

CHAPTER - 6

SUMMARY

CHAPTER - 1

In this chapter, the review of the literature have been summarized in three different sections. In first section, the earlier concepts concerning the structure and characterization of the clay minerals have been given. In second section, various aspects of clay-organic interactions and in the last section previous contributions regarding the influence of clay minerals on the polymerization of various monomers are introduced.

The present investigation embodies aqueous homopolymerization of methyl methacrylate and copolymerization of methyl methacrylate with acrylonitrile or methacrylonitrile using hydrogen montmorillonite/thiourea as polymerizing initiator. The mineral studied belongs to the general class of layer silicates. Basically, the clay minerals consist of a sheet of a silicon-oxygen tetrahedra in conjunction with an octahedral sheet containing aluminium or magnesium. The montmorillonite mineral consists of an octahedral alumina sheet surrounding by two tetrahedral silica sheets. The silicate layer exists in polymeric straight chain bridged by the O atoms of the basic SiO_2 unit. The alumina layers have the octahedral geometry with either O or OH groups. The layers are held together by some O atoms. The stacking of these sheet like structures, one on the top of the other, results in the formation of the layer silicate. Substitution of aluminium in octahedral coordination by iron and magnesium normally occur. The isomorphous

substitution of various ions in either the tetrahedral or octahedral sheet gives rise to a negatively charged silicate layer and this charge is compensated by associated cations on the mineral surface. In kaolinite, an alumina layer is linked with a silica layer through some oxygen atoms.

The clay minerals interact with many organic compounds depending on the nature of organic material and reaction media. The clay-organic complex results following the adsorption of the organic molecules in cationic form on the surface of the mineral. Also, the intercalation of polar organic compounds, hydrogen bonding and vander Waal's interaction between the mineral and organic compounds are extensive. Furthermore, the electron transfer reaction is evident in the interaction of the mineral with some organic compounds where the former acts as an electron acceptor.

Polymerization of vinyl monomers with clay minerals was studied in non-polar media in which the aluminium site (Lewis acidity) was responsible in the generation of cation-radicals. Cation-radicals of monomers e.g., styrene are stable enough for propagation whereas methyl methacrylate 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 the initiation of polymerization. The catalytic activity of the clay minerals in inducing polymerization in conjunction with free radical initiators like 2,2'-azo bis isobutyronitrile has already been shown by other authors. In a

study with clay mineral it was found that 2,2'-azobisisobutyramidine formed complex with clay which, subsequently decomposed easily to polymerize methyl methacrylate, 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. Other polymerization systems involving dry clay minerals in non-polar solvent are also available in the literature. Bentonite in combination with alcohols or thiols effectively initiate the aqueous polymerization of methyl methacrylate. Inter-lamellar complex formation between the monomer and clay favoured the propagation. Attempt has also been made to give a summary of previous contributions in the line.

CHAPTER - 2

In the second chapter, the scope and object of the present investigation have been outlined briefly.

A new initiating system, comprising of montmorillonite and thiourea is proposed for aqueous polymerization of vinyl monomers. Both extractable polymer and non-extractable polymer-clay adduct may presumably be obtained in aqueous polymerization of methyl methacrylate. High conversion with high molecular weight of uniform distribution would be favourable for this initiating system. The system may also be capable of producing copolymer of methyl methacrylate with acrylonitrile or methacrylonitrile with negligible amount of homopolymer of acrylonitrile and methacrylonitrile. In order to change the physical and chemical properties of the clays and thus to increase

their usefulness, the polymer grafted clay (in different proportion) would be obtainable with this initiating system. A most probable mechanism may be proposed and the ability of the initiating system may be tested with water insoluble monomers along with the influences of various reaction parameters.

CHAPTER - 3

This chapter consists of various experimental methods used in the present investigation have been given in nine different sections. These include preparation, purification, characterization and various techniques adopted in the polymerization processes.

Montmorillonite of average particle size less than two micron in suspension is collected by withdrawing suspension of the clay mineral at pH nearly to 8 at a regular interval of 24 hours. Exchangeable iron, oxides of iron and organic matters are removed by standard procedures. For the desired cationic form, the suspension is treated with cation and anion exchangers.

Monomers and other chemicals are purified adapting standard procedures.

The homopolymerization and copolymerization are carried out in 100 ml well-stoppered pyrex bottles in dark under nitrogen atmosphere. The solid product is centrifuged and the polymer is separated by benzene extraction and purified following repeated precipitation in methanol. The crude copolymers are extracted with dimethyl formamide followed by high speed centrifugation to separate traces of clay particles and finally precipitated from methanol.

The cation (H^+) exchange capacity of the prepared hydrogen montmorillonite suspension as determined by pH metric titration is 0.85 meqv./g. Exchangeable iron in a stored hydrogen montmorillonite suspension is estimated by exchanging the same with mono-, bi-, tri- and tetra-valent metal cations and measuring by visible spectroscopy as coloured Fe(III)-thiocyanate complex. Various chemical analyses have been carried out to determine the major constituents in the mineral quantitatively following the standard methods and found to contain 65.2% SiO_2 , 20.8% Al_2O_3 , 4.5% MgO and 2.141% iron.

