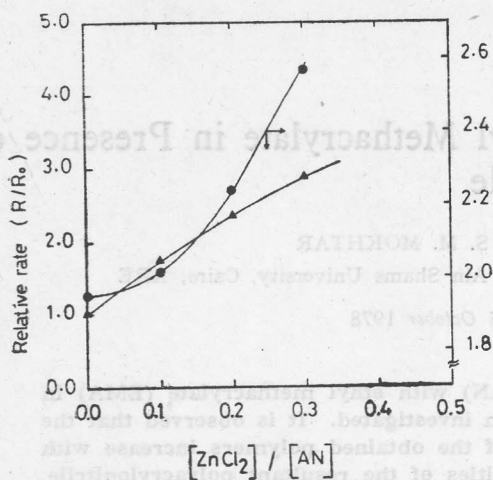


Fig. 1 — Acrylonitrile polymerization in dimethylformamide initiated by azobisisobutyronitrile at 60°C in presence of ZnCl<sub>2</sub>

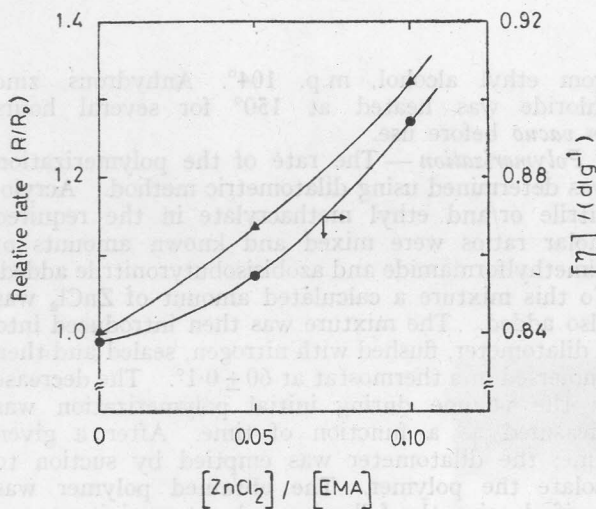


Fig. 2 — Ethyl methacrylate polymerization in dimethylformamide initiated by azobisisobutyronitrile at 60° in the presence of ZnCl<sub>2</sub>

function of  $[ZnCl_2]/[AN]$ . It is evident from Fig. 1 that as the concentration of ZnCl<sub>2</sub> increases, both the relative rate of polymerization ( $R/R_0$  where  $R_0$  is the polymerization rate of pure monomer) and the intrinsic viscosities of the obtained polymers increase.

The above experiments were repeated under identical conditions using ethyl methacrylate monomer. Fig. 2 shows that with increasing concentration of ZnCl<sub>2</sub> in the system, both the rate of reaction and the intrinsic viscosities of the obtained polyethyl methacrylate increase. Similar results were obtained previously by Imoto *et al.*<sup>8</sup>. It is observed that zinc chloride has a pronounced effect on the rate of polymerization of acrylonitrile monomer.

Copolymerization of acrylonitrile and ethyl methacrylate in the presence of ZnCl<sub>2</sub> was carried out using DMF as a solvent and with different concentrations of AN and EMA. The molar concentration ratio of acrylonitrile to EMA was taken as 90:10, 70:30 and 40:60. The total concentration of zinc

