CHAPTER - 1

INTRODUCTION

1. INTRODUCTION

A recent report put a value of nearly six billion dollars for the total world wide market in water soluble synthetic polymers (WSSP) reflecting their wide use in numerious products and processes. The wide field of application of these WSSP includes areas from adhesives to cosmetics, from explosives to medical products and from oil technology to paper technology[1]. Industrially, clay minerals are used as fillers and reinforcers in polymer systems such as elastromers, polyethylene, polyvinyl chloride and other thermoplastics and as coating agents for various types of paper.[2,3] All things being equal the efficiency of a filler in improving the physico-chemical properties of a polymer system is primarily determined by the degree of its dispersion in the polymer matrix.

The most effective way of achieving such compability is to graft a suitable polymer onto the filler surface and/or to encapsulate the mineral particles with the polymer layer.[2] Indeed, clay minerals specially those of phyllosilicates themselves are known to catalyze a variety of organic reactions including those which lead to polymer formation. The enormous success that has been achieved in the field of catalysis by molecular sieve zeolites has stimulated chemists to develop sophisticated ways of using clay as catalysts, for example, pillard clay catalysts.[4] Research on the intercalation chemistry of phyllosilicates is gaining momentum rapidly to transform these abundant minerals into new classes of selective heterogeneous catalysts. For example, the assymmetric synthesis of certain α-amino acrylates can be achieved with chiral rhodium complexes immobilized in smectite interlayers without sacrificing the high optical yields typified by the same complexes under homogeneous conditions.[4] The formation of stereoregular poly (acrylonitrile) and poly (acrylic acid) in the interlayer space of montmorillonite had been claimed[2].

1.1 POLYMERS OF ACRYLAMIDE

Acrylamide is a versatile, highly reactive monomer which readily undergoes vinyl polymerization to yield a broad spectrum of homopolymers and copolymers of controlled molecular weight and performance characteristics.[5] It is assuming increasing industrial importance as a chemical intermediate and as a monomer. Acrylamide is highly water soluble and tends to impart this same property to polymers and copolymers. Polyacrylamide is a very effective flocculant, a thickening agent and a pigment retension aid in paper making. It has found wide application in the treatment of ores, mineral and metal particles, sewage, industrial wastes etc. Polyacrylamide is usually fed as very dilute solutions which cause rapid agglomeration and sedimentation.

Extremely high molecular weight polyacrylamides have been found to be exceptionally effective flucculants.[6] Mixtures of acrylamide with small proportions of N, N^{l}-methylenebisacrylamide have been finding increasing application as chemical grouts. They are available commercially under the trademark "AM-9" (ref.7). Aqueous solutions of the monomer together with a redox catalyst are injected into soil formation. Copolymers of acrylamide and acrylic acid are being used as stock additives for improving the dry strength of paper.[8] These are particularly useful in the manufacture of printing papers. High molecular weight acrylamide copolymers have also shown considerable promises for increasing the retention of mineral fillers in paper making. Improvement in drawing rate and wet strength have also been obtained.

Copolymers of acrylamide and acrylic acid have been found to control the loss of fluid from oil well cements in hydraulic cementing operations.[9] Polyacrylamide with high molecular weight has been claimed to be useful as a thickening agent for water used in a secondary oil recovery method called water flooding. The thickened water is used to drive oil through the formation to a producing well[10]. Interpolymers of acrylamide and other monomers are useful for commercially important surface coatings[11-14].

On the other hand, a recent communication also describes a new series of antitumor agents which are derivatives of acrylamide, among which N-[(3-bromopropionamide) methyl] acrylamide was particularly effective[15].

1.2 MONTMORILLONITE

Montmorillonite possesses a layered structure and has strong sorptive properties due to expandability of the mineral layer. It is a 2:1 type or trimorphic layered phyllosilicate in which the central octahedral aluminium is surrounded by two tetrahedral silica sheets. The structure of montmorillonite was first given by Hoffmann, Endell and Wilm on the basis of its similarity with that of pyrophyllite[16]. This basic structure into which modifications by Marshall,[17] Maegdefrau and Hoffmann[18] and Hendricks[19] were subsequently incorporated, is now generally accepted[20,21]. The montmorillonite layer differs from that of pyrophyllite in that the substitution of Al (III) for other cations (e.g., Mg(II), Fe(II)) in octahedral positions, and less frequently of Si(IV) and Al(III) in the tetrahedral sheet always occurs. Although some internal compensating substitution may occur, the final result of the isomorphous replacement in the pyrophyllite structure is a layer which carries a permanent negative charge. The positive charge deficiency is balanced by sorption of exchangeable cation which, apart from those associated with external crystal surfaces are positioned between the randomly superposed layers within a crystals[18]. Water is also readily absorbed in the interlayer space. These concepts are illustrated in Figure 1. Water appears to enter the interlayer region as an integral number of complete layers of molecules, this number depends on the nature of the exchangeable cation.[21-23]

