CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Water-soluble polymers are those, which can either dissolve or swell in water to form either solution or hydrogel. Polyacrylamide is a very good water soluble functional polymer used extensively in a variety of applications including paper chemicals, mineral processing, water treatment, oil-well stimulation, friction retention etc [1]. Due to the random morphologies with a wide distribution of pore sizes [2,3] of acrylamide hydrogels, it has a broad field of application like electrophoretic media for the separation or purification of biomolecules, as model drug delivery system and matrix for enzymes in living cells [4].

Polymerization processes are broadly divided into two groups known as step growth and chain growth polymerizations. In step growth polymerization, also known as condensation polymerization, polymer is formed by the condensation of two multifunctional molecules to produce one larger multifunctional molecule, with or without the elimination of a small molecule such as water. Chain growth polymerizations on the other hand, involve a chain reaction in which the chain carrier can be an ion, a free radical, or a species that is covalently attached to a catalyst such as a transition metal. Free radical chain growth polymerizations are further classified into homogeneous and heterogeneous polymerizations. In a homogeneous polymerization, all components – monomer, polymer, and initiator, form a single phase throughout the reaction. This category includes both bulk and solution (using a solvent) techniques. Bulk techniques do not require separation of the polymer from a solvent. However, bulk polymerization of vinyl monomers is very difficult, since the reactions are highly exothermic; thus leading to problems associated with heat removal. Consequently, with the exception of poly (methyl methacrylate) and polystyrene, bulk polymerizations are seldom used commercially for the manufacture of vinyl polymers. Heterogeneous polymerizations consist of at least two phases at some point during the reaction. They can be classified into four types: suspension, precipitation, dispersion and emulsion polymerization. In suspension polymerizations, the initiator, monomer and the resulting polymer all are insoluble in the polymerization medium, which forms the continuous phase. Precipitation polymerization refers to a process in which the initial ingrediants (monomer, initiator) are soluble in the continuous phase, resulting in a homogeneous solution. The polymer chains grow in length and start precipitating once they reach a critical molar mass, beyond which they are not soluble in the continuous phase, thus resulting in the formation of a polymer phase. A dispersion polymerization is similar to a precipitation polymerization with respect to the solubility of the ingredients and the polymer. The difference is that surfactants are used to prevent coagulation or agglomeration of the polymer particles. In emulsion polymerization, in contrast to dispersion polymerization the reaction mixture is initially heterogeneous. The initiator and the monomer are segregated with the initiator soluble in the continuous phase and not in the monomer phase.

Water-soluble polymers are commonly synthesized from water-soluble monomers, e.g., acrylic acid and its sodium salt, acrylamide, hydroxyethyl methacrylate, hydroxyethyl acrylate and quaternary ammonium salts like, dimethyldiallyl ammonium chloride. Usually redox polymerization of acrylamide in aqueous medium yields polymer having not so high molecular weights primarily because of fast termination process via transfer of electrons to the oxidant of the redox couple (e.g. metal ions at higher oxidation state) from the growing polymer chain. However, it has been shown recently that if the polymerization is carried out in a constrained space of a reactor (e.g. interlayer space of a clay mineral) such that the growing polymer chain may not be able to transfer the electrons to the metal ions, high molecular weight polymers are formed [5]. The effect of microenvironment of a phyllosilicate in the polymerization process is not usually confined to delayed termination only; it also affects the mechanism of formation and sometimes the structure of the polymer.

1.2 HOMO AND COPOLYMERS OF ACRYLAMIDE

Acrylamide (2-propenamide) is a white crystalline solid soluble to 2.15 g/ml in water at 30°C, and prepared commercially from acrylonitrile, CH_2=CHCN. A solution of acrylonitrile in water when passed over a copper or raney nickel catalyst at 85°C results in a near total conversion to acrylamide, a method used by the major industries [6,7]. 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 [8]. It is assumed increasing industrial importance as a chemical intermediate and as a monomer. Polyacrylamide is a very effective flocculant, a thickening agent and a pigment retension aid in papermaking. It has found wide applications 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 flocculants [9]. Mixtures of acrylamide (AM) with small proportions of N,N-methylene-bis-acrylamide (Bis) have been finding increasing application as chemical grouts. They are available commercially under the trademark “AM-9” [10]. Aqueous solutions of the monomer together with a redox catalyst are injected into soil formation. Copolymers of AM and acrylic acid are being used as stock additives for improving the dry strength of paper [11]. These are particularly useful in the manufacture of printing papers. High molecular weight AM copolymers have also shown considerable promises for increasing the retention of mineral fillers in papermaking. 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 [12]. 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 thickening water is used to drive oil through the formation to a producing well [13]. Interpolymers of AM and other monomers are useful for commercially important surface coatings [14-17]. 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 [18].

Further, as has already been mentioned, recently hydrogels of acrylamide have found tremendous industrial applications and generated huge interests in research and development.

1.3 VERMICULITE

Vermiculite occurs in nature in the form of macroscopic crystals. Vermiculites, the geological name given to a group of hydrated laminar minerals, aluminium iron magnesium silicates, are similar in appearance to mica. Biotite and phlogopite are common parent minerals of vermiculite and mixed-layer mica/vermiculite (hydrobiotite or hydrophlogopite). Due to its structural features, vermiculite clays play an important role in many natural processes and industrial applications. These include oil and gas production [19] and the removal of organic contaminants from water etc [20-22]. Recently, these clays have also been used to produce new nanoporous materials [23]. Vermiculite crystals are constituted of stacking negatively charged sheets, which are held together by charge balancing interlayer counter ions [24]. The sizeable interlayer spacing of the clay plays an important role in the transport processes of natural and contaminant species in the soil. Modeling of clay minerals is, therefore, of significant interest for understanding the underlying physico-chemical processes in various phenomena, particularly clay swelling and the behaviour of metallic ions and organic compounds in the interlamellar space. This behaviour may well depend on the dynamics of the clay structure that is generally probed by the methods of vibrational spectroscopy.

