

CHAPTER I

INTRODUCTION

Dendrimers have become a particular interest to the polymer science community in the past 20 years. A wide variety of dendrimers with different chemistries has been synthesized to present new and well-defined architectures with interesting properties and applications. Many of the potential applications make use of two important properties of dendrimers, both of which are a direct consequence of their architecture: the large number of end groups and the nanoporous nature of the interior at higher generations (Tomalia et al., 1997). Poly(amidoamine) hyperbranched is an example of dendritic materials. Due to its molecular structure, both hydrophilic and hydrophobic characters are represented in the molecules of poly(amidoamine) via ionic character of ammonium salt and methylene spacer length and this should be useful in the application of waste water treatment.

Silicate clays are natural substances which have interesting geometry due to their surface area and electronegative charge. As a consequence, thousands of positively charged ions are attracted to each colloidal crystal (in expected – positive charge of ammonium salt of poly(amidoamine)). In addition, adsorptive surfaces of clays particles hold numerous water molecules that make up the clay micelle. The property of these clays could be modified by replacing the charge ions with different metal ions or attaching different ions to the clays (Wu et al., 1993).

In this thesis work, poly(amidoamine) and its nanocomposites with silicate clay were prepared and applied to several organic solvents. Properties of the nanocomposites in solution, such as viscosity and particle size, were studied and its ability to capture organic molecules was compared with linear PEO-clay nanocomposites.

1.1 Theoretical Background

1.1.1 Dendrimer

The name “Dendrimer” comes from two words: dendron and polymer. A dendrimer (from Greek *dendra* for tree) is an artificially manufactured or synthesized molecule built up from branched units called monomers. Such processes involve working on the scale of nanometers. Technically, a dendrimer is a polymer, which is a large molecule comprised of many smaller ones linked together.

Dendrimers have some proven applications, and numerous potential applications. They have been used in the production of industrial adhesives and are expected to serve as components in a variety of nanomachines. Dendrimers are of interest to researchers in medical technology, where they might help to carry and deliver drugs in the body, or serve as replacements for plasma components. Dendrimers might also prove to be useful in the manufacture of nanoscale batteries and lubricants, catalysts, and herbicides.

1.1.1.1 The Origin of Dendrimers

A major difference between linear polymers and dendrimers is that a linear polymer consists of long chains of molecules, like coils, crisscrossing each other. Dendrimers consist of molecular chains that branched out from a common center. They have fewer entanglements than polymers of equivalent molecular weight, but if the arms are long enough entanglements are still possible.

1.1.1.2 The Structures of a Dendrimer Molecule

Dendrimers have a globular configuration with monomer units branching out from a center core (Figure 1.1). The number of branches increases exponentially extending from core to the periphery. The branching would come to a stop when the steric hindrance stopped any further growth. There are three distinct architectural components (Figure 1.2). The multi-functionalized core (initiator core) forms the heart of the molecules; all branches emanate from this core.

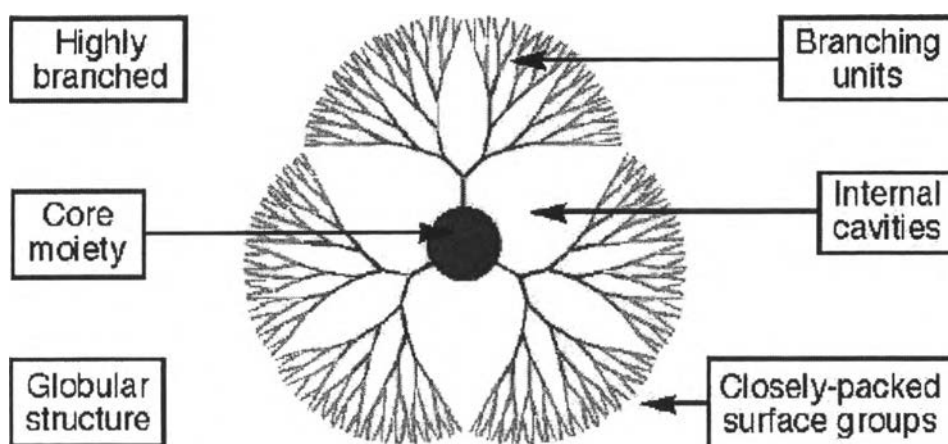


Figure 1.1 The dendritic structure (www.eng.buffalo.edu, March 2, 2002).

