

S U M M A R Y

CHAPTER - I : The present investigation embodies aqueous homo- and copolymerization of methylmethacrylate, acrylonitrile and methacrylonitrile, using hydrogen bentonite/alcohol initiating system. Clay minerals are essentially aluminosilicates in which the silicate layer exists in polymeric straight chain bridged by O atoms of the basic SiO_2 unit. Silicon is in tetrahedral form whereas the alumina layers have octahedral geometry with either O or -OH groups. Each alumina layer as $\overline{\text{Al}(\text{OH})_6}$ is followed by a silica layer $\overline{\text{Si}(\text{OH})_4}$. The layers are held by some O atoms. In bentonite one alumina layer is sandwiched between two silica layers. The other forms are kaolinite - one silica layer attached to one alumina layer and, vermiculite in which sheets of linked tetrahedra of $(\text{Si}, \text{Al})_4$ are pointed inward. Polymerizations of vinyl monomers with clay minerals were studied in non polar media in which the aluminium sites (Lewis acidity) were responsible in the generation of cation radicals. Cation radicals of monomers like styrene are stable enough for propagation whereas those of methylmethacrylate and the like, because of the instability of the cation radical, could not propagate. However, theories concerning the Bronsted acidity of the clay minerals were also put forward for the initiation of polymerization. The catalytic activity of the clay minerals in inducing polymerization in conjunction with free radical initiators like 2-2' -azobis-isobutyronitrile has already been shown by other authors. In a study with clay mineral it is found that aqueous polymerization of vinyl monomers, 2-2'-azobis-iso

butyra amidine formed complex with clay which, consequently, decomposed easily to polymerize methylmethacrylate, acrylamide, vinyl acetate etc. with much higher efficiency than the free radical initiator alone. The presence of transition metals in clay minerals are known to generate radicals with peroxy acids. Interlamellar complex formation between monomer and clay favoured the propagation. Other polymerization systems involving dry clay minerals in non polar solvent are also available in the literature.

CHAPTER - II

A new initiating system, comprising of hydrogen, sodium or copper forms of bentonite and alcohol, is proposed. This initiating system is incapable of homopolymerizing either acrylonitrile or methacrylonitrile but efficiently polymerized methylmethacrylate and copolymerized these monomers in aqueous medium. The system is, therefore, interesting and provides an easy, inexpensive, and elegant method to prepare copolymers exclusively when acrylo- or methacrylonitrile is used. This initiating has only been tested with water insoluble monomers. Thus the scope of future work with water soluble monomers is still left, that the polymer which is produced with insoluble monomers are not all soluble in solvents and are either chemically or physically associated with the clay minerals. This results are helpful in organizing plans to change the surface property of the clay minerals

following adsorption/chemical bond of any polar polymer molecule.

CHAPTER - III

Bentonite suspension was prepared by withdrawing suspension of the clay mineral at pH ~ 8 at a regular interval of 24 hrs, acidifying, treating with H₂O₂ and heating for a long time on a water bath (~ 100°C) till complete decomposition of H₂O₂ was achieved. For the hydrogen form the so formed suspension was treated with cation and anion exchangers.

Monomers and other chemicals were purified adapting standard procedures.

The homopolymerization and copolymerizations were carried out in 100 ml. dark, well stoppered pyrex bottles under nitrogen blanket. Polymethylmethacrylate/clay was centrifuged and the polymer was separated by benzene extraction and purified following repeated precipitation into a mixture of petroleum ether and methanol (50 : 50). The crude copolymers were extracted with tetra hydro furan followed by high speed centrifugation to separate traces of clay particles and finally precipitated from petroleum ether.