Chemical composition & structure of vermiculite

Vermiculite is a trioctahedral 2:1 layered silicate. Its empirical formula is: $Mg_{1.8}Fe^{2+}_{0.9}Al_{4.3}SiO_{10}$ $(OH)_2 \cdot 4(H_2O)$. The negatively charged layer of its structure is formed from a sheet of edge-connected XO_6 octahedra, where X is an octahedral atom (Mg, Al, Fe), which are symmetrically bound to two sheets of corner-connected TO_4 tetrahedra, where T is a tetrahedral atom (Si, Al), forming six-membered silicate rings [25]. The vermiculite structure, which is shown in Figure 1.1, contains three types of oxygen atoms. Oxygen atoms of the first type (O_I) link two Si atoms and are located at the corners of the SiO_4 tetrahadra. Oxygen atoms of the second type (O_{II}) are tetra-coordinated oxygen bound to a silicon atom and three magnesium atoms. Oxygen atoms of the third type (O_{III}) are tetra-coordinated oxygen coordinated to one hydrogen atom and three magnesium atoms. The external surfaces of the layer are built from oxygen of the first kind (O_I). The structure of vermiculite has a monoclinic unit cell and the unit cell is characterized by the following values of the lattice parameters: a = 5.33 Å, b = 9.18 Å, c = 28.90 Å, and β= 97° [25]. The interlamellar spaces are large enough to accommodate both inorganic and organic counter ions compensating the eventual charge of the layer. The amount of isomorphous substitution in vermiculite, however, is greater than in montmorillonite and much of this occurs in tetrahedral sheet [25]. Only in the fully hydrated phase (d(001) = 1.48 nm), all the available sites occupied by water molecules. As dehydration progresses, some of the unbound water are removed before the bound water. The interlayer expansion and collapse of vermiculite layers are influenced by the nature of the exchangeable cation as well as by that of the interlayer liquid [26]. In this respect its ability to form complexes with organic compound, vermiculite bear a striking resemblance to montmorillonite [27-29]. However, Mg-saturated vermiculite fails to expand beyond a basal spacing of ~1.45 nm with glycerol whereas all Mg montmorillonite appear to give double layer complex with glycerol (d(001) ~1.78nm). Weiss has reported that the basal spacing of vermiculite containing n-alkyl ammonium ions of increasing chain length (C_5 to C_{12}) increases in a stepwise fashion [30]. This behaviour was arised from the fact that on passing from an odd to next even number of carbon atoms the