The d(001) spacing of montmorillonite can vary over a wide range, the minimum corresponding to the fully colapsed state being 0.96 nm with large monovalent and divalent cations occupying interlayer exchangeable sites. Interlayer (or intercrystalline) swelling is limited to a d(001) spacing of about 1.9 nm. On the other hand, montmorillonite samples saturated with small

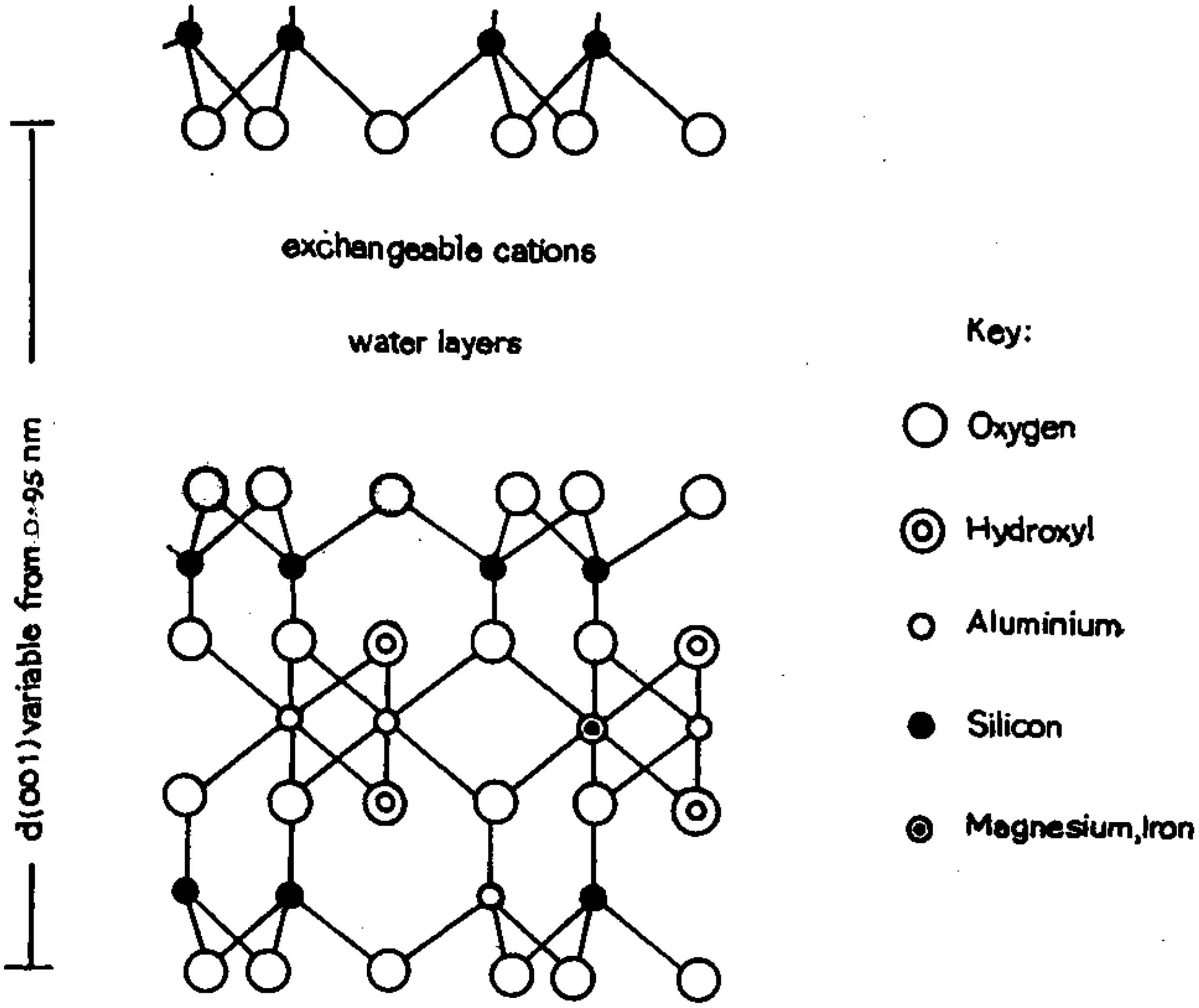


Fig. 1 The structure of a montmorillonite layer viewed along the a axis. The basal spacing is giving in nanometer units.

