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REVIEW ARTICLE

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A Study on Macrocyclic Polymers and Their Synthesis

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INTRODUCTION

The term supra-molecular chemistry, which was coined by Jean-Marie Lehn, means “Chemistry beyond the molecule”. While individual molecules consist of atoms joined by covalent bond, supra-molecular chemistry makes use of intermolecular interaction like hydrogen bonds, π-stacking and electrostatic forces bringing molecules together to form larger species. Hydrogen bonding enables compounds containing electronegative functional groups to interact with protons to form extended arrays. Molecules with aromatic rings can stack together by virtue of π-π interactions. Electrostatic interactions include ion-ion, ion-dipole and dipole-dipole interactions, where positively and negatively charged species associate. As supra-molecular chemistry focuses on how molecules interact with one another, there is emphasis on complementarity and pre-organization. Complementarity is the matching of a host molecule to the electronic and geometric needs of a guest. One can design supra-molecular complexes that can behaves as molecular machines, such as shuttles, switches, and sensors. Within the field of supra-molecular chemistry Lehn6 distinguished between ‘supra-molecule’ and ‘molecular assemblies’. Supra-molecules as were considered to be oligomers composed of a few components assembled via specific intermolecular associations whereas in molecular assemblies, large numbers of components assemble spontaneously into a structure that has reasonably well defined microscopic organization and displays characteristics typical of macromolecules, e. g., fibre formation, glass and melting transitions, chain entanglement and high property/ weight ratios7. It is because they exhibit these typical properties that extended –chain molecular assemblies are frequently referred to as ‘supra-molecular polymers’.

Macro-cyclic compound is an organic compound that contains a large ring. In the organic chemistry of alicyclic compounds, a closed chain of 12 carbon (C) atoms is usually regarded as the minimum size for a large ring. Macrocyclic compounds may be a single, continuous thread of atoms or they may incorporate more than one strand or other ring systems within the macrocycle or macro ring. Macrocyclic compounds play an important role in supramolecular chemistry. The macrocyclic compound often contains heteroatoms like O, N, S, and P or functional group that allow for the participation in intermolecular interactions. Crown ether is an early example of macro-cyclic compound, crown ethers are generally composed of repeating ethylene units separated by non-carbon atoms such as oxygen but as more intricate structures are prepared, nitrogen, sulfur, phosphorus, silicon, or siloxy residues are becoming much more common. Charles Pedersen, who was a chemist working at Dupont, discovered a simple method of synthesizing crown ether in 1967 when he was trying to prepare a complexing agent for divalent cations. Crown ethers have the remarkable property of recognizing and binding specific metal cations in complex mixtures. Consequently, since their discovery, crown ethers have found numerous applications in science and industry. In other words, due to the fix size of cavity, crown ethers are more selective for metal ions. The selectivity of the metal ion binding is controlled by changing the size of crown ether cavity and by introducing the various combinations of the O, N, S, heteroatoms in the crown ether ring.

Attachment of different functional group to crown ethers give unique metal complexing properties, due to their extensive ability to bind metal cations. The oxygen atoms of crown ethers are ideally situated to coordinate with a cation in the interior of the ring, whereas the exterior to the ring is hydrophobic. The result is that the complexed cation is soluble in non-polar solvents. The size of the interior of the crown ether determines the size of the cation it can solvate. Therefore, 18-crown-6 has high affinity to potassium cation, 15-crown-5 for sodium cation and 12-crown-4 for lithium cation. Pedersen, Lehn and Cram earned the nobel prize in chemistry in 1987 for their pioneering work in macrocyclic field.

The oxygen atoms in the ring enable the macrocycle to coordinate alkali metal cations. When one or two oxygen of crown ether is replaced with nitrogen atoms it is known as aza crown ether. The unmetalled crown ethers show a collapsed ring structure in the solid state.

Preorganized macrocycles maintain their structure in the absence of metal. That means the macrocyclic compound is a cyclic compound having high molecular masses. Some other macrocyclic compound like calixarenes, cyclodextrin, rotaxane and catanane are also included to the list of crown ethers.

Aza crown ethers have especially been focused on as useful ligands because of their versatility and applicability. The aza crown ethers have complexation properties that are intermediate between those of all oxygen atoms of aza crown ethers which strongly complex alkali and alkaline earths metal ions and those of all nitrogen cyclams which strongly complex with heavy-metal cations. These mixed complexation property make the aza crown ethers interesting to researchers in many areas. The property of aza crown ethers can be modified by altering its donating side arms as well as macrocycle itself. The metal ion complexing ability of aza crown can be significantly improved by functionalizing them with ligating sidearms. Aza crown ethers which are chemically modified are very interesting molecules because; they can be designed according to the need. The aza crown ethers have important applications in different field.