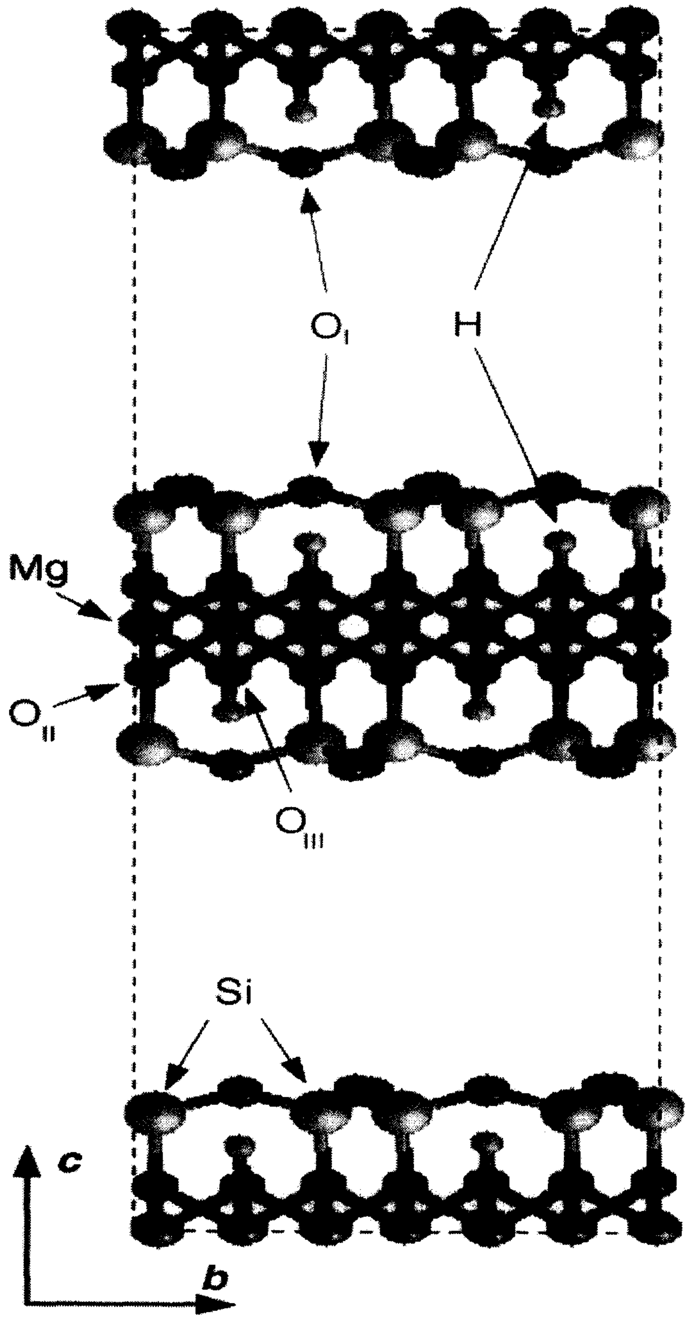

Figure 1.1: The layered structure of vermiculite

interlayer distance increases by 0.20-0.21 nm, but that on passing from an even to next higher odd number of carbon atoms – there is virtually no increase in this distance. Walker and co-workers demonstrated the presence of two distinct types of interlayer water in vermiculite crystal [33,36]. The existence of both types of water in vermiculite has since been substantiated by IR spectroscopy. Horward and co-workers observed that montmorillonite intercalated two layers of ethylene glycol or glycerol from their respective vapour phase whereas vermiculite did not yield regular double layer complexes with either ethylene glycol or glycerol, irrespective of the saturated cation and the pre-exposure to water vapour [31]. Rather, a series of complexes formed with basal spacing of about 1.36, 1.40, 1.43, 1.50, and 1.53 nm; two or more complexes may be present in the sample. Brindley has drawn the attention to the fact that about 1/6 of the diagonal sites are associated with monovalent cations in montmorillonite and with divalent cation in vermiculite [32]. In a double layer complex of extended amine molecules, 5/6 of the total sites are therefore available on each oxygen surface. This means that the amount of organic molecules, which can accommodate in a complex of this type far exceeds that which is present in the corresponding one-layer complex. With vermiculite, interlayer swelling is usually less pronounced, probably because the silicate layers are more strongly held compared to montmorillonite. The amide molecules tend to link to the cation by means of water bridges. Some vermiculite samples, however, may expand to a basal spacing of 6.3 nm after prolonged immersion in liquid N-ethylacetamide. This behaviour is reminiscent of that shown by n-butyl ammonium-vermiculite in water producing large interlayer separation. Extensive crystalline swelling of this type is attributed to the operation of osmotic repulsive forces giving rise to the formation of diffuse double layers when vermiculite crystals are immersed in strong amino acid solutions [33,34]. The effect of adsorbent charge and the kind of exchangeable cation present on the adsorption and retention of diquat and paraquat by 2:1 type layer silicates have been investigated by Weaver [35]. Maximum uptake by montmorillonite was close to the exchange capacity of the sample, being little influenced by nature of the saturating organic cations. On the other hand vermiculite adsorbed appreciably less than its exchange capacity and the extent of adsorption depended on the saturating organic cation decreasing in the order $Na^+ > Ca^{+2} > Mg^{+2}$. Vermiculite can also intercalate various amino acids. The relative lack of experimental data on vermiculite-amino acid complexes is perhaps explained by the fact that the interlayer sorption of the organic species is usually less readily achieved with vermiculite than with montmorillonite because of greater charge and hence greater electrostatic attraction between the vermiculite layers. Extensive interlayer expansion can occur in vermiculite complexes with amino acid cations [36]. Thus single crystal of vermiculite of which the inorganic cations initially present have been replaced by ornithine, lysine, and γ-amino butyric acid cations, swell in the respective amino acid solutions, when its concentration is below a critical value. Following Norrish, this type of swelling is initiated by the hydration of the interlayer amino acid cation, which dissociates from the clay surface [37]. This is followed by the development of diffuse double layer on interlayer surfaces so that subsequent interlayer expansion is controlled by osmotic repulsive interactions.

1.4 CLAY POLYMER INTERACTION

The interactions of clays with organic polymers have attracted the interest of soil scientists for a long time, being prompted by the biostability of soil organic matter ("humus") which, for the most part, is a mixture of dark-colored polyanions, and referred to as humic substances. It is now generally accepted that clay-humus interaction in soil plays an important and sometimes crucial role in many processes, such as mineral cycling, weathering, profile development and aggregate stabilization. Since early 1940, rapid advances have been made in understanding of the principles underlying the interactions of clays with organic compounds. For many systems involving small organic molecules, fairly accurate predictions can be made about the mode of bonding and orientation of the adsorbed species at the clay surface [38-39].

The clay polymer interaction has found many and varied practical applications in agriculture and chemical technology. One of the uses of polymers as flocculants of dilute clay and colloidal dispersions in which the particles are separated by relatively large distances. Flocculation involves both attachment of the polymer onto the particle surface and the bridging of several particles by the adsorbed molecule. Polymer adsorption on clay has long been a subject of both theoretical and experimental interest. The behaviour of polymers at solid-liquid interfaces is strongly connected with many technological importances such as colloidal stabilization, flocculation, adhesive, coating, and lubrication.

Clay minerals are known to catalyze a variety of organic reactions including those, which lead to polymer formation [39]. Some of these reactions, if not unique to clay systems, give yields much in excess of those obtained in homogeneous solutions. Examples of such reactions are the formation from their respective precursors of unusually bonded metal-arene complexes and higher molecular weight species [40-42], of polypeptides [43], of polynucleotides [44], and of porphyrins [45]. Clay minerals have the ability to transform and alter a variety of organic compounds through reactions, which in the absence of clays, would only proceed under extreme or special experimental conditions. Thus, clays can catalyze the oxidative degradation of amino acids and phenolic compounds [46]. Clay also act as strong Lewis and/or Brönsted acids, can transform purines and pyrimidines [47], sterols [48-49], and fatty acids [50] to yield products which occur or closely resemble those in sediments and crude oil. In a similar way clay minerals catalyze the dimerization and isomerization process of alkenes [51].

In the past decade, polymer nanocomposites have emerged as a new class of materials and attracted considerable interest and investment in research. There are several processes to make clay-based polymer nanocomposites, including in-situ polymerization [52-56], solution exfoliation [57-61] and melt intercalation [62-70] of different polymers such as nylon 6, nylon 12, nylon 66, polyimide, polypropylene, polyethylene, polystyrene, polyolefin, polycarbonate, polyethylene terephthalate etc. Layered solids used to prepare nanocomposites include graphite, clay minerals, transition metal dichalcogenides, metal phosphates, phosphonates and layered double hydroxides, etc. Among them, clay minerals have been widely used and proved to be very effective due to their unique structure and properties. Such minerals include both natural clays (e.g., montmorillonite, hectorite and saponite) and synthesized clays (e.g., fluorohectorite, laponite and magadiite). One can obtain two types of nanocomposites; intercalated structures and exfoliated structures. Especially exfoliated polymer–clay hybrids offer the improved mechanical and thermal properties because of the homogeneous dispersion of clay in polymer matrix, as well as large interfacial area of clay layers. Pristine clay is naturally hydrophilic, and polymers are often hydrophobic [71,72]. The hydrophilic nature of pristine clay impedes its homogeneous dispersion in polymer matrix. So, the clay modified with alkylammonium facilitates its interaction with a polymer because the alkylammonium makes the hydrophilic clay surface organophilic. Most of researches on synthesis of nanocomposites are focused on the organic modification of layered silicates (OLS) [73-82]. Many researchers have reported fabrication of polystyrene (PS)/clay nanocomposites [83-97] and polymethylmethacrylate (PMMA)/clay nanocomposites because of their big market volume [98-107]. Most PS and PMMA/clay nanocomposites, however, show the intercalated form of clay.