monovalent cations (Li^+, Na^+) may show extensive interlayer expansion in dilute aqueous solutions (0.3N) of their respective cation salt and in water, and under optimum conditioins the layers can dissociate completely.[23] The charge density of the clay surface as well as the nature of the exchangeable cation has a profound influence on the hydration properties of this 2:1 type phyllosilicates and obviously the hydration properties are affected more by the interlayer cation than by the silicate surface. Since uncharged polar organic molecules are absorbed essentially by replacement of the interlayer water, the behaviour of such molecules is likewise strongly influenced by the exchangeable cation. Evidence has accumulated to show that, at least at low water contents, cation-dipole interactions are of paramount importance in their effect on the absorption of polar molecules by clay minerals. Montmorillonite acquires its charge by the replacement of octahedral Al by Mg atoms. The structural formula is written as :

$$\begin{array}{c}[Si_8]^{IV}[Al_{4-x}Mg_x]^{VI}O_{20}[OH_4]\\ \downarrow\\ M_x\end{array}$$

(1)

This formula gives the composition of the planner unit cell. The number IV and VI indicate tetrahedral and octahedral positions respectively. The symbol M_x indicates the presence of compensator cations totalling x valencies per cell. The charge x is generally between 0.5 and 0.9 . Formula (1) is idealized. Fe(III) replaces a part of the Al's, Fe(II) replaces a part of the Mg's. Extensive chemical studies especially on the changes in composition of smectites by base exchange and the swelling effects in their geometrical significance, were made by M.D.Foster[24]. Swelling decreases with increasing octahedral replacement. In this respect the introduction of Fe(II) into the octahedral layers has greater depressing effect than that of Fe(III) which in turn appeared to have the same depressing effect as Mg(II).

An alternative and completely different structure (Figure 2) for

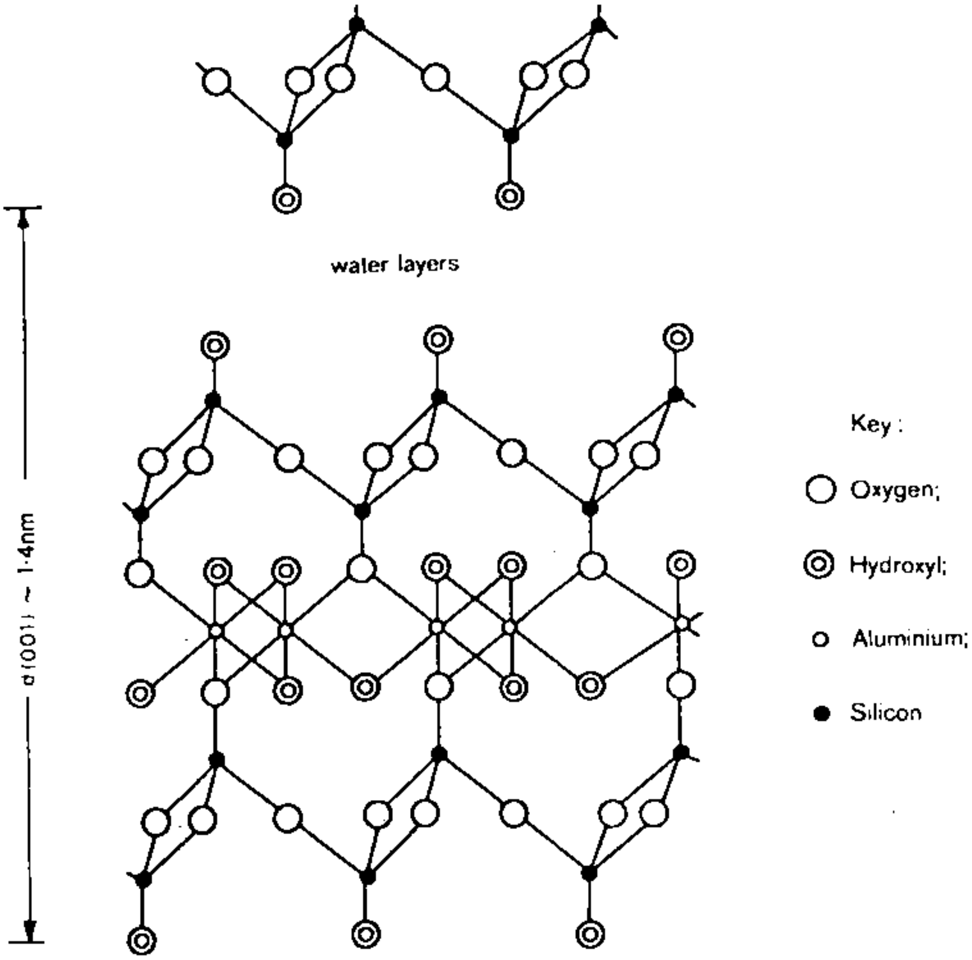


Fig. 2 The montmorillonite layer structure viewed along the axis according to Edelman and Favejee.