CHAPTER - IV

The polymerization of methylmethacrylate occurred with aqueous suspension of bentonites (H⁺, Na⁺, or Cu²⁺) only in the presence of alcohols and thiols. The conversions are dependent

on both clay, alcohol concentrations and temperature. In all polymerizations induction period of 60-185 minutes were observed depending upon the reaction conditions. Usually high molecular weight polymers $\sim 10^6$ and moderate to high conversions were obtained. With 1.08% (w/v) hydrogen bentonite (HB) and 0.374M Methyl Methacrylate the conversions at 60°C were 25.2%, 30.7%, 42.25%, 55.6%, 62.9% and 68.2% for 0.86×10^{-3} , 3.43×10^{-3} , 5.13×10^{-3} , 51.30×10^{-3} , 102.60×10^{-3} , 513.00×10^{-3} M ethanol respectively and with varied clay concentrations the conversion were 14.55%, 26.31%, 44.75%, 53.04% and 62.15% corresponding to 3.5, 5.0, 7.5, 10.0 and 12.1 gms per litre of the clay suspension when 0.562 M Methyl methacrylate and 0.34 M ethanol were used for the polymerization at 60°C for 12 hours.

The initial overall rate has 0.5th order dependance on ethanol concentration. Such dependence is followed by most aqueous free radical polymerization. Free radical nature of this system has been established by e.s.r. spectra and inhibiting effect by diphenyl picryl hydrazyl. Silicon sites are responsible for the free radical generation and has been established by blocking all the octahedral aluminiums of the clay mineral with sodium hexameta phosphate and by successful polymerization of MMA with ethanol treated quartz (200 mesh). It has been suggested that lower alcohols and thiols penetrate the clay surface beyond the first hydration layer and interact with the silicon. The free radicals are

presumably generated by the stretching of the unsymmetrical alcohol molecule by the d-orbital of the silicon.

Transfer to monomer is negligible. The M_n 's increased with increasing monomer concentration. The M_n 's increased with increasing monomer concentration. It has been suggested that the conversion and molecular weight increase are due to the adsorption of monomer molecules on the clay surface. The depletion of monomer concentration on the clay surface dictates for fresh monomer adsorption. This is probably because no measurable polymerization took place without intermittent shakings. The overall initial rate of polymerization is first order with respect to monomer. This, along with the 0.5 th order dependence on ethanol concentration and the free radical nature of the reaction suggest that classical equation is applicable.

$$R_p = k_p [M] \cdot \left[\frac{fk_d[I]}{k_t} \right]^{1/2}$$

The conversion of 55.11%, 56.02% of MMA and \bar{M}_v values of the product (PMMA) of 1.12×10^6 and 1.14×10^6 for HB and sodium bentonite (Na-B) under identical conditions concluded that the nature of the cation on the clay mineral is not going to influence the mechanistic behaviour of the polymerization reaction. The PMMA yield of 33% and 41.1% for shaken and 5.1% and 6.7% for the unshaken conditions for 0.3744 and 0.5620 M Methyl

methacrylate concentrations respectively leads to the view that the monomer has to come to the near surface of Si-surface for the polymerization to proceed.

Similar results have been obtained with increasing clay concentration. Parallel increase in molecular weight of the polymers is probable due to the increased viscosity, higher concentration of adsorbed monomer and lower termination rate. The failure of the polymerization with lower clay concentrations viz. 0.3% (w/v) or below is probably due to the very low concentration of radicals generated and some unknown side reactions.

The initiator efficiency of hydrogen bentonite/ethanol has been calculated with respect to ethanol from conversion, molecular weight and concentration of the alcohol. The initiator efficiency accounts for 33% with respect to ethanol. The value with respect to clay was not possible to determine because of the uncertainty in the calculation of hydration number of the clay mineral in the polymerizing system. However, with a knowledge of the basic composition of bentonite, Si sites are ~ 30% which, assuming 1:1 type of interaction between Si and alcohol, suggests 100% initiator efficiency.

Temperature has positive effect on the polymerization with this initiating system and the rate increased with increasing temperature. The polymerization was extremely slow at and below 40°C and hardly measurable amount of polymer could be isolated in 48 hrs. However, the rate increased significantly at higher

temperatures. Thus the rate increased from 5.72×10^{-6} Moles lit.⁻¹ sec.⁻¹ to 3.92×10^{-5} Moles lit.⁻¹ sec.⁻¹ at 50 and 80°C respectively. The apparent activation energy of 15.0 Kcal mole⁻¹ is slightly lower than that observed in homogeneous polymerization of methylmethacrylate with azo-bis-isobutyronitrile but higher than usually obtained for aqueous polymerization using various redox initiators.