Adsorption of polymers on mineral surfaces results from the combined effects of segment-surface, segment-solvent, and segment-segment interactions. Any parameter that can affect the relative importance of these interactions will be of central importance for the comprehension of adsorption process. Adsorption of polyelectrolyte chains on clay is quite different from adsorption of uncharged polymers. One of the most prominent differences is the occurrence of long-range electrostatic interactions, which are important in the adsorption of charged polymers, whereas, for uncharged polymers, only nearest-neighbour interactions play a role. Most theories of polyelectrolyte adsorption have been developed by incorporating electrostatic free energy in the partition function of the system based on the models for the uncharged polymer. Hesselink [108,109] developed the theory of Hoeve [110,111] for the adsorption of uncharged polymers by calculating the electrostatic free energy under the assumption that the charge in the adsorbed layer is homogeneously distributed. Schee and Lyklema [112] have presented an extension to the lattice theory of Roe [113], Scheutjens and Fleer [114] by adding an electrostatic free energy term to the existing nonelectrostatic term. Interactions between polyacrylamides (hydrolyzed and nonhydrolyzed) and clay minerals are the primary reactions in most applications of the water-soluble polymers, especially for enhanced oil recovery processes [115-118]. Deng and co-workers studied the adsorption of polyacrylamide (PAM) on clay minerals [119]. Three PAMs (anionic PAM, nonionic PAM, and cationic PAM) were used to react with three common clay minerals—smectite, kaolinite, and illite. In the polymer concentration range tested (0–1.2 g/L), the anionic PAM increased the dispersion of the clay suspensions but the cationic PAM promoted the flocculation. The strong flocculation function of cationic PAM made trapped clay particles inaccessible for adsorption despite its highest affinity for clay surfaces. The adsorption of the polymers was irreversible. Nonionic PAM and cationic PAM intercalated smectite but anionic PAM did not. The adsorbed polymer moderately altered the charge properties: the cation exchange capacity (CEC) and the abilities to remove heavy metals like Cu and Cr. Such an activity followed the order anionic PAM-clay > nonionic PAM-clay ≈ clay > cationic PAM-clay. These authors observed that the PAM-clay complexes did not show distinct adsorption for hydrophobic chlorophenols, indicating that the adsorbed polymers did not increase the hydrophobicity of the clay surfaces.

Dontsova and Bigham studied the effect of various clay minerals on polysaccharide sorption under different environmental conditions, including pH, ionic strength, and cation type. The sorption of xanthan, an anionic polysaccharide, was smallest with kaolinite and greatest with a low-charge (0.62 e layer charge per unit cell) smectite where layer charge originated mostly in the tetrahedral positions and the average sorption was two times greater for smectite than for kaolinite, indicating that clay mineral composition influenced polysaccharide sorption [120]. Page and co-workers investigated the influence of temperature on the adsorption of polyacrylamide and xanthan on siliceous materials and kaolinite [121].

Hofmann and Brindley reported appreciable adsorption of nonionic aliphatic compounds having chain length C_5-C_{10} on calcium montmorillonite [122]. 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 [123]. This deviation from chain length rule of Hofmann and Brindley has been supported by Bradley for adsorption of some aliphatic amines [124]. Larger molecules with more than five units–both aliphatic and aromatic, may be adsorbed to an appreciable extent on montmorillonite in the presence of excess water [125,126]. 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 vander Waals forces to the adsorption energy [127]. As the size of the molecule increases, vander Waals interactions become important because these forces are essentially additive and tend to orient the molecule so that the maximum number of contact points are established [128,129]. The adsorption of one organic molecule is accompanied by the disorption 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 [130,131]. 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 to C_7 organic compounds of different functional groups adopted on the clay mineral is in the order:

$\propto$ - methyl – acetyl acetone > acetoacetic ethyl ester > β - ethoxy propionitrile
hexanedione – 2,5 > hexane diol -1,6 > 2,4 - hexadiyne diol -1,6 [122].

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 Ca-montmorillonite invariably yielded as double layer complex whereas the corresponding Na-clay gave either a single or a double layer complex [132]. This difference between Ca and Na- montmorillonite in their behaviour towards polar organic liquids accords with later findings of German and co-workers for ethanol-montmorillonite and acetone-montmorillonite systems is ascribable to the grater solvation energy of the calcium ion compared to that of sodium ion [123,133]. The formation of double layer complexes of montmorillonite with some ethers and polyethers has been reported [124,132]. From X-ray data the basal spacing of 1.31-1.34 and 1.57-1.76 nm were suggested for both single and double layer complexes respectively [122].

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.

Weil-Malherbe and Wiss showed that both acid-base interaction and oxidation-reduction reactions were involved in the formation of coloured clay complexes with certain aromatic amines [134]. Briegleb showed that the association between clays and organic compounds may be termed electron donar-acceptor complexes [135]. Solomon and co-workers proposed a model based on charge transfer between the mineral and the absorbed organic species [136]. Toth and co-workers studied the thermal decomposition of complexes produced from bentonite and a linear polyacrylamide (PAM) by using TG-mass spectroscopy [137]. 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.

Bussetti and Ferreiro reported the adsorption of poly (vinyl alcohol) on calcium and sodium montmorillonite as a function of the pH value [138] The adsorption 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 [139-144]. The adsorption and polymerization of AM in the complex composite films which were prepared by adding AM and water to Na-fluortetrasilicic mica were investigated by Nagal and co-workers [145]. 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 differential scanning calorimetry (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.

1.5 CLAY CATALYZED POLYMERIZATION

Many of the common fillers (china clay, talc) belong to the classes of aluminium and magnesium silicates known as the clay minerals. Recently it has been shown that these minerals catalyze a number of polymerization reactions if adsorbed water is removed by drying under mild conditions [146]. Other reports also suggest that the clay minerals are not chemically inert. In some polymer compositions they are claimed to adversely affect crosslinking reactions, for examples, in the curing of unsaturated polyester with styrene [147,148], which involves free-radical intermediates. 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 [149], alkylation [150], isomerization [151], polymerization [152] etc. In 1960's and earlier clay initiated polymerizations of vinyl monomers emphasized on the use of dry clay minerals and non-polar solvents [153,154]. Although the carbocationic polymerizations of vinyl monomers have been investigated extensively with Lewis acid such as $AlCl_3$, $TiCl_4$, Et_2O, BCl_3, alkyl aluminiums etc. [155-161], the first report on such polymerization of styrene with acid clays [153] came in 1964. Almost 100% yield of polystyrene of molecular weights 500-2000 was achieved. The catalytic activity of the clay has been shown to be due to active protons associated with tetrahedral (due to dehydration of mineral) aluminium [162,163]. The formation of carbonium ion following surface adsorption of olefins on acid sites caused subsequent polymerization. Proton accepting contaminants such as water, amines etc., being preferentially adsorbed over styrene suppressed the polymerization. Styrene polymerized on the surface of homoionic clays [164]. It is argued that an electron transfer from adsorbed styrene to the aluminium produces radical cations, which dimerise rapidly. Both radical cation 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 Brönsted acidity rather than Lewis acidity to be responsible for the initiation of the polymerization of styrene by montmorillonite, a smectite clay mineral [165]. The inconsistency of their experiments, however, is in the reduction of polymer yield in the presence of trityl chloride, which selectively adsorbed on Lewis acid sites. They argued in favour of the Brönsted 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 [166]. This would apply equally well to the propagating process and therefore, the initiation by a radical ion mechanism cannot be ruled out [164]. The possibility of proton transfer to monomer leading to decreased average degree of polymerization, as in conventional cationic mechanism, has also been discussed [162]. The work of Matsumoto and co-workers along with Solomon and Rosser lead one to the conclusion that acidity of the clay cannot be solely ascribed to either Bronsted acidity or Lewis acidity [164,165]. It is 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 colorations of aqueous benzidine in the presence of oxidized montmorillonite [164,167]. Solomon and Rosser failed to find evidence of styrene interacting with the clay mineral which lead them to assume that styrene is either incapable of moving into the interlayer space or capable of doing so with difficulty. Blumstein and co-worker have studied the polymerization of MMA and methyl acrylate in montmorillonite interlayer induced by γ-radiation [168-171]. The interlayer polymer was 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 [172]. Glavati and co-workers found that the polymerization in acrylonitrile-montmorillonite complex by γ-radiation produced stereospecific polymers [172].