montmorillonite has been suggested by Edelmen and Favejee.[25] The main aspect of this structure is that every alternative SiO_4 tetrahedron in the tetrahedral sheet is inverted. The apical oxygens of such inverted tetrahedra, now pointed away from the surface, are replaced by hydroxyl groups which also fills the gaps left in the octahedral sheet. No isomorphous replacement within the structure is envisaged and the observed cation exchange capacity being solely ascribed to the dissociation of apical hydroxyl groups. Somewhat similar structure in which excess hydroxyl groups are present due to the replacement of some Si(IV) ions by $4H^+$ or $Al(III)H^+$ ions in the tetrahedral sheet has been suggested by McConnell.[26] On the other hand, Grim and Kulbicki postulated the existence of two types of montmorillonite, one confirming to the Hofmann-Endell-Wilm-Marshall-Maegdefrau-Hendricks structure and the other to the Edelman-Favajee structure.[27]

Because of the poorly crystalline nature of the clay mineral, X-ray diffraction patterns are generally broad and diffuse. Moreover, obtaining homogeneous and uncontaminated samples is not an easy task. These facts make it difficult to discriminate between the various possibilities using X-ray analysis alone. By a combination of X-ray, DTA, TGA and chemical analysis, it has been possible to distinguish between various types of montmorillonite samples.

1.3 CLAY-ORGANIC INTERACTION

Involvement of clay minerals in affecting organic reactions have now been well established by the contributions of Smith, Gieseking and co-workers[28-30], Hendricks[31], Jordon[32], Bradley[33], Mac.Dwan[34], and others. Excellent reviews of recent studies are available in books and journals (Grim[35], Eitel[36], Theng[2], Mc Ewan[34], Greenland and Hayes[37], Sposito[38], Bringley and Brown[39], Mortland[40] and others). Extensive studies on interaction of organic compounds with clay systems have also been the subject matter of research of different Indian scientists. In this context the noteworthy contribution of

Mukherjee[41,42], Chakravarty[43-48], Mukherjee and co-workers[49,50]. De and co-workers[51-54], deserve special mention.

On the basis of the above it has been abundantly clear that clays interact with many organic compounds to form complexes of varying stabilities and properties. Organic derivatives especially of montmorillonite have so far been obtained either by (a) ion-exchange reactions or (b) by direct introduction of the Si-C linkage.

The pronounced change in the physical properties of organo-clay complexes, particularly in relation to the development of organophilic characteristics, water proofness, exchange and other surface phenomena has been revealed by the work of Jordon[32], Gieseking[28-30], Mukherji[41], Chakravarty[47,48] and others. In the above studies some attempts have also been made to ascertain the nature of the bond in the clay organic complexes.

The absorption behaviour of quaternary ammonium compounds of varying chain length on surfaces of montmorillonite, soil colloids and clay mixtures has been critically studied by Chakravarty with the help of electrochemical, viscometric, electrophoretic and sedimentation volume techniques.[43-48]

The complicated process of interaction of larger ions with clays is accompanied by significant variation of exchangers, namely, charge reversal as shown by electrophoretic and sedimentation volume measurements.[43,49,51] In the formation of the clay organic complexes and for their stability the involvement of Van der Waals and hydrophobic bonds in addition to columbic bond has been reported by the authors.[44-47]

While most of these studies are on the interaction between clays and defined organic molecules of known structure, another interesting area of study that has gained importance in the recent past is "Clay polymer complexes".

Theng summarises the development in this area and the immense possibilities of studying interactions of clays with synthetic and naturally occuring polymers.[55] The contributions of Mortland, Boyd and Morland in this context are very significant.[56-59]

Hofmann and Brindley reported appreciable adsorption of non ionic aliphatic compounds having chain length C_5-C_{10} on Calcium montmorillonite[61]. But little or no adsorption of short chain organic compounds on montmorillonite from dilute solution (less than 0.5 M) occurred. However, German and Harding have reported that calcium and sodium montmorillonite adsorbed adequate amounts of primary n-alcohols viz, ethanol, propanol and butanol.[62] This deviation from chain length rule of Hofmann and Brindley has been supported by Bradley for adsorption of some aliphatic amines.[33] Larger molecules with more than five units – both aliphatic and aromatic may be adsorbed to an appreciable extent by montmorillonite in the presence of excess water.[61-64] That is, they can displace the water molecules associated with the exchangeable cations. The increase in affinity with molecular size or chain length can be generally applied to the adsorption of organic compounds of clays and is attributed to the increased contribution of Van der Waals forces to the adsorption energy.[60] As the size of the molecule increases, Van der Waals interactions become important because these forces are essentially additive and tend to orient the molecule so that the maximum number of contact points is established.[65,66]. The adsorption of one organic molecule is accompanied by the desorption of a number of water molecules initially co-ordinated to the cation, an appreciable amount of entropy is gained by the system, favouring adsorption.

