DESIGNER POLYMERS*

INTERDISCIPLINARY macromolecular science and engineering is emerging as a new and exciting frontier in the area of material science. This field lies at the confluence of materials science, engineering, chemistry, physics and biology. It promises to exert a profound impact on all future technologies, such as electronics, medicine and health care, information storage and transmission, energy harvesting and environment, areas which are critical to the new economy and the ultimate well being of human kind.

The key to the design of new polymer structures with novel properties are the synthetic methods which enable the fine control of macromolecular architectures. Properties of polymers are determined by four primary molecular characteristics, namely chain length, chain sequence, chain isomerism and chain topology. Most methods of forming polymers rely on statistics of chain growth reaction; hence properties of most known polymers are determined by averages of chain length. In spite of fifty years of intensive research, the ability to synthesize polymers with absolutely uniform chain length for a wide range of polymer structures is still a challenge. For many polymers, containing differing chemical compositions, chain sequence is an important feature, which controls many macroscopic properties. There are very limited choices in the tool-box of the synthetic chemist for preparing macromolecules with precisely defined sequences. Polymer stereochemistry defines many of the supramolecular properties of the polymer. Control of polymer stereochemistry through rational design of catalysts and initiating systems is, therefore, an area of significant contemporary interest. Lastly, chain topology is a critical design element in macromolecular structures. Polymer chains can assume, apart from linear and branched; newer shapes and forms, such as stars, hyperbranched, dendritic, catenanes/rotaxanes as well as two- and three-dimensional supramolecular assemblies. Apart from classical covalent chemistry, concepts such as molecular self assembly and self organization, through weak secondary valence forces, are playing a critical role in the creation of new polymer topologies. Nevertheless, control of topology as well as molecular geometry over large length scales in real spaces still poses a formidable challenge to the synthetic polymer chemist.

The ultimate goal of synthesis is to provide absolute control at a molecular level of macromolecular properties such as composition, composition distribution, functionality, functional group distribution, chain length, chain length distribution, regio- and stereo-chemistry of monomer insertion, branching, branching distribution and topology. Towards this end several new design paradigms in polymer synthesis have emerged during the last decade [1]. These are polymer synthesis through rational catalyst design, controlled polymer synthesis using the principles of living polymerization, step growth polymers (linear/branched) through iterative synthetic methodology as well as application of the principles of molecular self assembly for the synthesis of polymers with novel topologies. Some key features of these methodologies are discussed in the following sections.

Polyolefins via Rational Catalyst Design

Transition metal catalysts offer the most dramatic example of polymer structure control through rational design of catalyst structure (Table1, p53). Some dramatic effects of ligands on the nature of poly-

Table 1. Structure controlled macromolecules through rational catalyst design

- Early transition metal catalysts
- Metallocene and late transition metal catalysts
- Ring opening metathesis polymerization (ROMP)
- Acyclic diene metathesis polymerization (ADMET)
- Atom transfer radical polymerization (ATRP)
- Catalytic chain transfer polymerization (CCTP)
- Transition metal catalyzed living radical polymerization

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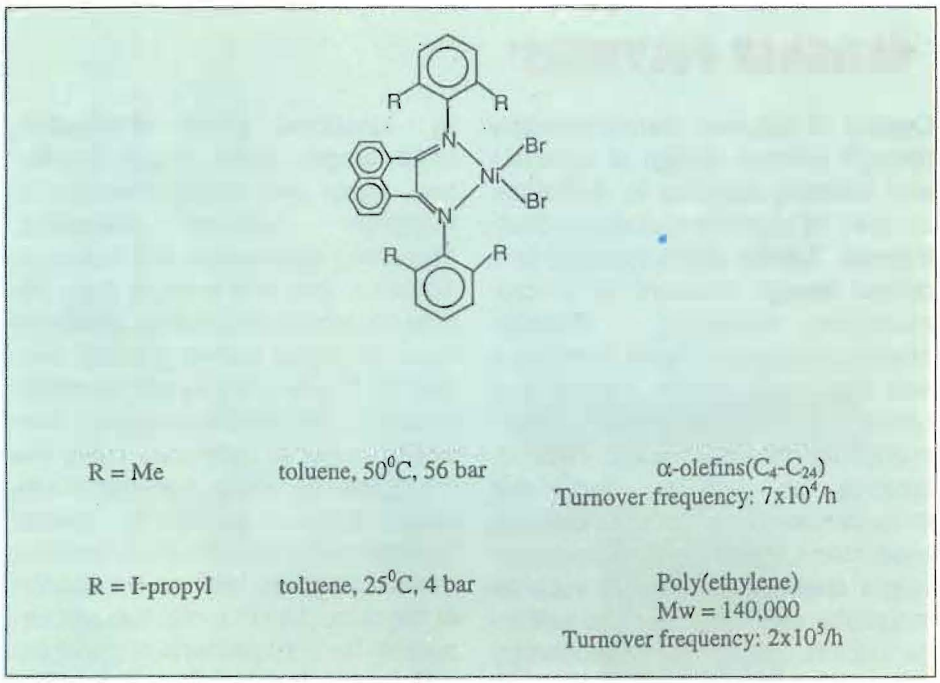