The monomers that attach to the core form the first branches (first generation). On the successive generations, two monomers will attach to the ends of the monomers in the previous generation. At the terminating generation, a terminal functional group is added to the tail of the monomer.

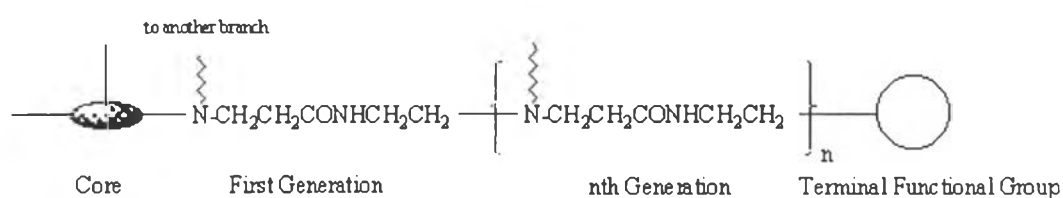


Figure 1.2 Components of a dendrimer, poly(amidoamine).

Most of the chemical properties of the molecule depend on types of terminal groups. The physical properties of the molecules, such as solubility and viscosity, are also affected by the terminal groups. Some of these dendrimers have diameters that are greater than ten nanometers. The molecular weights range from about 50,000 to 200,000 g/mol. The outer surface area of the molecule increases with the number of generations. There is a significant void space within the molecule. These voids consist of channels and cavities (Murat et al., 1996).

These unique geometries give the molecule special properties, such as adhesiveness and ability, to entrap foreign molecules.

1.1.1.3 Properties of Dendrimers

Theoretically, dendrimers are monodisperse. All molecules have the exact same molecular weight and structure. Due to minor defect during the synthesizing process, the polydispersity index is about 1.001. Polydispersity of 1.0007 for PAMAM has been reported (Bosman et al., 1999). The intrinsic viscosity of dendrimers has a peculiar behavior, it increases with increasing molecular weight (number of generations) and contrary to linear polymers, the viscosity will reach a maximum value then starts to decline (Hawker et al., 1995). The glass transition temperature (T_g) of dendrimers follows similar trend. It reaches to a maximum T_g and levels off at higher molecular weights (Hawker et al., 1995). This behavior is explained by the absence of entanglement at higher molecular weights.

1.1.1.4 Synthesizing and Designing Dendrimers

- Divergent growth method

There are two steps of this type of synthesis: the activation of the functional surface groups and the addition of branching monomer units. The reaction starts at the core. The initiator core contains several reaction sites. The first generation monomer units react with the core readily. Once all reactive sites are taken, the addition stops. Since the ends on the first generation are protected, addition of monomers to the end chain is impossible. The end groups must be activated before any further addition. The passive functionalities on the end groups are removed by a secondary reaction. Additional monomers are attached to the molecule. Steps are repeated for synthesizing higher generations. One of the great advantages of this method is the ability to modify the surface of the dendrimer molecule. By changing the end groups at the outermost generation, the overall chemical and physical properties of the dendrimer can be configured to specific needs (Fréchet, 1994).

- Convergent growth method

One of the shortcomings of divergent growth method is that the outermost generation has only one kind of functional group. Convergent growth method would eliminate such weakness. The reaction starts at the periphery and proceeds to the core. Similar to divergent growth, it involves two steps: the attachment of the outermost functional groups to an inner generation and the attachment of the inner generations to the core. Each wedge can have different function groups at the periphery. Thus, the making of unsymmetrical dendrimer is possible. This modification is useful in monolayer formation at the organic-aqueous interface (Hawker et al., 1990). Half of the dendrimer is submerged in the water phase, while the other half is in the organic phase. A combination of these two methods can be used to suit for special needs.