Thus, entropy effects arising from multiple bond formation between the organic compound and the water molecules in the primary hydration shell contribute to the strong adsorption of some uncharged linear polymers by montmorillonite[67,68]. Besides chain length (molecular size), the chemical character of the organic molecule influences adsorption behaviour. For many aliphatic compounds, a useful index of character is their "CH activity" arising from the activation of methylene groups by neighbouring electron withdrawing substituents like ⟩C=O and –C≡N. At equilibrium concentration, the amount of $C_6 - C_7$ organic compounds of different functional group adsorbed on the clay mineral is in the order :

α-methoxy - acetyl acetone > acetoacetic ethyl ester > β-ethoxy propionitrile hexanedione - 2,5 > hexane diol - 1,6 > 2,4 - hexadiyne diol - 1, 6 (ref. 61).

Complex formation with polar organic compounds is profoundly affected by the nature of exchangeable cation and by the water content (hydration status) of the clay. Apparently, hydration of the clay facilitates acetone uptake, presumably due to the expansion of mineral interlayers. In an attempt to prepare acetone complex, it was found that dehydrated calcium montmorillonite invariably yielded as double layer complex whereas the corresponding sodium clay gave either a single or a double layer complex.[69] This difference between calcium and sodium montmorillonite in their behaviour towards polar organic liquids accords with later findings of German, Harding, Bissada and co-workers for ethanol–montmorillonite and acetone–montmorillonite systems is ascribable to the greater solvation energy of the calcium ion compared to that of sodium ion.[62,70] The formation of double layer complexes of montmorillonite with some ethers and polyethers has been reported[33,69]. From X-ray data the basal spacings of 1.31 – 1.34 and 1.57 – 1.76 nm were suggested for both single and double layer complexes respectively.[61]

The complex formation between aliphatic or aromatic amines and 2:1 type clay minerals has received much attention. The basic information available are (i) the amines can exist in the cationic form like the corresponding alkyl ammonium ions which can replace the inorganic cation occupying exchange sites at the clay surface (ii) adsorption of some primary n-amines by hydrogen montmorillonite is influenced by the pH of the system and by the size (chain length) of the organic molecule.

In acidic media, amides may accept a proton on either the oxygen or the nitrogen atom. However, the weight of evidence from both spectroscopic and solution studies lies on the side of the former alternative.[2] From infrared studies of acetamide, Tahoun and Morland have confirmed that amides predominantly protonate on the oxygen atom in acidic montmorillonite system.[71] In acidic montmorillonite system, hemisalt formation is observed when excess amide is present, i.e. two amide molecules share a proton through a symmetrical hydrogen bond.

Weismiller has examined the interlayer expansion of montmorillonite crystals in N-ethyl acetamide.[72] Irrespective of the kind of interlayer cation present, montmorillonite apparently expands to a basal spacing of about 2.05 nm which is interpreted in terms of the intercalation of three layers of N-ethyl acetamide molecules with the exchangeable cations occupying positions midway between two opposing silicate layers. In the initial stage of adsorption, the amide molecule co-ordinates to the interlayer cation through the oxygen atom, but as the amount present increase the "excess" amide may form hydrogen bond of the cation-linked species and/or to the oxygen ion of the silicate surface.

Weil-Malherbe and Weiss showed that both acid-base interaction and oxidation-reduction reactions were involved in the formation of coloured clay complexes with certain aromatic amines.[73] Briegleb showed that the association between clays and organic compounds may be termed 'electron donar-acceptor complexes.[74] Solomon and coworkers proposed a model based on charge transfer between the mineral and the absorbed organic species.[75] Toth and Szepvolgyi and co-workers studied the thermal decomposition of complexes produced from bentonite and a linear polyacrylamide (PAM) by using TG - mass spectroscopy[76]. Thermal behaviour of bentonite-PAM complexes was mainly determined by PAM degradation and the decomposition of bentonite complexes above a temperature of 580°C proved to the formation of strong bonding between the constituents of the complexes.

Ogawa, Kuroda and co-workers suggested that acrylamide (AM) was intercalated in the interlayer spaces of montmorillonite through hydrogen bonds and co-ordination complexes in the Cu-montmorillonite-AM and Na-montmorillonite -AM intercalation compounds and that the molecular plane of AM was perpendicular to the silicate sheet[77]. Intercalated AM was polymerized to form montmorillonite - PAM intercalation compounds which adsorbed more water than raw montmorillonite .

The adsorption and polymerization of AM in the complex composite films which were prepared by adding acrylamide and water to Na-fluorterasilicic mica were investigated by Nagal and co-workers.[78] From X-ray diffraction it was observed that the interlayer spacing of the film was 9.6 Å for the Na-montmorillonite complex and 8.8 Å for the Na-fluortetrasilicic mica. From the DSC technique the quantity of uncrystaled AM was measured to be equal to that of AM intercalated into the interlayer space. AM in the films was polymerized upon irradiation. The extent of polymerization increased almost linearly with the irradiation time. The interlayer space of the polymered film did not change from that of the inirradiated film.