Figure 1. Ligand effects in polyolefin catalysts : Control of molecular weight

1 and 2. By a judicious choice of catalyst as well as reaction conditions, it is possible to change properties of polyolefins at a molecular level and independently of each other. These properties include, regiochemistry, degree and nature of tacticity, sequence of comonomer enchainment as well as molecular weight and its distribution. The recent discovery of metallocene and late transition metal catalysts has begun to provide a better understanding of how polymer properties depend upon the various elements of molecular architecture [2,3].

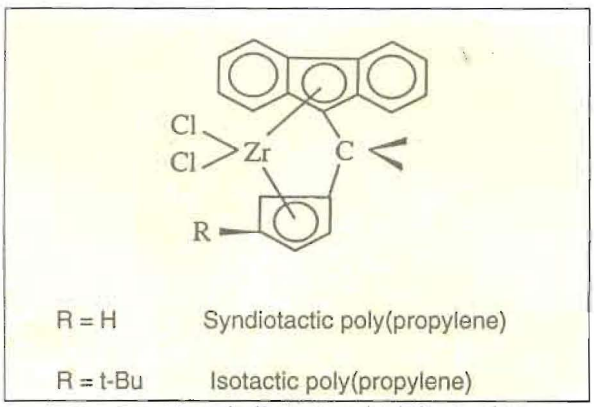


Figure 2. Ligand effects in polyolefin catalysts : Control on tacticity

Metal-catalyzed Living Radical Polymerization

Radical polymerization is one of the most important methods of synthesizing polymers with nearly 50% of synthetic polymers prepared through radical process. The commercial success of radical polymerization has several origins. Firstly, a relatively large number of monomers undergo radical polymerization. The polymerization technique is very forgiving, in the sense, that it can tolerate many functional groups. Additionally, radical polymerization occurs at 50°C or above, with minimal purification of monomers. It can be carried out in bulk, solution, aqueous suspension, emulsion, dispersion and so on. There are, however, several limitations to free radical processes. Using free radical processes, it has not been possible to prepare well defined polymers and copolymers with predetermined chain lengths and narrow distribution of molecular weights. Because of this block, graft and star shaped polymers cannot be prepared using radical processes. The main reason for this is the presence of unavoidable termination between growing radicals.

In the last decade, several approaches to control radical polymerization and to suppress contribution of chain breaking reactions while assuring quantitative initiation have been developed. These include Atom Transfer Radical Polymerization (ATRP) and transition metal catalyzed living radical polymerization [4-6]. Using these techniques new polymeric materials with novel compositions, topology and functionalities have become feasible [7] (Figure 3, p55). Many of these new materials have potential applications as components in coatings, adhesives, surfactants, dispersants, lubricants, additives and speciality material in electronic and biomaterial areas.

An example of this enabling science for the preparation of polymer nanoparticles has recently emerged out of the work at National Chemical Laboratory (NCL), Pune. The laboratory synthesized an oligomeric macrodiol by the controlled radical oligomerization of lauryl methacrylate using a free radical initiator. This oligomeric diol has proved to be a unique steric surfactant for the dispersion polymerization of an isocyanate with a diol, resulting in polyurethane microspheres with particle sizes in the range of 200 nm to 5 microns and relatively narrow particle size distributions [8] (Figure 4, p55).