Thermal polymerization of a number of vinyl monomers could be induced by montmorillonite/2-2-azobis-isobutyramidine (AIBA) system if AIBA was previously introduced to the clay mineral [173]. 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 initiating efficiency. The rate of polymerization with AIBA-montmorillonite complex initiator is greater than for AIBA alone [174]. 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. 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 polymethylmethacrylate (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 presence of mineral is not due to depolymerization has been established by heating PMMA with montmorillonite and determining the viscosity average molecular weight, M_V, before and after treatment. In a recent ESR study to assess the state of iron in montmorillonite, signals in the weak field at 'g; values of 7.6, 4.2 and 3.9 were assigned to Fe (III) ions in the octahedral layer of the mineral. The intensities of the wide bands of the spectra remain unchanged 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 structural properties of the polymers from clay catalyzed polymerizations of vinyl monomers have been made by several workers. Blumstein and co-workers studied the 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 [168-171]. Analyzing the NMR data they concluded that PMMA probably consisted predminantly of 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 polyacrylonitrile and polyacrylic acid using similar procedures [172]. It has been reported that the influence of clay minerals on polymerization reactions extends beyond direct action on monomers [174,175]. The minerals may also modify the chemical compounds used as polymerization initiators. It has been observed that clay minerals could affect both the rate and the rate of decomposition of initiators. Uskov and co-workers reported that polyvinylchloride (PVC) or a vinyl chloride copolymer modified by latex of butylacrylate-methylmethacrylate copolymer, butadiene-styrene copolymer, PMMA or a similar polymer was prepared by adding the latex to the reactor during the suspension polymerization [176]. The addition was made after 30-95% conversion of monomers. If inorganic compounds such as silica, montmorillonite or a calcium phosphate were added before or during the polymerization, the polymer with satisfactory particle size separated out from the aqueous suspension. Talapatra, Saha and co-workers reported that bentonite in conjunction with alcohols or thiols effectively initiate aqueous polymerization of vinyl monomers on the surface of the minerals [177-181]. 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, dicyandiamide and amidinothiourea [182]. The product markedly improved aggregation of clay containing soils. Ono and co-workers, however, polymerized MMA in H_2O containing phyllosilicates in presence water and azo initiators [183].

1.6 REFERENCE

1. H.R. Lin, *Eur Polym J*, **37**, 1507(2001).
2. D.G. Liu, *Anal Biochem*, **339**, 351(2005).
3. C.L. Lester, S.M. Smith, G.C. Allan, *Maromolecules*, **34**, 8587(2001).
4. D. Yankov, *Enzyme Microb Technol,* 34, 603(2004).
5. P. Bera and S.K. Saha, *Macromol Rapid Commun*, **18**, 261(1997).
6. D. Lipp and J. Kozakiewicz, 1991, ' Acrylamide polymers' in *Encyclopedia of Chemical Technology*, ed. J.I. Kroschwitz, John Wiley and Sons, New York.
7. C.E. Habermann, 1991, Acrylamide' in *Encyclopedia of Chemical Technology*, ed. J.I. Kroschwitz, John Wiley and Sons, New York.
8. The Chemistry of Acrylamide: A review with many references, American Cyanamid Company, New York, (1956).
9. E.R. Kolodny and R.B. Booth, *Canadian Pat.* 616,976, (1961), (to American Cyanamid Company).
10. AM-9 Chemical Grout, American Cyanamid Company, New York, 1960.
11. Accostrength Paper Resin 2386, American Cyanamid Company, New York, 1959.
12. R.L. Mongan and E.R.Kolodny, *U.S. Pat.*2, 868,753 (1959) (to American Chamical Company).
13. E.R. Kolodny, *U.S. Pat.* 3,002, 960 (1961), (to American Chamical Company).
14. C.L. McCormick and G.S. Chen, *J Polym Sci Polym Chem Ed,* **22**, 3649(1984).
15. R.M. Christenson and H.A. Vogel, *U.S.Pats*, 919, 254(1959), 2,940, 943 and 2,940, 944(1960), (to Pittsburgh Plate Glass Company).
16. H.A. Vogel and H.G. Bittle, *U.S. Pats*, 2,870,116 and 2,870,117(1959), (to Pittsburgh Plate Glass Company).
17. "Thermosetting Acrylic Resins", a symposium in *Ind Chem*, **53**, 458(1961).
18. A.S. Tomcufeik, S.D. Willson, A.W. Vogel and A. Sloboda, *Nature*, **191**, 611(1961).