1.4 CLAY CATALYZED POLYMERIZATION

Synthetic and naturally occurring clay minerals due to their favourable structures, are used in a number of widely diversified roles in the chemical industry as catalyst for cracking or depolymerization[79], alkylation[80] isomerization[81], polymerization[82] etc. In 1960's and earlier clay initiated polymerizations of vinyl monomers emphasised on the use of dry clay minerals and non-polar solvents.[83-85] Butadiene, trans and cis-butene-2 was found to be spontaneously polymerized on the external surface of neutral and acidic montmorillonite at room temperature and atmospheric pressure without additional catalysts.[83] The olefins were adsorbed on dry clay from systems like (i) solid-gas at reduced pressure and at various temperatures, (ii) solid-gas at room temperature and (iii) solid-liquid at –78° or 0°C for neat monomer or monomer dissolved in solvent.

Although the carbocationic polymerizations of vinyl monomers have been investigated extensively with Lewis acid such as $AlCl_3$, $TiCl_4$, BF_3, Et_2O, BCl_3 alkyl aluminiums etc.[86-92], the first report on such polymerization of styrene with acid clays[84] came in 1964. Almost 100% yield of polystyrene of molecular weights 500 to 2000 was achieved. The catalytic activity of the clay has been shown to be due to active protons associated with tetrahedral (due to dehydration of the mineral) aluminium.[93,94] The formation of carbonium ion following surface absorption of olefins on acid sites caused subsequent polymerization. Proton accepting contaminants such as water, amines etc., being preferentially absorbed over styrene suppressed the polymerization. Styrene polymerized on the surface of the homoionic clays.[95] It is thought that an electron transfer from adsorbed styrene to the aluminium produced radical cations which rapidly dimerized. Both radical cations and dimers are involved in the initiation step but the propagation being cationic. Using activated clay minerals, however, styrene did not polymerize in the presence of ethanol, dioxane, ethyl acetate and methyl methacrylate (MMA) within 30 minutes of the reaction. All these data lead to postulate that the active sites are the octahedral aluminium at the crystal edges. The aluminium acts as electron acceptors.

Matsumoto, Sakai and Arihara preferred the concept of Bronsted acidity rather than Lewis acidity to be responsible for the initiation of the polymerization of styrene by montmorillonite[96]. The inconsistency in their experiments, however, is in the reduction of polymer yield in the presence of trityl chloride which selectively absorbs on Lewis acid sites. They argued in favour of the Bronsted acidity on the ground that the replacement of exchangeable hydrogen ions by sodium or ammonium ions almost completely inhibited the polymerization. On reacidifying the mineral, however, the activity to polymerize styrene was restored. Since the degree of polymerization increased with the dielectric constant of the medium and was almost independent of the initial concentration, cationic mechanism for the initiation process was favoured.[97]

This would apply equally well to the propagating process and therefore, the initiation by a radical ion mechanism cannot be ruled out.[95] The possibility of proton transfer to monomer leading to decreased average degree of polymerization, as in conventional cationic mechanism, has also been discussed.[93] The work of Matsumoto and coworkers along with Solomon and Rosser lead one to the conclusion that acidity of the clay can not be solely ascribed to either Bronsted acidity or Lewis acidity.[95-96] It is to be understood that dry mineral surface is very acidic due to the polarization of residual water molecules by the exchangeable cations. Such acidity is influenced by the solvent as evident from the blue colouration of aqueous benzidine in the presence of oxidized montmorillonite. Instead a yellow colour appeared when a benzene solution of benzidine was treated with dry clay mineral.[95,98] Solomon and Rosser failed to find evidence of styrene interacting with the clay mineral which lead them to assure that styrene is either incapable of moving into the interlayer space or capable of doing so with difficulty.

The polymerization of MMA on such clay minerals has not yet received much attention. The failure of MMA to polymerize can be accounted for in the light of well accepted mechanism of charge transfer from the monomer to the clay mineral to produce a radical cation which is a non-propagating species for the polymerization of MMA. However, Dekking could prepare MMA-montmorillonite complex using the conventional free radical initiator, 2-2^{I} azo-bis-isobutyramidine (AIBA).[105] The polymerization of MMA and methyl acrylate in montmorillonite interlayer induced by γ-radiation has been studied by Blumstein and co-workers.[99-102] The interlayer polymers were difficult to isolate by the usual solvent extraction and could only be isolated by treating the clay-polymer complex with hydrofluoric acid which damaged most polymers. Glavati and co-workers found that polymerization of acrylonitrile / montmorillonite complex by γ-radiation produced stereospecific polymers.[103]

Thermal polymerization of number of vinyl monomers e.g. MMA, acrylamide, vinyl acetate, 4-vinyl pyridine could be induced by montmorillonite if AIBA was previously introduced to the clay mineral.[104] The cationic form of AIBA goes to the exchange sites in montmorillonite to form AIBA-clay complex which decomposes thermally to generate free radicals. The complex has high initiating efficiency. The rate of polymerization with the AIBA-montmorillonite complex initiator was greater than for AIBA alone.[105] It has been proposed that free radicals remain attached to the adjacent planes of AIBA-montmorillonite dispersed in water, and on heating these planes move away from each other allowing more water to penetrate. This situation is represented in Figure 3 and 4.

