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Introduction

Dendrimers are highly branched, three-dimensional macromolecules with a branch point at each monomer unit[1,2]. Although industrial applications are relatively recent, dendrimers are a common macromolecule in nature. The Greek prefix dendr means treelike. Figure 1. demonstrates this similarity.

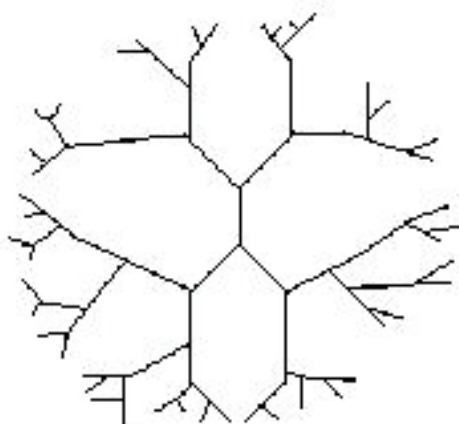


Figure 1: A tree-like structure called a dendrimer

A dendrimer consists of four main components: a central or core unit, arms of identical size, linking or branched points and end functional groups. They can be formed by two general methods. The divergent method, illustrated in figure 2, starts with a polyfunctional core molecule and proceeds outwardly through successive reactions involving two or more branched points at each step.

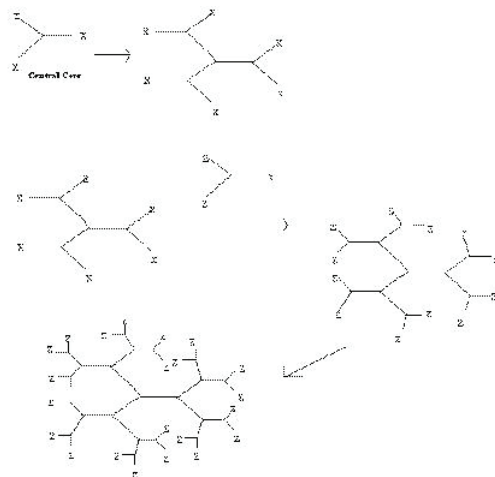


Figure 2: Synthesis of a divergent dendrimer

In the convergent method, each generation involves the same number of coupling reactions at the branching sites. This allows for better control of purity. See Figure 3.

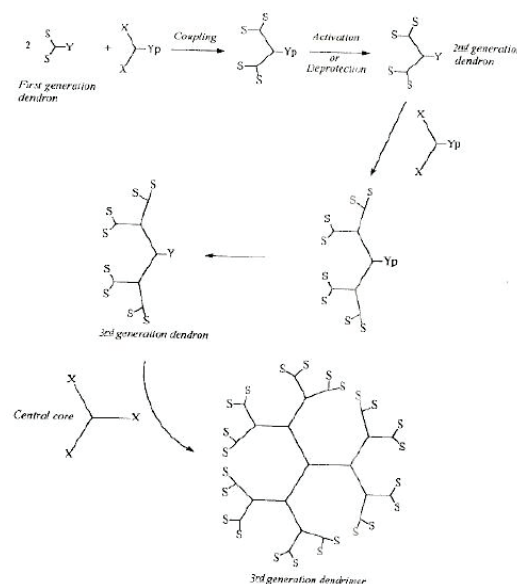


Figure 3: Synthesis of a convergent dendrimer

Special Properties and Reverse Osmosis Antiscalant Applications of Dendrimers

Polydispersity/Purity

Polydispersity is defined as the ratio of the weight average molecular weight to the number average molecular weight, (M_w / M_n). Dendrimers are in theory monodisperse structures. However, a significantly low level of impurities does occur under normal synthesis. The convergent method results in fewer impurities. These dendrimers have a polydispersity of the magnitude 1.002, while linear, branched and cross-linked polymers such as polyacrylic, polycarboxylate, polyacrylamide homopolymers and copolymers vary statistically in number average and weight average molecular weights having polydispersities greater than 1.2.

This yields a wide distribution of molecular structures that dilute the desired macromolecular form and properties. This diluted molecular structure adversely affects the application performance of the polymer[3]. When applied to the control of colloid dispersion, the presence of a polydispersity affects particle dispersion leading to destabilization. Further, during crystal formation, polydispersion causes depletion and structural force changes resulting in the early formation of numerous small crystals.

The Physical Behavior of Dendrimers

Because of their unique geometry, dendrimers behave quite differently from linear and cross-linked macromolecules. In solution, the dendrimers' occupied volume varies cubically with increasing size. However, the mass increases exponentially. This results in different solution properties for dendrimers than linear molecules. This difference of density leads to enhanced solubility, reactivity and viscosity.

When dendrimers are compared to their linear isomers they are found to have greatly increased solubility in common solvents and the dendrimer form quite often has solubility in solvents that are not effective solvents for the linear isomer. Figure 4 illustrates the geometrical difference between a dendrimer and its linear isomer[5].