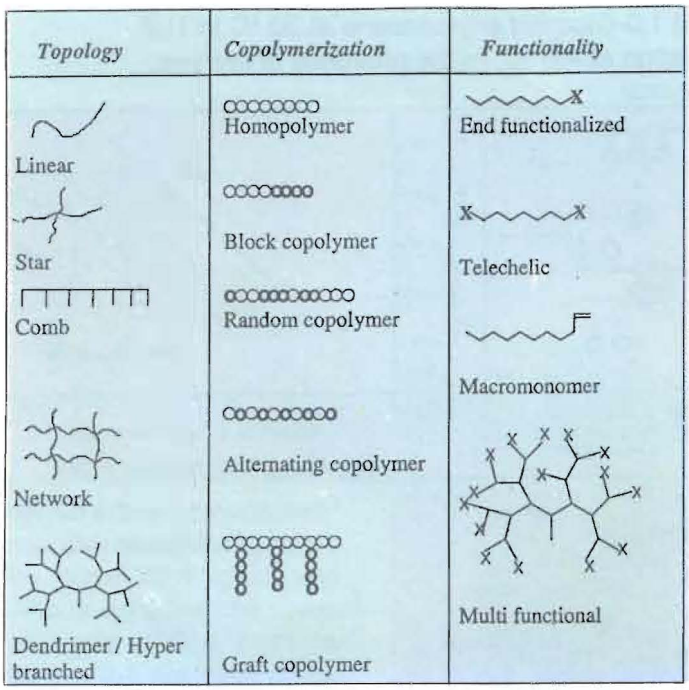


Figure 3. Macromolecular motifs accessible through controlled living radical polymerization

Living Anionic Polymerization

Living anionic polymerization, wherein the growing chain end is a carbanion, has been known since the early seventies. Under appropriate conditions, the chain ends are indefinitely "living", in the sense that one can synthetically exploit the reactive chain end carbanions for functionalization using electrophilic terminating agents [9] or for growing a new polymer chain, leading to well defined block, graft or star copolymers. Recently, a novel approach to hyperbranched vinyl polymers has been developed in NCL. This method, called "living anionic self condensing vinyl polymerization" leads to complex branched structures of vinyl polymers with multiple carbanionic sites, which can be functionalized to yield a hyperbranched polymer with a very high density of peripheral functionalities [10] (Figure 5, p56). Such polymers are expected to be useful in applications, such as, speciality surfactants and supports for catalysts.

Conjugated Macromolecules with Precise Length and Constitution

Due to the statistical nature of polymerization processes, most synthetic polymers are mixtures of macromolecules, with varying chain lengths. Such heterogeneity is of little consequence when the polymer is used for bulk applications. However, for more specialized applications there exists a need for oligomers or polymers with precisely controlled length, size and shape. Molecular inhomogeneities are detrimental in applications where individual chains are used for molecular functions (e.g. catalysis, host-guest interaction). Future materials needed for nanoelectronic or nanophotonic process will likely require monodisperse materials. In fact, for many conjugated polymers useful in electronic and photonic applications, oligomers are sufficient. For example, hexamer of thiophene shows significantly better performance in field effect transistors. Similarly, octamer of thiophene is a good photoactive component in photovolatic cell. Yet, synthesis of oligomers of precise chain length is notoriously difficult using the methods generally known in polymer chemistry.

To overcome this difficulty, new synthetic methodologies have emerged in the last five years. The key element of this methodology is the use of iterative synthetic manipulations for growing the chain stepwise. These are illustrated for the synthesis of a pentamer of thiophene [11] (Figure 6, p57) and a 10 nm

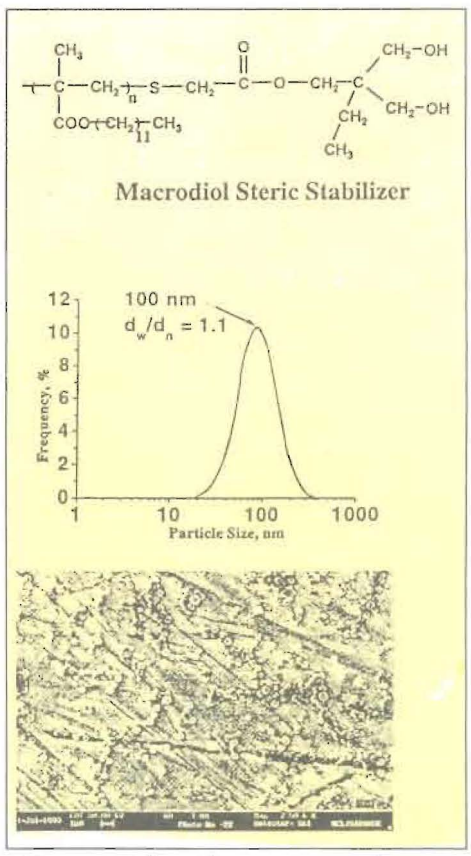
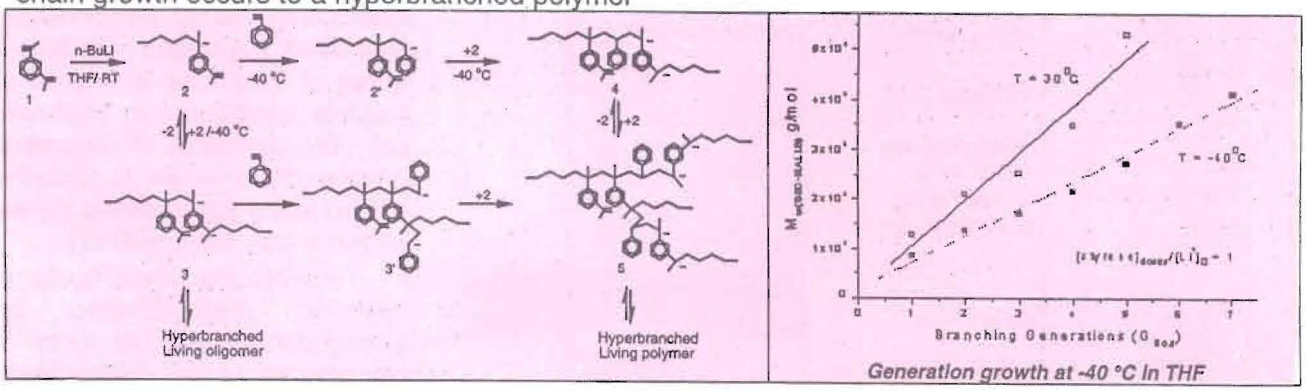