19. S. Karaborni, B. Smit, W. Heidug, J. Urai and E. Oort, *Science*, **271**, 1102(1996).
20. S.A. Boyd, J. F. Lee and M. Mortland, *Nature (London),* **333**, 345(1988).
21. G.D. Williams, N.T. Skipper, M.V. Smalley, A.K. Soper and S.M. King, *Faraday Discuss Chem Soc*, **104**, 295(1996).
22. L.S. Kajita, *Clays Clay Miner*, **45**, 609(1997).
23. R. Dhamodharan, J.D. Jeyaprakash, S. Samuel and M.K. Rajeswari, *J Appl Polym Sci*, **82**, 555(2001).
24. A.C.D. Newman, in *Chemistry of Clay and Clay Minerals*, Mineralogical Society, London, 1987.
25. A. Mathieson and G. F. Walker, *Am Mineral*, **39**,231(1954).
26. J.A. Bittles, A.K. Chaudhuri and S.W. Benson, *J Polym Sci*, **A2**, 1221(1964).
27. W.D. Johns and R.T. Tetenhorst, *Am Mineralogist*, **44**, 894(1959).
28. G.W. Brindley, K. Wiewiora and A. Wiewiora, *Am Mineralogist,* **54,**1635(1969).
29. A. Amil and D.M.C. Macewan, *Kolloid Z,* **155**, 134*(*1957).
30. A. Weiss, *Angew Chem Int Edit Engl,* **2,**134(1963).
31. M. Harward, D.D. Carstea, and A.H. Sayegh, *Clays Clay Minerals,* **16,** 437 (1969).
32. G.W. Brindley, *Clay Minerals,* **6**, 91(1965).
33. G.F. Walker and W.G. Garrett, *Nature*, **191**, 1389(1961).
34. I. Barshad, *Soil Sci Soc Am Proc*, **16**, 176(1952).
35. C.E. Weaver, *Am Mineralogist*, **43**,839(1958).
36. G.F. Walker and W.G. Garrett, *Nature*, **191**,1389(1961).
37. K. Norrish, *Disc Faraday Soc,* **18,**120**(**1954).
38. M.M. Mortland, *Advan Agron*, **22**, 75(1970).
39. B.K.G. Theng, *The Chemistry of Clay-Organic Reactions*: Adam Hilger, London, p 343 (1974).
40. H.E. Doner and M.M. Mortland, *Science,* **166**, 1406(1969).
41. M.J. Tricker, D.T.B. Tennakoon, J.M. Thomas and S.H. Graham, *Nature*, **253**, 110(1975).
42. M.M. Mortland and L.J. Halloran, *Soil Sci Soc Amer J*, **40**, 367(1976).

43. M.P. Horowitz, *J Mol Evol*, **11**, 101(1978).

44. J.D. Ibanez, A.P. Kimbal and J. Oro, *Science*, **173**, 444(1971).

45. S.S. Cady and T.J. Pinnavaia, *Inorg Chem*, **17**, 1501(1978).

46. T.D. Thomson and A. Tsunashina, *Clays and Clay Minerals*, **21**, 351(1973).

47. W. Vander Vender, G.J.F. Chittender and A.W. Schwartz, (Advan. Org. Geochem, Proc. 6th Int. Congr, 293-304(1973).

48. J.W.D. Leeuw, V.A. Correia and P.A. Schenck, Advan Org Geochem, Proc 6th Int Congr, 993-1004(1973).

49. O. Sieskind, G. Joly and P. Albrecht, *Geochim Cosmochim Acta*, **43**, 1675(1979).

50. W.R. Almon and W.D. Johns, (1976) Petroleum forming reactions: clay catalyzed fatty acid decarboxylation: in Proc. Int. Clay Conf, Maxico City, 1975, S.W. Bailey, ed., Applied Publishing, Wilmette, Illinois, 399-409.

51. J.R. Sohn and A. Ozaki, *J Catalysis,* **61**, 29(1980).

52. A. Usuki, M. Kawasumi, Y.Kojima, A. Okada, T. Kurauchi and O. Kamigaito, *J Mater Res*, **8**, 1174(1993).

53. A. Usuki, Y. Kojima, M. Kawasumi, A. Okada, Y. Fukushima, T. Kurauchi and O. Kamigaito, *J Mater Res*, **8**, 1179(1993).

54. T.M. Wu and C.S. Liao, *Macromol Chem Phys*, **201**, 2820(2000).

55. A. Matsumura, Y. Komori, T. Itagaki, Y. Sugahara and K. Kuroda, *Bull Chem Soc Jpn*, **74**, 1153(2001).

56. T.M. Wu and E.C. Chen, *Polym Eng Sci*, **42**, 1141(2002).

57. K. Yano, A. Usuki and A. Okada, *J Polym Sci Part-A: Poly Chem,* **35**, 2289(1997).

58. M. Kato, A. Usuki and A. Okada, *J Appl Polym Sci*, **66**, 1781(1997).

59. M. Kawasumi, N. Hasegawa, M. Kato, A. Usuki and A. Okada, *Macromolecules*, **30**, 6333(1997).

60. N. Hasegawa, M. Kawasumi, M. Kato, A. Usuki and A. Okada, *J Appl Polym Sci*, **67**, 87(1998).

61. D. Wolf, A. Fuchs, U. Wagenknecht, B. Kretzschmar, D. Jehnichen and L. Haussler, in Eurofiller'99, Lyon-Villeurbanne (1999).