From X-ray studies it was concluded that type 'c' and 'd' radicals do not recombine but move apart due to driving force of water. Once the radicals are separated some 30 Å, they can initiate the polymerization of the three types of free radicals formed during the decomposition of AIBA-clay complex, only type 'a' (Figure 4) can form homopolymer, and type 'a' radicals are free to be deactivated through recombination with type 'b'. Figure 4 also explains how the formation of homopolymer may be greatly decreased while the formation of graft polymer (from clay) is increased by decomposing the AIBA-montmorillonite complex. If the clay is dispersed in methanol, the later surrounds the intercalated free radicals inhibiting their separation and thus facilitating the graft polymer formation. From X-ray studies, Solomon and Loft suggested an interlamellar complex formation between a series of acrylate and methacrylate monomers and montmorillonite[106], as illustrated by Figure 5.

Only type III (Figure 5) is responsible for spontaneous polymerization of acrylic monomers in presence of peroxide initiator[106]. The polymerization of

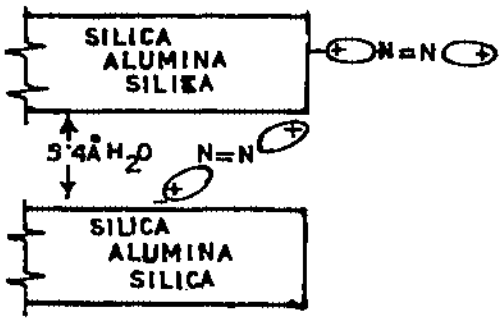

SILICA
ALUMINA
SILICA
N=N
5·4Å
H2O
N=N
SILICA
ALUMINA
SILICA

FIG- 3

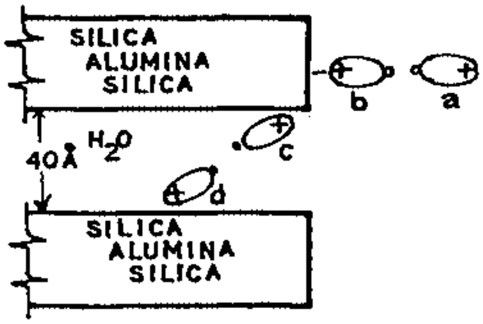
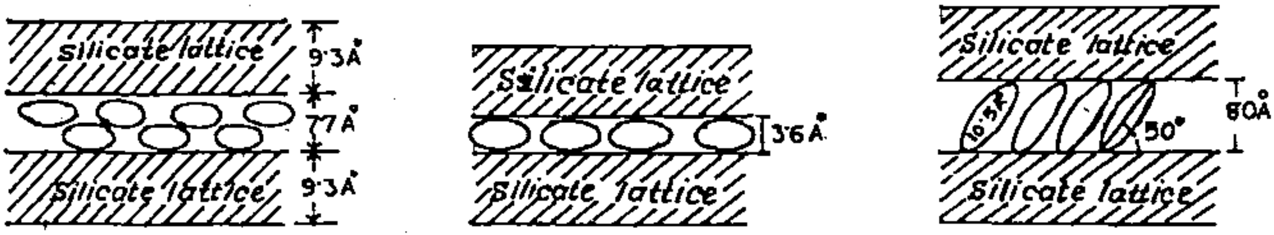

SILICA
ALUMINA
SILICA
b
a
40Å
H2O
c
d
SILICA
ALUMINA
SILICA

FIG - 4



TYPE I

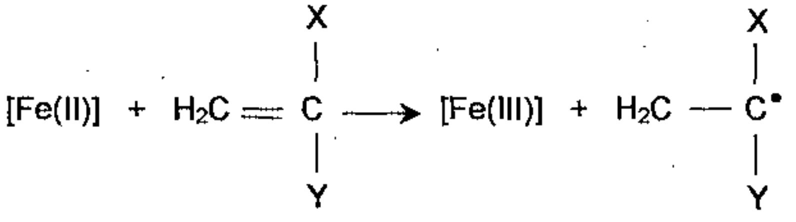
Fig. 5 Two monomer layers lying flat. (Spacing shown is for methyl methacrylate)

TYPE II

One monomer layer lying flat (Spacing shown is for dimethyl amino ethyl methacrylate)

TYPE III

One layer of inclined molecules. (Spacing shown is for hydroxyethyl methacrylate) hydroxy methacrylates has been suggested to be due to the presence of electron donating sites within the silicate layers. The inclined orientation of the hydroxyl groups gave a favourable orientation for initiator, and the propagation involved radical anions. The following mechanisms have been forwarded.