Figure 4. Polyurethane nanoparticles via dispersion polymerization of isocyanate with diol using a macrodiol steric stabilizer

Reaction of equimolar amounts of *n*BuLi and 1,3-diisopropenylbenzene at 30 °C in THF forms *Inimer* which undergoes self-condensation at -40 °C. In the presence of styrene, chain growth occurs to a hyperbranched polymer



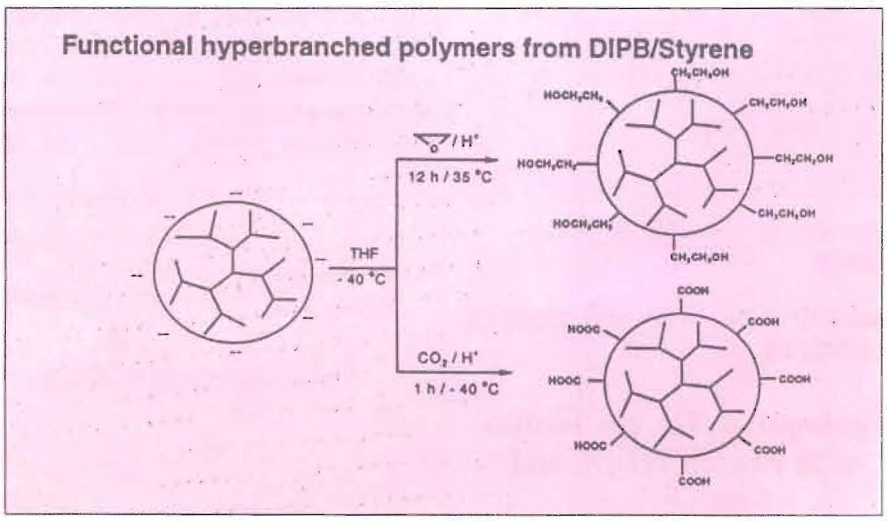


Figure 5. Hyperbranched vinyl polymer using living self condensing anionic polymerization.

chain of an alternating copolymer of thiophene and acetylene [12] (Figure 7, p58). By repeating steps (a), (b) and (c) (Figure 7), three times, one can make a precise oligomer chain of sixteen thiophene and acetylene units each with a chain dimensions of 100 Å.

Such precisely controlled structure of conjugated molecules [13] forms the basis of a new discipline of material science, called molecular electronics. Design of molecular wires and switches, molecular logic gate providing the functions of field effect transistors, polymeric photovoltaics based coatings with sunlight harvesting abilities [14] all require these enabling synthetic methodologies. Similarly, the burgeoning field of polymeric light emitting diodes has also significantly gained from new developments in stepwise synthesis of step growth polymers.

Dendrimers : Emergence of Nanoscopic Macromolecules

The elegance of the iterative synthetic strategy for the construction of macromolecules was first demonstrated for the synthesis of densely branched polymers (often called dendrimers). Such a synthetic strategy invokes the concept of "directionality" in the design and synthesis of molecule with considerable branching. A monomer with one reactive site will grow in one direction, whereas, a monomer with three reactive sites will grow in three directions. Apart from this, the geometry of the core molecule will dictate the overall directionality. A planar three directional branching core will have a different topology than a pyramidal three dimensional branching core.