The molecular weights of the polymers are determined by the viscosity measurements of the polymers in benzene at $30^\circ C$ with Ubelhode Viscometer following the equation:

$$[\eta] = 8.69 \times 10^{-5} \bar{M}_n^{0.76}$$

A dye partition test with disulfine blue VN-150 has been employed for the detection of amine end groups in the poly (methyl methacrylate).

CHAPTER - 4

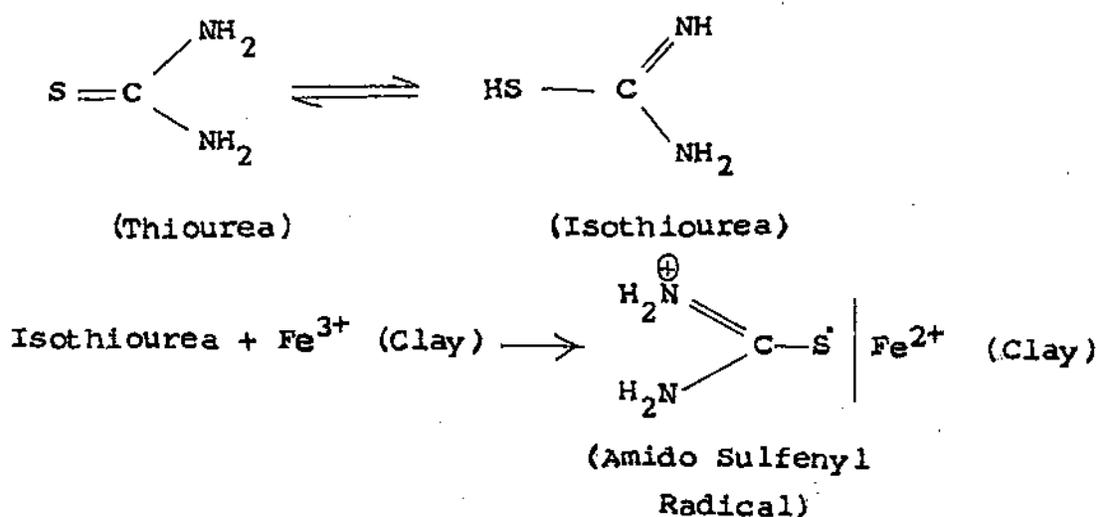
In the fourth chapter, the present investigation on the heterophase aqueous polymerization of methyl methacrylate with hydrogen montmorillonite/thiourea initiating system have been detailed in five sections. These include the results and discussion of various aspects of the polymerization processes, effect of various reaction parameters, spectroscopic and the electrochemical experiments.

A combination of HM and TU is an effective initiating system for heterophase MMA polymerization while either aqueous HM or TU alone could not initiate MMA polymerization. Upto 70 wt% of total PMMA formed is grafted onto 1.25% (w/v) HM from which it can not be extracted by repeated and prolonged boiling in benzene. The overall initial rates of the polymerization R_p , increase from 0.45×10^{-5} to 1.18×10^{-5} mole.l⁻¹ s⁻¹ for nearly 65 fold increase in HM content. The number of polymer molecules (determined from \bar{M}_n and yield) remain nearly constant over the entire range of clay concentration although both yield and \bar{M}_n increase gradually. The slight increase in R_p may be attributed to the increased extent of adsorption of MMA between the layers and not due to any change in the radical concentration at a fixed amount of TU. It is therefore, possible that an equilibrium between MMA adsorbed HM and TU exists.



On increasing TU concentration from 1.0×10^{-3} to 40×10^{-3} M at fixed concentrations of HM and MMA, R_p and \bar{M}_n increase 2.5 and 2.6 fold respectively. It is of interest to note the constancy in \bar{M}_n within error ($7.2-7.8 \times 10^5$). Large excess of TU possibly acts as transfer agent. Attempts to polymerize MMA with quartz/TU, alumina/TU, kaolinite/TU, laponite/TU and hydrated Fe₂O₃/TU fail, whereas, HM treated with sodium hexametaphosphate to block Al-sites is effective in conjunction with TU. Besides H-form, other forms e.g. K-, and Cu(II) — montmorillonite with TU are almost equally efficient in

MMA polymerization. The R_p with HM/TU are also examined as a function of pH. The results indicate that H^+ has no bearing on the polymerization under the conditions of this study. The presence of lattice substituted Fe^{3+} is established by esr spectra and chemical analysis of the montmorillonite sample. This Fe^{3+} undergoes oxidation-reduction reaction as evident from electrochemical study. This has also been observed that TU completely oxidized by HM and it suggests that Fe^{3+} in lattice of the montmorillonite acts as an electron acceptor site. It is clear, therefore, that neither Bronsted nor Lewis acidity of the mineral is responsible for initiating species generation and the lattice Fe^{3+} on HM is the effective initiator with TU. The free radical nature is established by the inhibition with 2,2-diphenyl-1-picrylhydrazil or hydroquinone when added to the system. Unlike $FeCl_3$ and $Fe(ClO_4)$, aqueous HM is neither an inhibitor nor a retarder when used in large excess. In line with these results along with the positive test with disulfine blue VN-150 for amine groups in the PMMAs' harvested with TU/HM, TU/KM or TU/CuM suggest the formation of amido sulfenyl radicals:



The overall initial rate has 0.5th order dependence on TU concentration. Such dependence is followed by most aqueous free radical polymerization. This, along with first order dependence on monomer concentration suggest the rate equation as

$$R_p = k_p [M] (fk_d [I] / k_t)^{1/2}$$

Assuming that chain transfer to HM/TU is insignificant, a plot of $1/\overline{DP}_n$ vs $R_p / [M]^2$ found to be linear. From such plots, the values of $k_{tr,M}/k_p$ and k_p^2/k_t are calculated. The transfer to monomer is quite small and k_p^2/k_t values are higher than for homogeneous polymerization. The increase in k_p^2/k_t with temperature is probably due to the increase in k_p while k_t is relatively small because of the occlusion of free radical ends by growing polymer chains inside layers of the clay mineral. In the aqueous polymerization of MMA with HM/TU initiating system, HM becomes hydrophobic following MMA adsorption and tends to be solvated by MMA. TU is also adsorbed on clay surface and the amido sulfenyl radicals produced on the surface (mostly internal) of the montmorillonite initiates the polymerization on the surface. Propagation is favoured over termination because most of the growth takes place either in the intercalated or MMA solvated loosely bound chains. The view is substantiated by i.r. and X-ray studies.

Temperature has positive effect on the polymerization with HM/TU initiating system and the rate increases with increasing temperature. The overall initial rates are 1.10×10^{-5} , 1.68×10^{-5} , 2.18×10^{-5} ,

3.6×10^{-5} and 5.87×10^{-5} mole.l.⁻¹ s⁻¹ at 40, 50, 60, 70 and 77°C respectively. The induction period is found to be dependent on temperature and it varies from 58 to 10 minutes within the temperature range 40 to 77°C. The overall activation energy is of 9.2 Kcal/mole for this system. This value so obtained, however, is apparent activation energy since correction due to the heats of adsorption of MMA on montmorillonite surface has not been made. The value is lower than that observed with Fe(III)/TU redox system in t-butyl alcohol medium but close to the value with Ce(IV)/TU redox system in aqueous medium.

In immiscible mixed solvent systems e.g., benzene-water and carbon tetrachloride-water, no polymer are produced but in miscible mixed solvent system, e.g., t-butyl alcohol-water, polymer is produced but at a slower rate than that observed in pure water. It is believed that for effective polymerization the monomer molecules have to be adsorbed or intercalated in the mineral or have to be in the proximity of the surface of the mineral. Out of the total PMMA formed, a major amount remain non-extractable and this may be ascribed to the formation of hydrogen bond between the oxygens of polymer molecules and the hydroxyls of clay lattice and also intercalated PMMA formation in the interlamillar space of the mineral. A fair amount of polymer in clay-polymer adduct decomposes at a higher temperature.

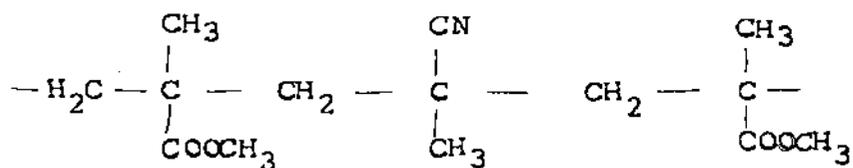
CHAPTER - 5

In this chapter, the reviews, experimental, results and discussion concerning the copolymerization experiments of methyl

methacrylate with acrylonitrile or methacrylonitrile have been put forward in four sections.

The copolymerization of acrylonitrile (ACN) and methacrylonitrile (MACN) with methyl methacrylate (MMA) by the present HM/TU initiating system is important because of the failure of both the nitrile monomers (ACN and MACN) to homopolymerize. The purification of the copolymer excludes the step for the separation of the copolymers from one of its homopolymer i.e. polyacrylonitrile or polymethacrylonitrile. The copolymers, poly(MMA-co-ACN) and poly(MMA-co-MACN), are not much stable and degrade considerably with rise in temperature beyond 50°C.

The analysis of carbon, hydrogen and nitrogen of both the copolymers suggested the triad sequence in the copolymer as shown below:



Such a sequence is also a best fit from the nmr spectral observations.

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 analytical data for copolymer prepared from

different monomer concentrations. The compositions of monomers are then known to both in the monomer feed and in the copolymer, and thus the reactivity are calculated to be 1.21 and 1.40 for poly(MMA-co-ACN) and poly(MMA-co-MACN) respectively.

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