1.1.2 Clay

The inorganic colloidal matter in soil is presented almost exclusively as clay of various kinds. In a broad way, two groups of clays are recognized—the *silicate clays* so characteristic of temperate regions, and the *iron and aluminum hydrous-oxide clays* found in the tropics and semitropics. Our immediate concern will be with the silicates, because they are dominant in the most developed agricultural regions of the world.

1.1.2.1 The General Constitution of Silicate Clays

Shape: The particles of clays are laminated, that is made up of layers of plates or flakes (Figure 1.3). Their individual size and shape depend upon their mineralogical organizations and the conditions under which they have developed. Some of these particles are mica-like and definitely hexagonal; others are irregularly plate- or flakelike; still others seem to be lath-shaped blades or even rods.

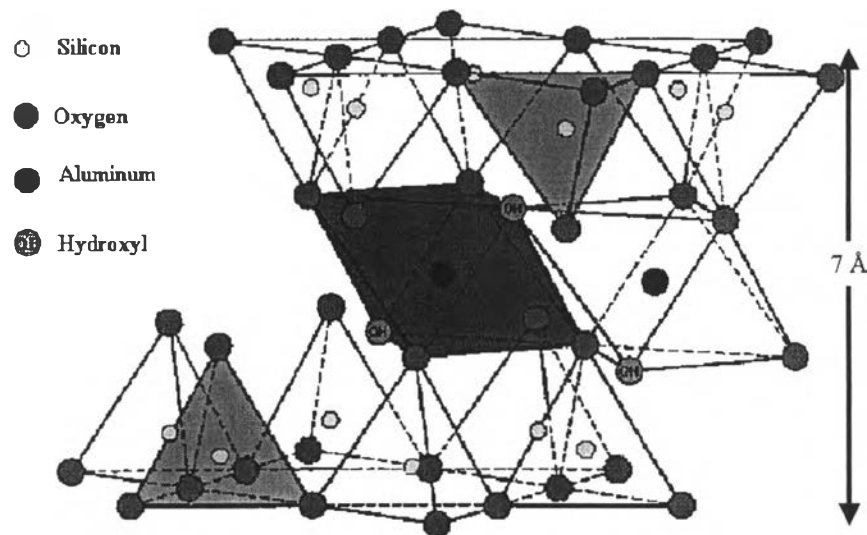


Figure 1.3 Montmorillonite clay structure.

Surface area: Clay particles, merely because of their fineness of division, must expose a large amount of *external* surface. But this is by no means all. In some clays there are *internal* surfaces as well. This internal interface occurs between the platelike crystal units that make up each particle. Thus, the tremendous surface area that characterizes clay is accounted for not only by fineness of division but also by the platelike structure of the fine particles.

Electronegative charge and adsorbed cations: The silicate-clay colloid particles, which are referred to as *micelles*, ordinarily carry a *negative* charge. As a consequence, thousands of positively charged ions or *cations* are attracted to each colloidal crystal. This gives rise to what is known as an ionic double layer. The colloidal particle constitutes the *inner* ionic layer, being essentially a huge *anion*, the surfaces of which are highly negative in charge. The *outer* ionic layer is made up of a swarm of rather loosely held cations which surround and in some cases penetrate the particle. Thus, a clay particle is accompanied by a tremendous number of adsorbed cations. Moreover, water molecules are adsorbed by the crystal surfaces and by the layer of cations that make up the clay micelle. Properties of clay are affected by the type of adsorbed cations (Buckman et al., 1971).

1.1.2.2 *The Adsorbed Cations*

Although all cations may be adsorbed by clay micelles, certain ones are found in natural conditions. For humid region, the balance charges in the order of their numbers are H^+ , Ca^{2+} , Mg^{2+} , K^+ and Na^+ . For well-drained arid-region soils, the order of the exchangeable ions is usually Ca^{2+} , Mg^{2+} , Na^+ , K^+ and H^+ .