Dendrimers are a special class of branched polymers which possess a dimensionally layered arrangement of chemical bonds that arise from the introduction of a branch point at each monomer unit. Therefore, these are potentially the most highly branched structures that exist. A dendrimer essentially consists of four main components, namely a central core, arms of identical length linking branching points and end reactive functions [15].

Some of the largest organic macromolecules (C1398 H1278, molecular weight = 18,054 daltons and a diameter of 12.5 nm) have been prepared by using the above synthetic strategy [16]. Several applications have been explored for dendrimers (Table 2, p57). One of the most successful application is a dendrimer with 24 complexed gadolinium ions used as an MRI contrast

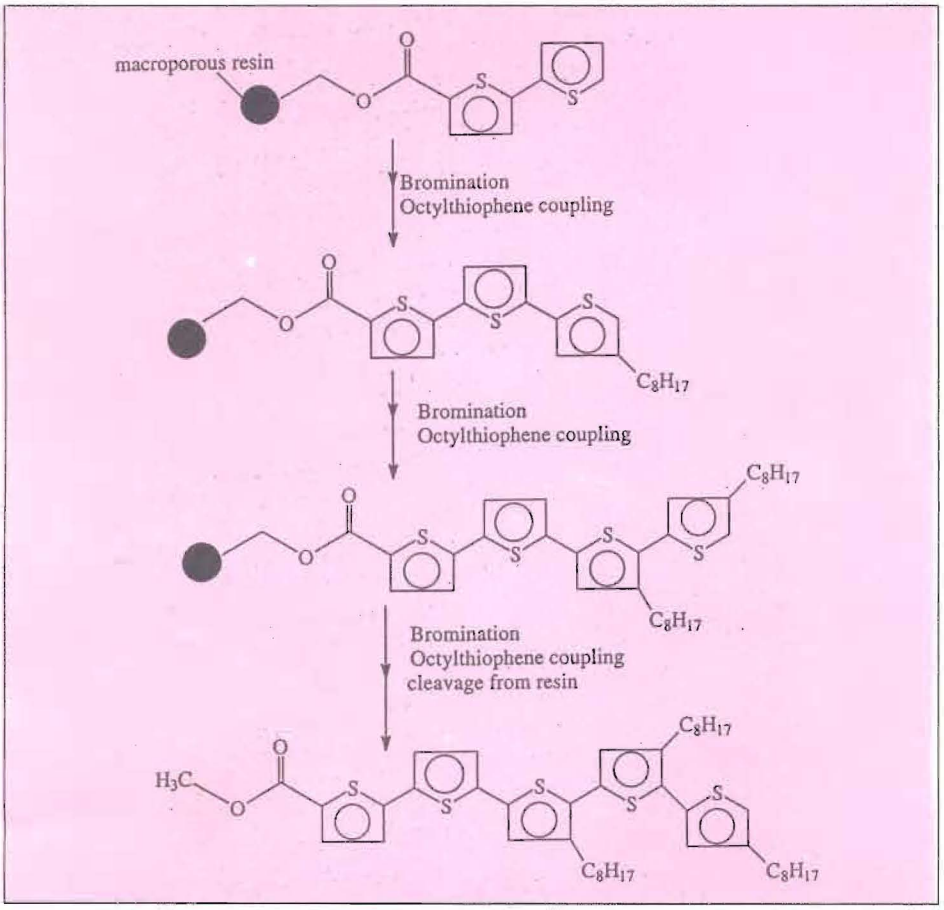


Figure 6. Stepwise synthesis of thiophene pentamer

agents. The intravenous application of small doses of this dendrimer, therefore, promises a highly resolved and contrasted visualization of blood vessels in coronary angiography.

Supramolecular Polymers

One of the most interesting developments in the area of polymers over the past ten years has been the advent of supramolecular polymers. These polymers are arrays of small molecules held together through weak non covalent interactions, such as hydrogen bonding, van der Waals forces or ionic interactions. The polymers can take various structures, although the basic form is described as a main chain supramolecular polymer. Main chain supramolecular polymers can be formed using either self associating molecules or mixtures of mutually associating molecules. These supramolecular polymers are similar to step growth polymers made from bifunctional monomers. Unlike step growth polymers, for supramolecular polymers in solution the degree of polymerization very much depends on concentration. While step growth polymers do not attain high molecular weights until the end of the reaction, supramolecular polymers only attain long chains at high monomer concentrations.

Because of the weak non covalent bonds that hold together supramolecular polymers, there are potential advantages. For example, they could flow like small molecules at elevated temperature or in dilute solutions. Similarly, they are expected to behave differently in terms of their rheological characteristics. Because the non covalent interactions in supramolecular polymers are reversible, the materials should reach a thermodynamically favorable state with the maximum possible crosslinking. This should significantly affect polymer mechanical properties.

