CHAPTER II
LITERATURE SURVEY

2.1 Dendrimer

The first synthesis of "cascade" poly(propylenimine) is credited to Buleier and coworkers in 1978. It consisted of Michael addition of acrylonitrile to primary amine groups. Each successive step involved reductions of the nitrile groups followed by additions of acrylonitrile.

In 1985, Tomalia and coworker's poly(amidoamine) dendrimers are synthesized. These are the first dendritic structures that have been thoroughly investigated and that have received wide spread attention. There are three distinct architectural components. The multi-functionalized core (initiator core) forms the heart of the molecules; all branches emanate from this core. The paper includes calculations of the molecular weight and other useful quantities about the dendrimer molecules.

In 1990, Hawker and Fréchet introduced the convergent approach toward dendrimers. The reaction starts at the periphery and proceeds to the core while Tomalia's PAMAM dendrimers were synthesized using divergent method, starting with an initiator core and expanding to the periphery. In the first step, 2 mol of a benzylic bromide is condensed with the two phenolic groups of the monomer, 3,5-dihydroxybenzyl alcohol, under phase-transfer conditions. After transformation of the benzylic alcohol functionality of the growing molecule into the corresponding bromide, the procedure is repeated with stepwise addition of the monomer followed again by activation of the benzylic site. After several generations of growth, the resulting dendritic wedges, in their benzylicbromide form, can be coupled to a polyfunctional core such as 1,1,1-tris(4′-hydroxyphenyl)ethane to form the final hyperbranched macromolecule.

The unique feature of "dendritic box" is explored by Tomalia's group in 1997. The modified dendrimers Gn(C12) show the ability to host the hydrophobic dye in aqueous solution. Moreover, the interaction of these dendrimers with anionic surfactants generates supramolecular assemblies which greatly enhance their ability to accommodate the dye. The capability of hosting small organic molecules in water is the key to transport biological molecules.

Bosman and coworkers, 1999 proposed that hydrophilic dendrimers with hydrophobic functionalities on the periphery form micelles in organic solvents. These types of dendrimers can extract organic compound from the water phase to the organic phase. In addition, there are small differences in structural features of the divergently and convergently produced structures. It is regardless the way in which they have been prepared. In the same year, hyperbranched analogues of the Tomalia's PAMAM dendrimer have been prepared from a series of A_2B aminoacrylate hydrochloride monomers using Michael addition chemistry by Hobson and Feast. The synthesis of these monomers involves classical protection/deprotection chemistry using t-BOC protecting group, where control over both molecular weight and extent of branching through B_n unit. The materials exhibit a branching factor close to one.

One year later, Chang and coworkers, 2000 synthesized a new class of amphiphilic linear-dendritic diblock copolymers based on hydrophilic linear PEO and hydrophobic dendritic carbosilane using a divergent approach at the allyl end group of the allyl-terminated PEO. The amphiphilic nature of these block copolymers was highly dependent on the size of the hydrophobic dendritic block. The block copolymer with the dendritic moiety of a third generation could not be dispersed in water. The block copolymers with the first (PEO-Si-1G) and, the second (PEO-Si-2G) generation of dendritic carbosilane blocks form micelles in an aqueous phase.

2.2 Polymer-Clay Nanocomposite

In 1993, Wu and Lerner prepared layered nanocomposites from Na-montmorillonite and PEO. The nanocomposites were characterized using X-ray diffraction, impedance spectroscopy, DTA and TGA. Two reaction stoichiometries were used to obtain uniform clay's gallery expansions. Materials prepared with intermediate stoichiometric yield diffraction profiles characteristic of solid solutions of these two phases. The details of composition and structure provide strong evidence that the polymer conformation was not helical as in crystalline PEO but more closely resembles an adsorbed layer. Moreover, sodium salts such as $NaClO_4$ could also be incorporated into the polyether/clay phases.