This is probably due to the preoccupation of the monomer layer in the interlamellar space of the clay mineral before the propagation starts. The monomer reaches the near vicinity of the clay surface where it gets free radicals already produced on the surface.

CHAPTER - V.

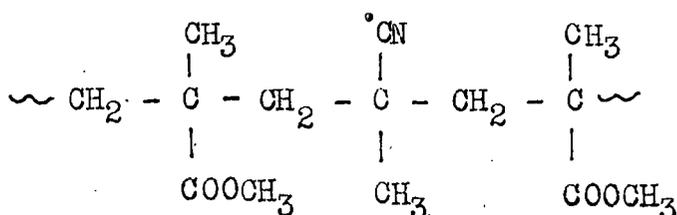
The copolymerization of acrylonitrile (ACN) and methacrylonitrile (MACN) with methylmethacrylate (MMA) under the present investigating HB-ethanol initiating system were important in respect to the failure of both the former monomers (ACN and MACN) to homopolymerize. The purification of the copolymer avoided a step for the separation of the copolymer from one of its homopolymer i.e. polyacrylonitrile or poly methacrylonitrile.

The copolymers, poly (MMA-Co-ACN) and poly (MMA-Co-MACN), were not much stable and degraded considerably with rise in temperature beyond 50°C. Gel permeation chromatographic study with poly (MMA-Co-ACN) showed that \bar{M}_w/\bar{M}_n value of 2.2 changed to 2.5 when the conditioning values of the sample changed from 30°C (1 mm pressure) to 40°C (1 mm pressure). Both \bar{M}_w and \bar{M}_n changes. When \bar{M}_n changes from 7×10^5 to 4.5×10^5 , the \bar{M}_w changes from

1.54×10^6 to 1.125×10^6 (Figs. 37/39). An examination of the nmr spectra of the samples showed that it is the polymeric acrylonitrile group which is degraded from the copolymer chain.

The reactivity ratio of the nitrile monomers in both the copolymers being zero, the same for the other monomer i.e., MMA is calculated from the analysis data for carbon, hydrogen and nitrogen in the copolymer prepared from different monomer concentrations. The compositions of monomers were then known to both in the monomer feed and the copolymer and the reactivity ratios were calculated to be 1.28 and 1.35 for Poly (MMA-Co-MACN) and poly (MMA-Co-ACN) respectively.

The analysis of carbon, hydrogen and nitrogen of both the copolymers further suggested the tirad sequence in the copolymer and having the following structure:



Such a sequence is also a best fit from the nmr spectral observations. Of the two copolymers, poly (MMA-Co-MACN) was taken as a model for the configurational study by ^{13}C nmr spectrum. The analysis of the spectrum leads to the conclusion that the heterotactic triad had a little predominance over the syndiotactic form.

The observed relative intensities of the peaks of approximately 2:5:4 are consistent with the free radical generated copolymer having essentially a random configuration. Furthermore, the chain termination did not occur either through the water molecule or through the alcohol molecule because in that case both the copolymers would produce the line segments beyond 140 for ^{13}C nmr spectrum. It is then reasonable that the chain termination occurred through recombination. This is consistent with the high molecular weight ($\bar{M}_w \sim 1.5 \times 10^6$) of the copolymer yield.

List of Publications

1. Aqueous Polymerization of clay surface 1. The Polymerization of methyl methacrylate on Hydrogen Bentonite : Effect of alcohols.

S. Talapatra, S.K.Saha, S.K.Chakravarti and S.C.Guhaniyogi
Polymer Bulletin, 10, 21-27 (1983)

2. Aqueous Polymerization on clay surface 2. The Polymerization of methyl methacrylate on Hydrogen Bentonite : Effect of monomer concentration and temperatures.

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