1.1.2.3 *The Various Types of Silicate Clays*

On the basis of clays crystalline properties, three major groups of silicate clays are now recognized:

1. Kaolinite group
2. Montmorillonite group (MMT), was used in this thesis
3. Hydrous micas

The flakelike crystal units of montmorillonite are made up of two tetrahedral (silica) sheets with an octahedral (alumina) sheet tenaciously bound in between by mutually shared oxygen atoms. The crystal lattice is, therefore, a 2:1 type.

The structural units are so loosely held together by very weak oxygen-oxygen linkages and the crystal range in diameter from 0.01 to 1.00 microns. Cations and water molecules are able to move in between the crystal units of montmorillonite because of its easily expanded crystal lattice. Thus, in addition to the surface of the outside of the particle, *internal surfaces* of very much total magnitude are presented. This internal surface is also negatively charged. Consequently, this 2:1 type of colloid has a high cation-adsorption capacity- perhaps 10 to 15 times that of kaolinite. Moreover, because of the movement of water between crystal units, the swelling of montmorillonite greatly exceeds that of kaolinite.

1.1.3 Polymer-Clay Nanocomposite

Composite materials prepared to have inhomogeneity in smaller scale than submicron ($10^{-7}m$) are called nanocomposites. Research on nanocomposites aims at developing materials with outstanding mechanical properties as well as optical, electrical, magnetical, chemical and so-called smart functionalities. In

general, the dispersion of clay particles in a polymer matrix can result in the formation of three general types of composite materials (Figure 1.4). Conventional composites contain clay tactoids with the layers aggregated in unintercalated face-face form. The clay tactoids are simply dispersed as a segregated phase. Intercalated clay composites are intercalation compounds of definite structure formed by the insertion of one or more molecular layers of polymer into the clay host galleries and the properties usually resemble those of ceramic host. In contrast, exfoliated polymer-clay nanocomposites have a low clay content, a monolithic structure, a separation between layers that depends on the polymer content of the composite, and properties that reflect those of the nano-confined polymer.

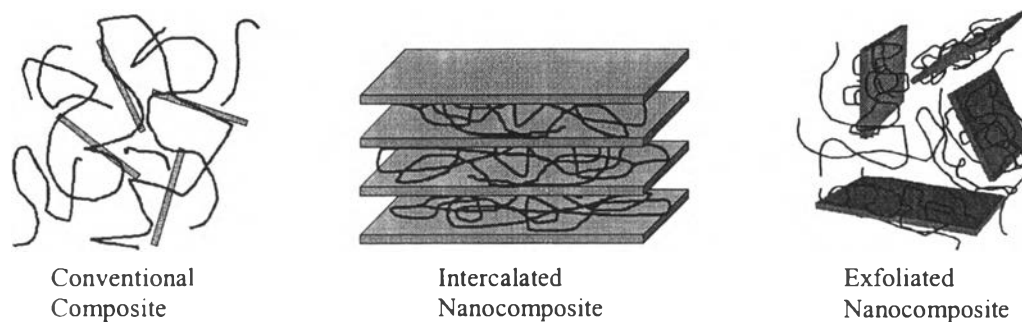


Figure 1.4 Schematic illustration of the three possible types of polymer-clay nano composite.

Intercalated polymer-clay nanocomposites have been synthesized by direct polymer intercalation, and *in situ* intercalative polymerization of monomers in the clay galleries. Owing to the spatial confinement of the polymer between the dense clay layers, intercalated polymer-clay nanocomposites can exhibit impressive conductivity and barrier properties. The exfoliation of smectite clays provides 10Å^o-thick silicate layers with high in – plane bond strength and aspect ratios comparable to those found for fiber reinforced polymer composites.

Exfoliated clay nanocomposites formed between organocation exchanged montmorillonites and thermoplastic Nylon-6 have recently been described by Toyota researchers. Clay exfoliation in Nylon-6 matrix gave rise to greatly improved mechanical, thermal and rheological properties, making possible new

materials applications of this polymer. However, it is relatively difficult to achieve exfoliation of smectic clays into a continuous polymer matrix, because of the strong electrostatic attraction between the silicate layers and the intergallery cations (Chow et al., 1996).