$$\mathrm{[Fe(II)]} + \mathrm{H_2C}{=}\overset{\mathrm{X}}{\underset{\mathrm{Y}}{\mathrm{C}}} \longrightarrow \mathrm{[Fe(III)]} + \mathrm{H_2C}{-}\overset{\mathrm{X}}{\underset{\mathrm{Y}}{\mathrm{C}^{\bullet}}} \qquad \text{(A)}$$

(in lattice) (in lattice) (adsorbed)

$$\mathrm{[Fe(II)]} + \mathrm{ROOH} \longrightarrow \mathrm{[Fe(III)]} + \mathrm{RO}^{\bullet} + \mathrm{OH}^{-} \qquad \text{(B)}$$

(in lattice) (in lattice)

Iron is shown as a oxidizable atom in the silicate lattice although other transition metals may be present. In mechanism (A), the radical anion is formed via electron transfer from the mineral to the double bond. The mechanism is similar to that proposed for the polymerization of olefins by transition metal catalysts.

The influence of aluminosilicates and magnesium silicates on the free radical polymerization of MMA has been studied in terms of termination reaction and supported by studies of the reaction of stable free radicals with the minerals. In the absence of clay mineral the yield of PMMA was 3.68% (mol.wt. 1.36×10^6) whereas with montmorillonite the yield was 0.68% (mol.wt. 3.05×10^6). That the decreased amount of polymer in the presence of the mineral is not due to the depolymerization has been established by heating PMMA with montmorillonite and determining the viscosity average molecular weight before and after the treatment. A recent work involved ESR study to assess the state of iron in montmorillonite.[109] The absorbtion bands in the weak field as 'G' values

7.6, 4.2 and 3.9 were assigned to Fe(III) ions in the octahedral layer of montmorillonite. The intensities of the wide bands of the spectra remain unchange when the cations were altered as the exchanging sites. This indicated that the montmorillonite had particularly no iron in the ion exchangeable positions.

Studies on the structural properties of the polymers from clay catalyzed polymerizations of vinyl monomers have been made by several workers. Blumstein and co-workers studied dilute solution properties of the polymers prepared in the presence of clay minerals which differed significantly from those obtained using conventional free radical technique and suggested that the interlayer PMMA developed a two-dimensional sheet structure in the presence of a cross linking agent during the polymerization.[99-102] Analysing the n.m.r. data they concluded that PMMA probably consisted predominantly of short isotactic sequences. Small scale stereo-regularity of this kind could be ascribed to the orientation induced in the intercalated monomer by ion-dipole and the ester carbonyl group of the monomer. Earlier, Glavati and co-workers obtained oriented stereo-regular poly (acrylonitrile) and poly (acrylic acid) using similar procedures.[104]

Theng reported that the influence of clay minerals on the polymerization reactions extends beyond direct action on the monomers.[107-108] The chemical compounds used as polymerization initiators may also be modified by the minerals. It has been observed that clay mineral could affect both the rate and products of decomposition of initiators.

Uskov and co-workers reported that PVC or a vinyl acetate-vinyl chloride copolymer modified by a latex of Butyl acrylate-methylmethacrylate copolymer, Butadiene-styrene co-polymer, PMMA or a similar polymer was prepared by adding the latex to the reactor during the suspension polymerization.[109] The addition was made after 30-95% conversion of monomers. If inorganic compounds such as silica, montmorillonite or calcium phosphate was added before or during the polymerization, the polymers with satisfactory particle size separated out from the aqueous suspension.

Recently, Talapatra and co-workers reported that bentonite in conjuction with alcohols or thiols effectively initiate the aqueous polymerization of vinyl monomers on the surface of the mineral[110-114]. A granular soil amendment was formulated from acrylamide polymers, silicic acid or silicate and one or more of phosphates, nitrates and sulfates, or free form of urea, guanidine, dicynidiamide, and amidinothiourea.[115] The product markedly improved aggregation of clay containing soils. T. Ono and co-workers, however, polymerized MMA in H_2O containing phyllosilicates such as montmorillonite in presence of water and azo- initiators.[116]

Powder minerals encapsulated with PMMA were formed when the montmorillonite-encapsulated minerals were extracted with hot benzene or methyl acetate, a fraction remained unextractable. The PMMA encapsulated mineral composites had good processability and charpy impact strength. The polymerization of formaldehyde with o- and p- cresol in the presence of Na-montmorillonite results in the formation of linear, short copolymer chains (oriented parallel to the silicate group) in the interlamellar spaces of Na-montmorillonite.[117] The polymerization of HCHO with m-cresol did not result in copolymer formation in interlamellar spaces i.e., the high reactivity of the m-cresol resulted in the formation of 3-dimensional copolymers.