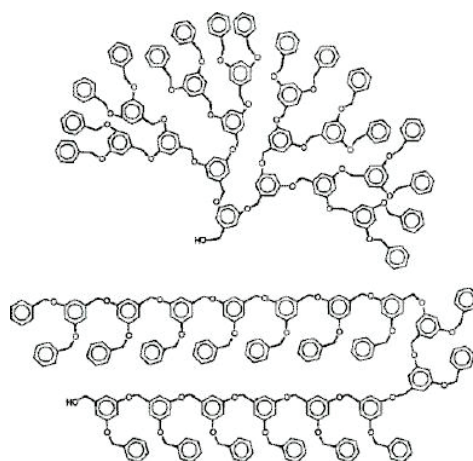


Figure 4: Dendrimer compared to its linear isomers

Linear molecules obey the Mark-Houwink-Sakurada equation and viscosity increases with molecular mass. Dendrimer intrinsic viscosity reaches a certain maximum and remains constant even with increasing molecular mass [4]. In general, dendrimers are several orders of magnitude less in viscosity than their linear isomer. This leads to better flow characteristics.

While linear macromolecules generally become entangled as ionic strength increases, dendrimers do not. In fact, dendrimers will generally decrease uniformly in volume leading to higher molecular and functional group density. Also, a corresponding uniform increase in partial charge density occurs with increasing ionic strength.

The linear analogue of many dendrimers crystallize while the dendrimer of similar molecular size are amorphous. This effect can usually be explained by the geometry of the dendrimer, the functional group distribution and the lower hydrogen bonding properties of the dendrimer.

Extremely interesting work has been conducted concerning the surface-active behavior of dendrimers at the air-water interface.

The linear analogues form a brush-like aggregate at the air-water interface (see figure 5.)



Figure 5: Linear analogue at air-water interface

The hydrophilic heads form a linear aggregate with spacing determined by the molecular area in the compressed state and the number of end groups per molecule inside the air-water surface. The hydrophobic chains stand out of the surface. Figure 6 illustrates the surface aggregate of a dendrimer with hydrophilic surface-end groups. The dendrimer is compressed in an egg-like shape with the surface groups in the interface.



Figure 6: Dendrimer with hydrophilic surface-end groups

Figure 7 presents a dendrimer that contains hydrophobic surface end groups. While the egg-like core sits on the surface, the hydrophobic groups stand away from the surface. (see next page)



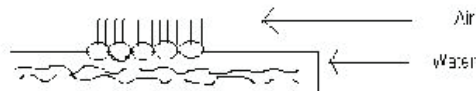


Figure 7: Dendrimer with hydrophobic surface-end groups

Because of these differences, the surface and inter-phase properties are drastically different from the linear analogues. Where the linear analogues require many separate polymers to form micelles in an aqueous matrix, the dendrimer forms a unimolecular micelle.

These unimolecular micelles have unique properties. Dendrimers have been found to suspend and stabilize iron and other metal ions in an aqueous matrix at levels far above their linear analogues. These metals can be protected by the dendrimer and make them less reactive. Further, because of the specific fractal geometry of the unimolecular micelles, it is possible to design specific micelle formations that have predictable physical properties such as dipole moments, intrinsic viscosity and energy transfer.

Dendrimer Based Antiscalants

The uniqueness of dendrimers allows the design of specific antiscalant performance far superior to their linear analogues.

These properties include stability in high TDS waters composed of metal ions such as iron. All acrylic, maleic and amido linear and branched polymers and copolymers have precipitation problems in the presence of metal ions.

Linear and branched acrylic, maleic, amido and other monomer-based polymers and copolymers coil and entangle on themselves in high TDS waters, leaving them less effective. Dendrimers do not entangle on themselves because of their specific geometry and they actually become more effective in high TDS waters.

Linear and branched acrylic, maleic, amido and other monomer-based polymers and copolymers are able to hydrogen bond to the membrane surface, thereby, causing instability that leads to fouling of the membrane surface. The unique geometry of the dendrimer eliminates hydrogen bonding and is free from membrane fouling problems.

Linear and branched acrylic, maleic, amido and other monomer-based polymers' and copolymers' viscosities increase with molecular weight. Dendrimers by structure have very low viscosity.

Special Properties and Reverse Osmosis Antiscalant Applications of Dendrimers

Linear and branched acrylic, maleic, amido and other monomer-based polymers and copolymers act only as sub-stoichiometric chelants and crystal modifiers between .5 ppm and 5 ppm. As crystal modifiers, they produce small crystals that cover the surface quicker than unmodified pristine crystals that don't cover as much surface area of the membrane. Above 5 ppm, they start to form gels near the surface of the membrane when metals are present. Dendrimers remain stable because of the unique geometry.

Linear and branched acrylic, maleic, amido, and other monomer-based polymers and copolymers have high polydispersity that leads to the destabilization of colloids. Dendrimers have ultra-low polydispersity that allows them to stabilize colloids in even high TDS water.

References

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