1.1.4 Symplex

Symplexes, i.e., polyanion-polycation complexes formed by a predominantly coulombic interaction between anionic and cationic polymers usually in aqueous solution, are of practical interest in connection with membranes, coatings, microcapsules and flocculation processes, and they are of scientific relevance with regard to highly organized polymer systems and molecular recognition. The principle of symplex formation can be realized by a neutralization reaction between a polyacid and a polybase, reacting the alkali salt of a polyacid with the halide salt of a polybase and a polymerization of an ionic monomer aligned along the chain of an oppositely charged polyion.

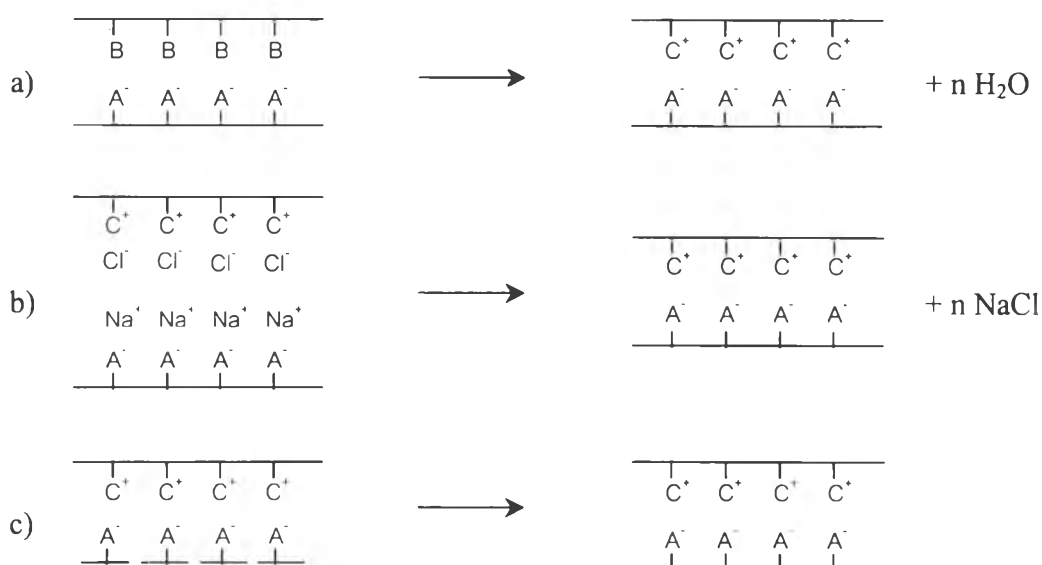


Figure 1.5 Principle of symplex formation. (a) Neutralization of a polybase with a polyacid; (b) interaction between the halide of a polybase and the alkali salt of a polyacid; (c) matrix polymerization of an anionic monomer preordered along a polycation. A⁻ = anionic group; C⁺ = cationic group; B = free base group.

A special case of symplex formation is the interaction between the anionic and the cationic sites of polyampholytes leading to a symplex like precipitates at suitable conditions of pH and ionic strength. Complexes showing some similarity to symplexes and being of some relevance to polymer analysis can be formed between a macroion and surfactant or dye molecules of opposite charge.

In polyanion-polycation interactions, coulombic forces are usually assumed to be responsible for the stability of the aggregates formed. This holds true in general, especially with regard to symplex formation between oppositely charged macroions. But intermolecular interactions of different kinds, such as H-bond formation, polar forces and hydrophobic interactions, also have to be taken into consideration (Mitchell, 1991).

1.1.5 Adsorption Process

1.1.5.1 Adsorption in Wastewater Treatment

Water is a common solvent used in many industrial processes. Hence, it is expected to contain a diverse range of organic, inorganic, metallic, hydrocarbonic and biological effluents of all classes and properties. In effect, many types of pollutants have been identified in the municipal water in the U.S. such as humic substances, volatile organic carbon and dyes. However, the diversity of water pollutants necessitates a wide range of treatment methods too. The methods used for wastewater treatment are air stripping or aeration which involves the removal of volatile organic carbons by transferring them from solution to the gas phase, chemical oxidation, a widespread operation that uses ozone (ozonation), permanganate and chlorine dioxide chemical reagents. Compared with those methods, adsorption has demonstrated efficiency and economic feasibility as a wastewater treatment operation. It is an attractive option for industrial water treatment, especially the removal of specifically selected toxins. It is used for the removal of toxic trihalomethanes and their intermediates, for dechlorination and for groundwater cleanup operations. It is also used for elimination of humic substances that result in THM production. Moreover, adsorption is applied for the removal of dyes from wastewater effluent from textile industry (Mckay, 1996).