62. B. Han, G.D. Ji, S.S. Wu and J. Shen, *Eur Polym J*, **39**, 1641(2003).

63. F. Chavarria and D.R. Paul, *Polymer*, **45**, 8501(2004).
64. Z.Z. Yu, C. Yan, M.S. Yang, and Y.W. Mai, *Polym Int*, **53**, 1093(2004).
65. Q. Zhang, K. Wang, Y. Men, and Q. Fu, *Chin J Polym Sci*, **21**, 359(2003).
66. E.C. Lee, D.F. Mielewski and R.J. Baird, *Polym Eng Sci*, **44**,1773(2004).
67. Y. Wang, F.B. Chen, Y.C. Li, and K.C. Wu, *Compos Part-B: Eng*, **35**, 111(2004).
68. X.Q. Zhang, M.S. Yang, Y. Zhao, S.M. Zhang, X. Dong, X.X. Liu, D.J. Wang and D.F. Xu, *J Appl Polym Sci*, **92**, 552(2004).
69. C.M. Koo, J.H. Kim, K.H. Wang, and I.J. Chung, *J Polym Sci Part-B: Polym Phys*, **43**, 158(2005).
70. M.J. Chung, L.W. Jang, J.H. Shim and J.S. Yoon, *J Appl Polym Sci*, **95**, 307(2005).
71. T.J. Pinnavaia, *Science,* **220**, 365(1983).
72. H.H. Murray, *Appl Clay Sci*, **17**, 207(2000).
73. R.A. Vaia, R.K. Teukosky, E.P. Giannelis, *Chem Mater*, **6**, 1017(1994).
74. R. Krishnamoorti, R.A. Vaia, E.P. Giannelis, *Chem Mater*, **8**, 1728(1996).
75. R. Krishnamoorti, E.P. Giannelis, *Macromolecules,* **30**, 4097(1997).
76. R. Limary, S. Swinnea, P.F. Green, *Macromolecules*, **33**, 5227(2000).
77. J. Ren, A.S. Silva, R. Krishnamoorti, *Macromolecules*, **33**, 3739(2000).
78. Y. Lyatskaya, A.C. Balazs, *Macromolecules*, **31**, 6676(1998).
79. A.C. Balazs, C. Singh, E. Zhulina, *Macromolecules*, **31**, 8370(1998).
80. E. Zhulina, C. Singh, A.C. Balazs, *Langmuir*, **15**, 3935(1999).
81. A.C. Balazs, C. Singh, E. Zhulina, Y. Lyatskaya, *Acc Chem Res*, **32**, 651(1999).
82. V.V. Ginzburg, A.C. Balazs, *Adv Mater*, **12**, 1805(2000).
83. A. Akelah, N. Salahuddin, A. Hiltner, E. Baer, A. Moet, *Nanostruct Mater*, **4**, 96(1994).
84. A. Akelah, A. Moet, *J Mater Sci*, **31**, 3589(1996).
85. A. Moet, A. Akelah, *Mater Lett*, **18**, 97(1993).
86. E.P. Giannelis, *Adv Mater*, **8**, 29(1996).
87. B. Hoffmann, C. Dietrich, R. Thomann, C. Friedrich, R. Mulhaupt,

Macromol Rapid Commun, **21**, 57(2000).

88. X. Fu, S. Qutubuddin, *Mater Lett*, **42**, 12(2000).
89. X. Fu, S. Qutubuddin, *Polymer*, **42**, 807(2001).
90. M.W. Weimer, H. Chen, E.P. Giannelis, D.Y. Sogah, *J Am Chem Soc*, **121**, 1615(1999).
91. R. Vaia, H. Ishii, E. Giannelis, *Chem Mater*, **5**, 1694(1993).
92. M. Sikka, L.N. Cerini, S.S. Ghosh, K.I. Winey, *J Polym Sci, Part-B: Polym Phys*, **34**, 1443(1996).
93. P. Kelly, A. Akelah, S. Qutubuddin, A. Moet, *J Mater Sci*, **29**, 2274(1994).
94. R.A. Vaia, K.D. Jandt, E.J. Kramer, E.P. Giannelis, *Macromolecules*, **28**, 8080(1995).
95. H.Z. Friedlander, C.R. Grink, *J Polym Sci Polym Lett*, **2**, 475(1964).
96. C. Kato, K. Kuroda, H. Takahara, *Clays Clay Miner*, **29**, 294(1981).
97. G. Chen, Z. Ma, *Scripta Mater*, **44**, 125(2001).
98. A. Blumstein, *J Polym Sci Polym Chem*, **3**, 2653(1965).
99. A. Blumstein, *J Polym Sci Polym Chem*, **3**, 2665(1965).
100. J. Bhattacharya, S.K. Chakraborti, S. Talapatra, *J Polym Sci Polym Chem*, **27**, 3977(1989).
101. G. Chen, X. Chen, Z. Lin, W. Ye, K. Yao, *J Mater Sci Lett*, **18**,1761(1999).
102. M. Okamoto, S. Morita, H. Taguchi, Y.H. Kim, T. Kotaka, H. Tateyama, *Polymer*, **41**, 3887(2000).
103. D.C. Lee, W.J. Lee, *J Appl Polym Sci*, **61**, 1117(1996).
104. A. Biasci, M. Aglietto, G. Ruggeri, F. Ciardelli, *Polymer*, **35**, 3296(1994).
105. H. Sato, H. Taguchi, N. Sato, M. Okamoto, T. Kotaka, *Polym Prep Jpn*, **46**, 2719(1997).
106. X. Huang, W.J. Brittain, *Macromolecules*, **34**, 3255(2001).
107. C. Zeng, J.L. Lee, *Macromolecules*, **34**, 4098(2001).
108. T.T. Hesselink, *J of Colloid and Interface Sci*, **60**,448(1977).
109. T.T. Hesselink, in "Adsorption from Solution at the Solid/Liquid Interface" (G.D. Parfitt and C.H. Rochester, Eds.), Academic Press, London (1983).

110. C.A.J. Hoeve, *J Chem Phys*, **44**, 1505(1966).
111. C.A.J. Hoeve, *J Chem Sci,* (C)**30**, 361(1970).
112. H.A. Vander Schee and J. Lyklema, *J Phys Chem*, **88**, 6661(1984).
113. R.J. Roe, *J Chem Phys.* **60**, 1192(1974).
114. J.M.H.M. Scheutjens and G.J. Fleer, *J Phys Chem*, **83**, 1619(1979); **84**, 178(1980).
115. L.T. Lee, R. Rahbari, J. Lecourtier and G. Chauveteau, *J of Colloid and Interface Sci,* **147**, 351(1991).
116. J. Lecourtier, L.T. Lee and G. Chauveteau, *Colloids Surf*, **47**, 219 (1990).
117. J. Lecourtier and G. Chauveteau, *Third Coll Eur RAP*, **32**, 178 (1985).
118. L. Pefferkorn, L. Nabzar and R. Varoqui, *Colloid Polym Sci*, **265**, 889(1987).
119. Y. Deng, J.B. Dixon and G.N. White, *Soil Sci Soc of Am*, **70**, 297(2006).
120. M.D. Katerina and J.M. Bigham, *Soil Sci Soc of Am,* **69**, 1026(2005).
121. M. Page, J. Lecourtier and C. Noik, *J Colloid and Interface Sci*, **161**, 450(1993).
122. R.W. Hofmann and G.W. Brindley, *Geochim Cosmochim Acta*, **21**,15(1960).
123. W.L. German and D.A. Harding, *Clay Minerals*, **8**, 213(1969).
124. W.F. Bradley, *J Am Chem Soc*, **67**,975(1945).
125. R.W. Doehler and W.A. Young, *Clays and Clay Minerals*, **9**, 468(1962).
126. C.A. Bower, *Soil Sci*, **95**,192(1963).
127. D.J. Greenland, *Soil Fertilizers*, **28**,415(1965).
128. J.H.De Boer and G.Heller, *Physica*, **4**, 1045(1937).
129. H.C. Mahaker, Physica, **4**, 1058(1937).
130. D.J. Greenland, *J Colloid Sci*, **18**,647(1963).
131. R.L. Parfilt and D.J. Grenland, *Clay Minerals*, **8**, 305(1970).
132. D.M.C. McEwan, *Trans Faraday Soc*, **44**, 349(1948).
133. K.K. Bissada, W.D. Johns and F.S. Cheng, *Clay Minerals*, **7**,155(1967).
134. J.W. Malherbe and J. Weis, *J Chem Soc*, 2164(1948).
135. G. Briegleb, Electronen-Donator-Acceptor-Complex, Pringer verlag, Berlin.