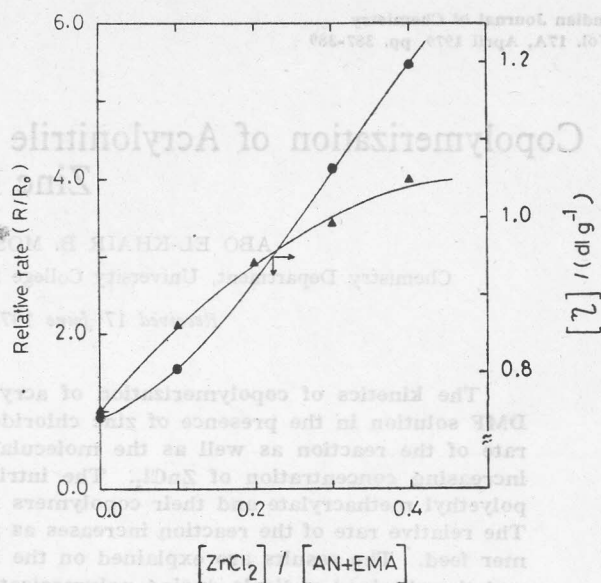


Fig. 3 — Dependence of copolymerization rates of acrylonitrile and ethyl methacrylate and their intrinsic viscosities on the concentration of ZnCl<sub>2</sub> {[AN]/[EMA] = 90:10 (molar ratio)}

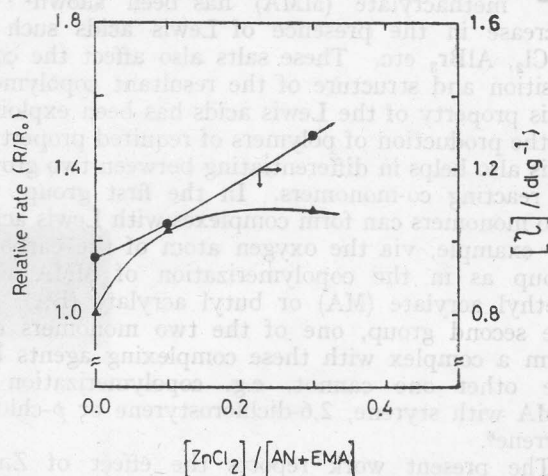


Fig. 4 — Dependence of the copolymerization rates of acrylonitrile and ethyl methacrylate and their intrinsic viscosities on the concentration of ZnCl<sub>2</sub> {[AN]/[EMA] = 70:30 (molar ratio)}

chloride as compared to the total concentration of the two monomers was varied from 0.0 to 0.4 molar ratios. The concentration of ABIN used was 0.2% of the weight of the two monomers. It is observed that the relative rate of the reaction increases four times for AN:EMA ratio of 90:10 as the concentration of zinc chloride increases from 0.0 to 0.4 mol (Fig. 3). The intrinsic viscosities of the obtained copolymers also increase with increasing concentration of zinc chloride in the system (Fig. 3). Though a similar trend is also discernible at AN:EMA ratio of 70:30 or 60:40, the relative rates at these ratios of the monomers is less than that observed at AN:EMA ratio of 90:10 (see Fig. 4 as representative for copolymerization at AN:EMA ratio of 70:30).

From the above results, it can be suggested that  $ZnCl_2$  could form a complex with the nitrile group of acrylonitrile or with the ester group of ethyl methacrylate. The formation of such complex is considered to have a close relation to the acceleration effect of  $ZnCl_2$  and to the increase in molecular weights of the obtained polymers. This can be confirmed from the IR analysis. The IR spectrum of acrylonitrile with zinc chloride shows that while the absorption band of nitrile group at 2270 and 2220  $cm^{-1}$  undergo shift, the vinyl absorption bands at 1600 and 900-1000  $cm^{-1}$  remain unchanged. This indicates that the nitrile group in AN participates to form the coordination type complex with  $ZnCl_2$  (ref. 8).

The IR spectrum of ethyl methacrylate with  $ZnCl_2$  shows that the band due carbonyl group of the acrylic ester shifts towards higher frequency region, compared to that of the pure monomer.

From IR observations, it can be concluded that the formation of such complexes increase conjugation energy and intensifies the electron orbital polarization of monomers, i.e. the conjugation energy of the  $\pi$ -electrons of the C=C double bond being somewhat increased. Therefore, the observed effects of  $ZnCl_2$  on the polymerization of AN and EMA may be due to the action of zinc chloride on the rates of all the elementary polymerization reactions.