The convergence of various polymers, which are substituted by attaching different functional group and macro-cyclic compounds like crown ethers, cryptands and calixarenes are known as polymeric macrocyclic compound. The use of crown ethers and analogous compound on a large scale for industrial purposes is inhibited by their expense. A potentially useful way around this problem lies in attaching the crown ethers to a polymeric matrix and thus facilitating it retrieval. Other benefits of polymeric supported aza crown ethers are that the properties of these macromolecules do not change even after long term use. The insoluble cross-linked polymer supported aza crown ethers are of considerable interest to the synthetic chemist. Such polymers that can be used as starting materials for the preparation of solid supported catalyst and ligands, have been recently reported.

SUPRAMOLECULAR POLYMER

The field of supramolecular chemistry has been developed over the past 25 years by synthetic chemists. A SP (supramolecular polymer) is based on the reversible association of many monomers through weak labile interactions self-assembling in to an infinite network. Unlike finite supramolecular systems, whose synthons form thermodynamically stable finite architectures, monomer synthons having multiple recognition sites complex *ad infinitum* until all available synthons have been consumed. When the supramolecular recognition is due to the coordination between a functionalized ditopic ligand and a ditopic metal complex the metalla-supramolecular polymers are called coordination polymers (CP). Strong, highly directional, reversible interactions are required to form liner supramolecular polymers.

Otherwise, the polymer gel forms microphase-separated structure. The repeat units of the molecular assembly must only interact with their intended partners. In hydrogen-bonded supra-molecular polymer system where there is no anisotropy, single or double hydrogen bonds are not sufficiently stable to allow self-assembly to occur. High purity monomers must be used in preparing supra-molecular polymers because mono-functional impurities or unreacted repeat units cap the growing polymer chain. A first step towards the synthesis of supra-molecular polymers was taken as far back as 1984. While studying the liquid crystalline behavior of polymeric gycols, Lenz and coworkers prepared dicarboxylic acid derivatives of glycol polymers13 hoping to obtain liquid crystals by varying the position of mesogenic group and flexible spacers along the polymer chain. Adjacent acid groups were found to have hydrogen bond, doubling the length of the mesogenic groups and giving stiffer, more anisotropic, liquid crystals.

The first truly main chain supramolecular polymer was self-assembled by Lehn et al.14 using uracil (A) and 2, 6 diaminopyridine (B). The polymer consisted of a molecular assembly composed of an equimolar mixture of repeat units bearing uracil (A) and 2,6 diaminopyridine (B) groups, which are associated via triple hydrogen bonding. This polymer adopted a well-defined structure and displayed physical properties similar to conventional polymers. Ka of polymer is approximately 103 M-1 in apolar solvents. These polymers had liquid crystalline behavior and a helical pitch owing to the chirality of the tartarate backbone. This study and others relied on a small number of repeated H-bonding interactions to give interesting solution properties such as liquid crystallinity or light harvesting15. No complications have been reported regarding its long-term stability. For these reasons, it has become a benchmark in the field of supramolecular polymer chemistry. Since then increasing interest has developed in extended self-assembled structure such as one dimensional chains, two-dimensional sheets and three-dimensional networks. Much research into supramolecular polymers has been concerned with preparing liquid crystalline molecular assemblies that display similar characteristics to that prepared by Lehn's polymers.

Meijer and coworkers have designed derivatives of the ureidopyrimidinone motif for use as an associating end group to overcome the limitation imposed by weakinteractions mentioned previously. Ureidopyrimidinones offer strong, directional hydrogen bonding, and have been shown to form dimers following a predictable recognition and assembly process. Polymer derived from ureidopyrimidinones may also have potential for preparing soft materials whose flow properties can be accurately controlled. Viscoelasticity in polymers arises from entanglements between chains. While conventional high molecular weight polymers are elastic, they have long relaxation times. Ka of dimerization is approximately 108 M-1 in apolar solvents, 17, 18. SPs with polymeric properties in both concentrated and dilute solutions, with improved polymeric properties, allowed for processing in to the quadruple H-bonded array stabilized by favorable secondary H-bonding interactions. Meijer's polymer and its analogues, such as telechelic polysiloxanes, -ethers, -esters, -ethylene/butylenes and –carbonates, were shown to have viscoelastic properties similar to those of traditional polymers.

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