There are several design principles that needs to be borne in mind while synthesizing supramolecular polymers [17,18]. The most important aspect is the nature of interaction that will hold the monomers to-

Table 2. Dendrimers : Emerging applications

Life sciences

- Dendrimer conjugates
- Biomimetics
- Immuno assays
- Medical diagnostics

Interfacial science

- Catalysts
- Monolayers
- Coatings

Nanodevices

- Molecular antennae
- Electroconductive dendrimers

Materials science

- Liquid crystal constructs
- Molecular ball bearings

Supramolecular sciences

- Molecular encapsulation
- Host guest interaction
- Dendrimer box
- Micelle mimics
- Lock/key complexes

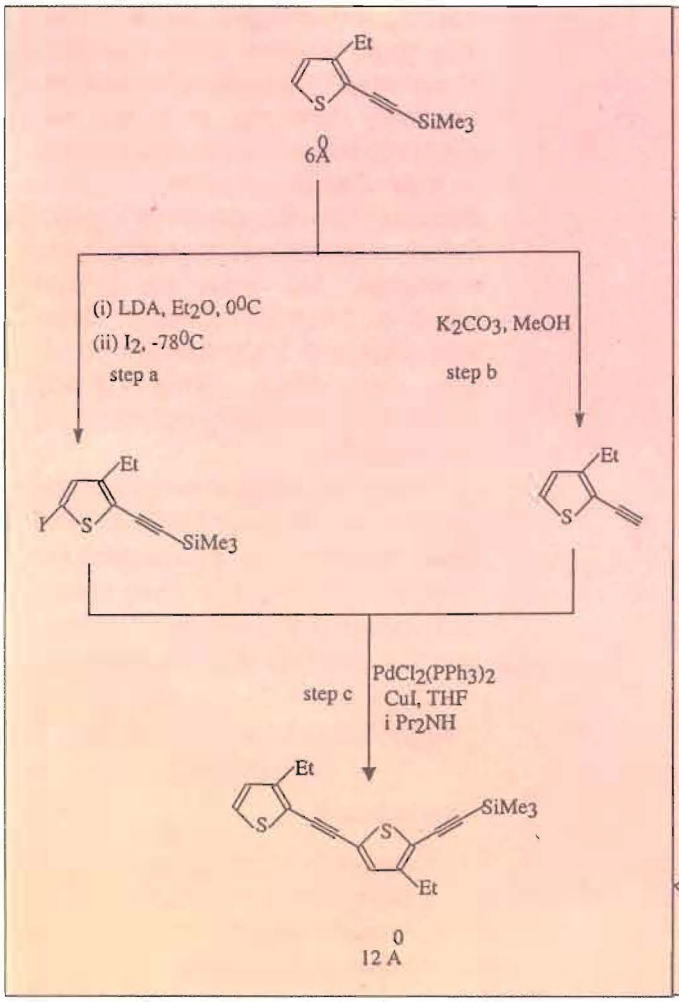


Figure 7. Iterative synthesis of oligo (thiophene ethynylene)s

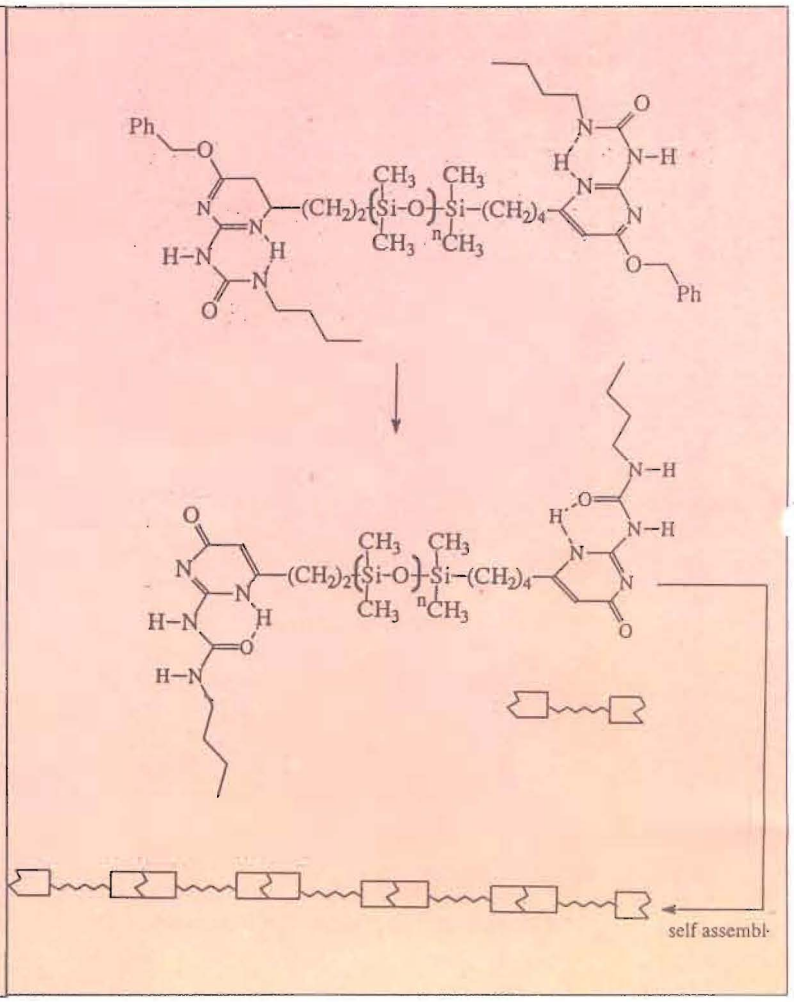


Figure 8. Urido-pyrimidone bifunctionalized siloxane (Mn=6000) gives oligomer upon debenzylation

gether. The interaction must be stronger than the van der Waals forces between the polymer chains, but weak enough to allow reversible dissociation under applied stress. Hydrogen bonding is the most frequently used bonding technique because it combines directionality with simplicity (Figures 8 and 9, pp58 &59). Ionic interactions have also been useful in the synthesis of threaded catenanes. Metal coordination bonds are highly directional and have been used to create molecular scaffolds [19,20].