Earlier ESR investigation<sup>9</sup> of complexed acrylic ester propagating radicals (as polymethyl methacrylate radical with Lewis acid) have shown a partial transfer of an unpaired electron to the atomic orbital of the complexing agent metal.

On the basis of the observation recorded, the copolymerization of acrylonitrile and ethyl methacrylate in the presence of  $ZnCl_2$  can be considered

as a multicomponent system, since the two monomers can form complexes with  $ZnCl_2$  and sixteen elementary polymerization reactions can be suggested as follows: (i)  $AN \cdot + AN$ ; (ii)  $AN \cdot + EMA$ ; (iii)  $AN \cdot + AN \dots ZnCl_2$ ; (iv)  $AN \cdot + EMA \dots ZnCl_2$ ; (v)  $EMA \cdot + AN$ ; (vi)  $EMA \cdot + EMA$ ; (vii)  $EMA \cdot + AN \dots ZnCl_2$ ; (viii)  $EMA \cdot + EMA \dots ZnCl_2$ ; (ix)  $AN \cdot \dots ZnCl_2 + AN$ ; (x)  $AN \cdot \dots ZnCl_2 + EMA$ ; (xi)  $AN \cdot \dots ZnCl_2 + AN \dots ZnCl_2$ ; (xii)  $AN \cdot \dots ZnCl_2 + EMA \dots ZnCl_2$ ; (xiii)  $EMA \cdot \dots ZnCl_2 + AN$ ; (xiv)  $EMA \cdot \dots ZnCl_2 + EMA$ ; (xv)  $EMA \cdot \dots ZnCl_2 + AN \dots ZnCl_2$ ; and (xvi)  $EMA \cdot \dots ZnCl_2 + EMA \dots ZnCl_2$ ; where AN, EMA, AN...  $ZnCl_2$  and EMA...  $ZnCl_2$  are free and complexed monomers and  $AN \cdot$ ,  $EMA \cdot$ ,  $AN \cdot \dots ZnCl_2$  and  $EMA \cdot \dots ZnCl_2$  are free and complexed propagating radicals of acrylonitrile and ethyl methacrylate.

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The following evidence clearly indicated the formation of grafted starch: (i) The infrared spectrum of grafted material showed absorptions at 2300 ( $C \equiv N$ ) and 1746  $cm^{-1}$  ( $C=O$ ) which were not present in starch. (ii) An intimate physical mixture of starch and homopolymer (PMA) was subjected to water and benzene extraction under conditions used for purification of graft copolymer. After benzene extraction the residue was treated with 1N HCl for 2 hr at 100°. All the material went into solution and no polymer could be isolated indicating that benzene extraction completely removed homopolymer. The grafted material on the other hand after solvent

extraction on grafted of vinyl monomers and starch. Russell and coworkers<sup>10</sup> have reported that vinyl monomers can be grafted to starch by conventional initiation method. Grafting onto starch using radical initiator has not received much attention. In a recent study Mita & Wada<sup>11</sup> have reported that benzoyl peroxide (BPO) is capable of effecting grafting of acrylonitrile (AN) onto starch. Russell and coworkers<sup>12</sup> have studied grafting of AN, methyl methacrylate (MMA) and vinyl acetate (VA) onto starch using cation technique. They observed that the relative activity of monomers towards grafting followed the order  $AN > MMA > VA$ . No attempt, however, has been made to determine relative activity of AN and methyl acrylate (MA) towards grafting onto starch using conventional radical initiator BPO. The mechanism of grafting by cation technique is quite different from that of BPO initiated grafting. It was therefore thought desirable to compare monomer reactivities towards grafting onto starch by radical initiator BPO. In the present paper we report the results of a detailed study on grafting of AN and MA onto starch using BPO as a radical initiator.

Materials and Methods

Dried starch (BDH) was used in all experiments. The monomers vinyl acetate (BDH), methyl acrylate