1.1.5.2 Criteria for Adsorption as a Separation Process

The first step to an efficient adsorption process is the search for an adsorbent with high selectivity, high capacity, and long life. The selectivity of adsorbents is determined by the separation factor and is measured on three bases:

1. equilibrium studies
2. kinetic and diffusional properties
3. molecular sieve separation

Based on equilibrium studies, the separation factor of an ij mixture is defined by the (solid/fluid) concentrations of component i related to the (solid/fluid) concentrations of j , i.e.,

$$\alpha = \frac{Y_i/X_i}{Y_j/X_j} \quad (1.1)$$

Where Y is the solid phase concentration or particle loading and X is the fluid phase concentration-in solution. Naturally, the separation factor α depends on each adsorbate/adsorbent system. Also, it is a function of temperature and composition of the system, and therefore the process conditions are to be carefully decided to obtain the highest possible selectivity. Compared to distillation, though, for the same number of stages, adsorption is a more economical process; it has a largely higher separation factor than distillation.

In kinetic separation the selectivity is measured by the ratio of micropore diffusion. It is based on the difference in diffusivities induced by difference in molecular diameters of species. For molecules of comparative diameters, the separation factor becomes significant only in the presence of steric hindrances, i.e., when the molecular diameters are comparable to pore diameters causing multidirectional interactions. This approach is only valid in the case of activated carbons and molecular sieves as there is a bidisperse and polydisperse internal structure, respectively.

Molecular sieve separation factor is based on the complete exclusion of one species due to its relatively large molecular diameter. This factor has a limited application as it requires a stringent adsorbent internal structure.

However, it can be pointed out that while analyses for separation factors give information about the suitability of an adsorbent for a separation process, they also supply information about the system kinetics and equilibrium.

Apart from high selectivity and separation factor, a suitable adsorbent must have a large surface area and a well-developed, well-defined inframicrocrystalline structure. In principle, any porous solid may be an adsorbent. Common natural adsorbents are fly ash, bone char, sawdust, fuller's earth, aluminum oxide (bauxite), charcoal, woodmeal, bagasse pith, peat, and lignite. Some adsorbents are natural, but treated to develop their infrastructures, such as silica gel, activated alumina, activated carbon, and carbon molecular sieves. However, on an industrial scale adsorbents are to be present in tonnages, be resilient to shear, have long life, be relatively easily regenerable and have economical costs (Mckay, 1996).

1.1.5.3 The Mechanism of Adsorption

The selectivity of an adsorbent is strongly connected to its inframicrocrystalline structure. It consists of microcrystallites linked together by surface functional organic groups. Adsorption occurs by the donor-acceptor complexation mechanism where atoms of the surface functional group donate electrons to the sorbate molecules. The position of these functional groups on the sorbent surface determines the type of sorbate/sorbent bond and therefore decides whether the process is physisorption or chemisorption.

In physisorption, Van der Waals and physical bonds are produced, the process is reversible, and the system has a low heat of adsorption. It is a nonspecific process with no electron transfer occurring, though sorbate polarization is likely. On the other hand, chemisorption involves ionic or covalent bond formation, requires high energy, and is irreversible. It is a highly specific process that is possible over a wide temperature range while physisorption occurs more at lower temperatures. Due to its irreversibility, monolayer is expected to form in chemisorption while multilayer is encountered in physisorption. In an adsorption system, both sorts are expected to occur and therefore, upon analysis, properties of both appear. However, most adsorptive separation processes depend on physical adsorption (Mckay, 1996).