Swenson and coworker, 2001 investigated the interlayer structure of a four-component clay-polymer-salt-water system consisting of n-butylammonium vermiculite, poly(ethylene oxide) (PEO), n-butylammonium chloride and heavy water using neutron diffraction and H/D isotope substitution of the butylammonium and PEO chains. They found that the PEO molecules, salt ions, and water molecules are located in the interlayer regions between parallel and regularly spaced clay platelets. The results showed that the added PEO does not cause any significant alteration in the distribution of butylammonium ions, when compared with the corresponding three-component system without added PEO. The clay surfaces are covered by, first, one layer of adsorbed ethylene oxide segments and water molecules, second, another molecular layer of water and third, the layer of butylammonium ions. From the ordered structure around each clay platelet, they obtain a picture of an approximately 30 Å thick dressed macroion. The polymer segments that are not adsorbed onto the clay surfaces are rather homogeneously distributed in the interlayer region, at least in the present case with a high molecular weight PEO. Each polymer molecule adsorbs onto both clay surfaces and thereby induces a reduction of the interlayer spacing by a phenomenon known as polymer bridging flocculation.

In 2002, Månson and coworker prepared hyperbranched polymer layered silicate nanocomposite from -OH terminated hyperbranched polyesters (HBP) and Na-MMT. HBP was prepared by condensation of 2,2-bis-hydroxymethyl propionic acid (bis-MPA) with a tetrafunctional ethoxylated pentaerythritol core to give structures analogous to the dendrimer. HBP-clay nanocomposites with varied amount of clay were prepared by mixing the required amount of Na-MMT with aqueous dispersions of HBP at suitable condition. As the result, at 10 wt % clay, exfoliation was confirmed to dominate by XRD and TEM.

2.3 Organic Impurities Adsorption from Water

Wibulswas and coworker, 2000 investigated the feasibility of utilizing montmorillonite as an adsorbent for removing organic toxicants from wastewater. Montmorillonite was modified in a manner that considerably improves their capacities to remove organophilic impurities by using QACs (Quaternary Ammonium Cations) like TMA, BDHDMA, HDTMA and TDMA. They found that the larger organic QACs increase the spacing between the tetrahedral sheet and the organophilic sorption zone is created between the layer of the clay. The study has evaluated the ability of organoclay to remove various organic compounds from water by means of hydrophobic interaction. The results shown that the anionic, like methyl orange, and the nonionic, like phenols and naphthalene, organic components do not adsorb on the montmorillonite while the presence of long alkyl chain length QACs causes significant adsorption of those organic components. The adsorption of humic acid, anionic and nonionic organic components on clays were enhanced significantly with an increasing of organic carbon content on montmorillonite.

In the same year, Sheng and Boyd, 2000 studied the sorptive properties of hexadecyltrimethylammonium (HDTMA) clays prepared by using a high charge smectite (HDTMA-Saz-1), a low-charge smectite (HDTMA-Swy-2) and an illite (HDTMA-ILL). The resultant organoclays were used to sorb aqueous phase 1,2-dichlorobenzene (*o*-DBC), 1,3-dichlorobenzene (*m*-DBC) and 1,4-dichlorobenzene (*p*-DBC). Sorptive characteristics of these compounds were determined by their molecular polarities (*o*-DBC > *m*-DBC > *p*-DBC) and the HDTMA-clay interlayer distance. HDTMA-ILL was used for comparison to HDTMA-Saz-1 and HDTMA-Swy-2. All dichlorobenzene isomers were directly intercalated in the interlayers of HDTMA-SAz-1, causing interlayer expansion. *o*-DCB and *m*-DCB were not intercalated in the interlayers of HDTMA-SWy-2 at low concentrations, but intercalation occurred at higher concentrations, which caused interlayer expansion. The concentration needed to produce interlayer expansion depended on the solute molecular polarity, hence a higher concentration of *m*-DCB than *o*-DCB was required. *p*-DCB was sorbed primarily by the HDTMA phase on the external surfaces of HDTMA-Swy-2.