Complex supramolecular organization requires information rich molecules that display high definition molecular surfaces. Supramolecular polymer chemistry enables synthesis of mesoscale molecules which can act as mechanical components of molecule sized machines [21] (Figure 10, p59). One can imagine a future, wherein, machines of the size of molecules, will sail through our blood stream to find and destroy clots or will open/close switches in nanoscopic electrical circuits.

Initially, the macrocyclic loop resides solely at the -NH_2+-station, but deprotonation of this (removing the positive charge) removes the stabilising interaction, making the loop move to the bipyridine station (+2 charge) instead. Adding acid regenerates the -NH_2+-group, and the macrocycle move back.

Conclusion and Prognosis

During the last five decades of this century polymers matured from their initial inception as poorly characterized organic compounds to versatile materials with great utility in critical areas of human needs such as shelter, clothing, transportation and health. In the next millenium, polymers, apart from meeting these established needs, are poised to

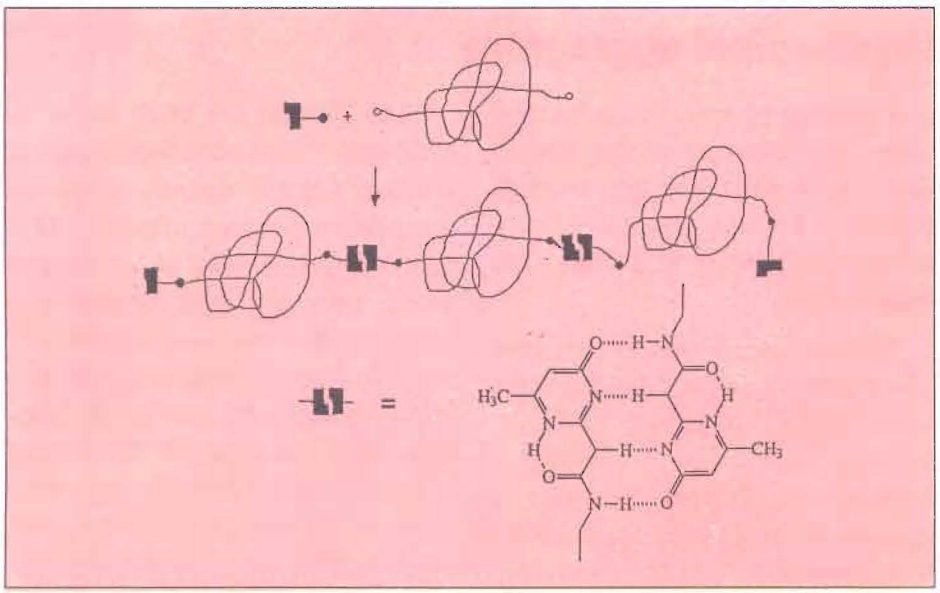


Figure 9. Functionalization of telechelic polymers with quadruple hydrogen-bonded ureido-pyrimidone units

capture many new areas of demanding applications, such as information storage and amplification technologies, low energy separation technologies, molecular electronics and photonics, sensor as well as biomedical technologies. These applications require polymers with precise control of structure and function at a molecular scale. New design principles of synthesis and powerful methods of polymer characterization, now under evolution, will ensure that these goals are fulfilled. Polymers, more than ever, are likely to become an integral part of human endeavor on this earth.