136. D.H. Solomon, B.C. Loft and J.D. Swift, *Clay Minerals*, **7**,389(1968).

137. L. Toch, J. Szepvolgyi, J. Emma, P. Szabo and T. Szekey, *Thermochim Acta*, **170**,155(1990).

138. G.B. Silvia and A.F. Eladio, *Clays and Clay Minerals*, **52**(3), 334(2004).

139. S.K. Chakraborti, *Sci Cult*, **22**,170(1956).

140. S.K. Chakraborti, *J Ind Soc Soil Sci*, **5**,185(1957).

141. S.K. Chakraborti, *J Ind Soc Soil Sci*, **5**, 65(1957).

142. S.K. Chakraborti, *J Ind Soc Soil Sci*, **6**, 239(1958).

143. S.K. Chakraborti, *J Ind Soc Soil Sci*, **7**, 27(1959).

144. S.K.Chakraborti, D.Phil.Thesis, Calcuta University (1959).

145. H. Nagae, K. Kawase, H. Sakami, S. Lida and Hayakawa, *Kiyoshi Kabunshi Ronbunshu*, **47**(8), 631(1990).

146. D.H. Solomon and M.J. Rosser, *J Appl Polymer Sci*, **9**,1261(1965).

147. N.G. Stanko, *Lakokrasochnye Minerals*, **3**,14(1961).

148. J. Samois, *Oil Colour Chemicals Assoc*, **47**, 906(1964).

149. C. Kemball and J.J. Rooney, *Proc Roy Soc Japan*, **52**, 43(1949).

150. S. Mohil, Oil Co, INC, Brit.Pat.896, 864(1962).

151. Y. Suehiro, M. Kuwabara and V. Ayukawa, *J Chem Soc Japan*, **52**, 43 (1949).

152. F.E. Shephard, J.J. Rooney and C. Kemball, *J Catalysis*, **1**,379(1962).

153. H.Z. Friendlander, *J Polym Sci*, **C4**, 1291(1964).

154. D.H. Solomon, J.D. Swift and A.J. Murphy, *J Macromol Sci*, **A5 (3)**, 587 (1971).

155. P.H. Flesch, Cationic Polymerization and Related Complexes, Academic Press, New York (1953).

156. D.C. Pepper, *Trans Faraday Soc*, **45**, 3979(1949).

157. D.C. Pepper, *Trans Faraday Soc*, **45**, 404(1949).

158. D.C. Pepper and M.J. Hayes, *Proc Chem Soc*, 228(1958).

159. A.G. Evans and G.W. Meadows, *Trans Faraday Soc*, **46**, 327(1950).

160. G.F. Endres and C.G. Overberger, *J Am Chem Soc*, **77**, 2201(1955).

161. J.P. Kenedy, Cationic Polymerization of Olifins. : A Critical Inventory, Wiley-Interscience, (1975).

162. J.A. Britles, A.K. Choudhuri and S.W. Benson, *J Polym Sci*, **A2**, 1847(1964).

163. J.A. Britles, A.K. Choudhuri and S.W. Benson, *J Polym Sci*, **A2**, 3203(1964).
164. D.H. Solomon and M.J. Rosser, *J Polym Sci*, **9**, 1261(1965).
165. T. Matsumoto, I. Sakai and M. Arihara, *Chem High Polymers (Japan)*, **26**, 378(1969).
166. M.M. Mortland, Trans. 9th Intern. *Cong Soil Sci Adelaide*, **1**,691(1968).
167. W. Bodenheimer, L. Heller and S. Yariv, *Internat Clay Conf Jerusalem*, **I**, 251(1966).
168. A. Blumstein, *J Polym Sci*, **A3**, 2653(1965).
169. A. Blumstein and F.W. Bilmeyer, *J Polym Sci*, **A4**, 465(1966).
170. A. Blumstein and R.Blumstein, *Polymer Letters*, **5**, 69(1967).
171. A. Blumstein, S.L. Malhotra and A.C. Waterson, ACS, *Polymer Reprints*, **167** April(1968).
172. O.L. Glavati, L.S. Polak and V.I. Shchexin, *Neftekhimiya*, **3**, 905(1963).
173. H.G.G. Dekking, *J Appl Polym Sci*, **9**, 1641(1965).
174. H.G.G. Dekking, *J Appl Polym Sci*, **11**, 23(1967).
175. D.H. Solomon and B.C. Loft, *J Appl Polym Sci*, **12**, 1253(1968).
176. I.A. Uskov, Y.G. Tarasenco, V.P. Solomko, *Vysokomolekhul Soedin*, **6**, 1768(1964).
177. S. Talapatra, S.K. Saha, S.K. Chakroborti and S.C. Guhaniyogi, *Polym Bull*, **10**, 21(1983).
178. S. Talapatra, S.C. Guhaniyogi, and S.K. Chakraborti, *J Macromol Sci Chem*, **A22 (11)**, 1611(1985).
179. J. Bhattacharya, S.K. Chakraborti, S. Talapatra, S.K. Saha and S.C. Guhaniyogi, *J Polym Sci Part-A: Polymer Chemi*stry, **27**, 3977(1989).
180. J. Bhattacharya, S.K. Saha and S.C. Guhaniyogi, *J Polym Sci Part-A: Polymer Chemistry*, **28**, 2249(1990).
181. S.K. Saha and D.J. Greenslade, *Bulletin of Chemical Society of Japan*, **65**, 2720(1992).
182. Jpn. Patent, 58, 28, 313, June 15, 1983, Nilto Chemical Industry Co. Ltd.
183. T. Ono, T. Takahashi, M. Konno and T. Mikawa, *Ken Kyu Kiyomiyagi, Kagyo Koto Senmon Gakko*, **18**, 57(1982).