References

1. Hatada, K.; Kitayama, T.; Vogl, O. *Macromolecular Design of Polymeric Materials*, Marcel-Dekker, Inc., New York, **1997**.

2. Schiers, J.; Kaminsky, W. *Metallocene based Polyolefins*, John Wiley & Sons, New York, **2000**.

3. Bajgur, C.S.; Sivaram, S. *Curr. Sci.* **2000**, *78*, 1325-1335.

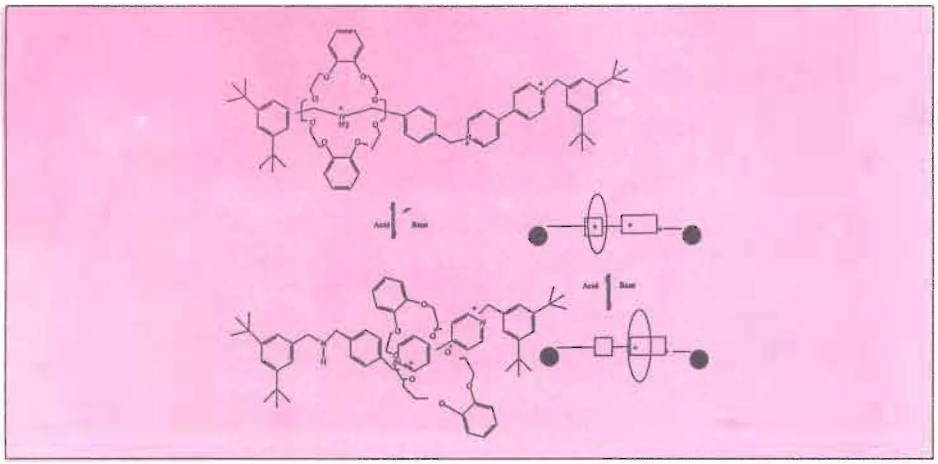


Figure 10. Linear movement of a rotaxane : A molecular shuttle

4. Matyjaszewski, K. *Chem. Eur. J.* **1999**, *5*, 3095-3102.

5. Patten, T.E.; Matyjaszewski, K. *Adv. Mater.* **1998**, *10*, 901-915.

6. Sawamoto, M.; Kamigato, M. *CHEMTECH*, **1999**, 30-38.

7. Malmslrom, E.E.; Hawker, C.J. *Macromol. Chem. Phys.* **1998**, *199*, 923-925.

8. Ramanathan, L.S.; Sivaram, S. U.S. Patent 6,123,988, **2000**; U.S. Patent 6,022,933, **2000**.

9. Hirao, A.; Hayashi, M. *Acta Polym.* **1999**, *50*, 219-231.

10. Baskaran, D. unpublished results, NCL.

11. Malenfunt, P.R.L.; Frechet, J.M.J. *Chem. Commun.* **1998,** 2657-2658.

12. Tour, J.M. *Chem. Rev.* **1996**, *96*, 537-553.

13. Petty, M.C.; Bryce, M.R.; Bloor, D. *An Introduction to Molecular Electronics*, Edward Arnold, London, **1995.**

14. Wallace, G.G.; Dastoor, P.C.; Officer, D.L.; Too, C.O. *CHEMTECH*, 15-22.

15. Fischer, M.; Vogtle, F. *Angew. Chem. Intl. Ed. Engl.* **1999**, *38*, 884-905.

16. Xu, Z; Moore, J.S. *Angew. Chem. Intl. Ed. Engl.* **1993**, *32*, 1354-57.

17. Philp, D.; Stoddart, J.F. *Angew. Chem. Intl. Ed. Engl* **1996**, *35*, 1154-1196.

18. Zimmerman, N.; Moore, J.S.; Zimmerman, S.C. *Chem. Ind.* **1998**, 604-610.

19. Moore, J.S. *Curr. Opin. Coll. Interface Sci.* **1999**, *4*, 108-116.

20. Folmer, J.B.B.; Sijbesma, R.P.; Versteegen, R.M.; Van der Rijt, A.J.; Meijer, E.W. *Adv. Mater.* **2000**, *12*, 874-878.

21. Ward, M.D. *Chem. Ind.* **2000**, 22-26. ❑