MOLECULAR NECKLACES: POLYESTER ROTAXANES

by

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(ABSTRACT)

Polyrotaxanes consisting of 30-60 membered aliphatic crown ether macrocycles whose cavities are pierced by polysebacate chains were synthesized by several polymerization approaches including transesterification polymerization, the acid chloride method, and interfacial polymerization.

The polyrotaxanes were purified by multiple reprecipitations into good solvents for the crown ethers. In some cases the threaded macrocycles are constrained onto polymer chains by the incorporation of monofunctional blocking groups at polymer chain ends, or by the copolymerization of a difunctional blocking group with other monomers.

The compositions and the physical properties of the polyrotaxanes were determined by a variety of characterization techniques including NMR, UV, VPO, GPC, DSC, TGA, and intrinsic viscosity measurements. Significant amounts, up to 51 mass %, of the macrocyclic components were incorporated. Because of incorporation of flexible and polar macrocycles, polyrotaxanes

display special behavior in solution and in the solid state. In solution the linear components of polyrotaxanes are stiffened by the threaded macrocycles, resulting in increased hydrodynamic volumes. The solubilities of linear polymers in polar solvents are enhanced by the incorporated crown ethers. The glass transitions are also affected by the crown ether component. Due to the movement of the macrocycles along the backbone, the macrocycles are able to aggregate and crystallize without dethreading from the polysebacate backbones.

The threading and dethreading processes were systematically studied in the diol/diacid chloride system. Due to the hydrogen bonding between the cyclic and linear species, the macrocycle contents of unblocked polyrotaxanes are significantly affected by the feed ratio of macrocycle to linear monomers up to a value of 2 but are independent of reaction time and the length of diol monomers. The macrocycle content of polyrotaxanes increases non-linearly with the size of the macrocycles, presumably due to changes in the fraction of threadable conformations of the macrocycles. Although some macrocycles near the unblocked polymer chain ends are apparently susceptible to the dethreading from polymer chains, most of the macrocycles are prevented on resonable time scales, e.g., months in solution, from the dethreading by the entanglement of cyclic and linear species.

In the Memory of My Father

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CHAPTER I

POLYMER ARCHITECTURES

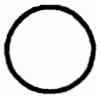
Polymers are large molecules made up of a large number of low molar mass base units which are connected by primary bonds (Greek *poly meros* = many parts). Since German chemists developed a synthetic "methyl" rubber to replace the natural rubbers in 1917, the requirements of replacing traditional materials, such as wood, metals, ceramics, and natural fibers by synthetic polymers have increased dramatically. This development requires a fundamental understanding of relations of structure-property which can be examined under two broad aspects. (a). The chemical level which is concerned with structural information, including the order in which the specific atoms are connected; the type of covalent bonds; and the three dimensional arrangements around rigid centers. For some chemical systems this level is not sufficient. (b). The architectural level which deals with the properties being invariant for various structures consistent with the chemical level. Topological isomerism in chemistry refers to differences in the way in which molecules are imbedded as a whole in three dimensional space.

I. TOPOLOGIES OF POLYMERS

Molecular chemistry, the chemistry of the covalent bond, deals with the natural rules governing the structures, properties, and conversions of molecules. In the molecular chemistry point of view, polymers can be classified by their molecular

topology as cyclic, linear, branched and network polymers (1), as depicted in Figure 1:

I. Cyclic Polymers (No Chain Ends)



II. Linear Polymers (Two Chain Ends)

Homopolymer — AAAAAAAAAAAAAAAA

Random Copolymer — ABBABAAABABAABAA

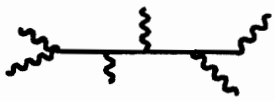
Alternating Copolymer — ABABABABABABABAB

Block Copolymer — $-(A)_x-(B)_n-$

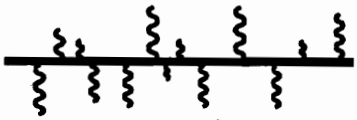
III. Branched Polymers
(More than Two Ends)

Star Polymers (Homo- or Block-)

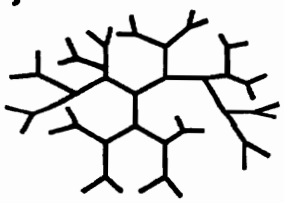
Randomly Branched Polymers



Graft/Comb Polymers
(Long Chain- &
Short Chain- Branching



Dendritic



IV. Network Polymers
(One Enormous Molecule with few chain ends)

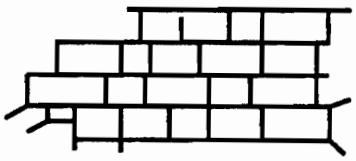


Figure 1. Polymer topologies

Cyclic polymers have no chain ends. They represent the extreme case in the whole spectrum of polymer topology. Because of their non-chain-end structure, cyclic polymers display special dilute solution, diffusional and rheological properties such as lower hydrodynamic volumes, lower melt viscosity, and higher glass transition temperatures than linear polymers [2,3].

A linear polymer has two chain ends and has no branching other than the pendant groups associated with the monomers. If the polymer is prepared from a single monomer, the product is referred to as a homopolymer. The intermolecular interactions of homopolymers determines their physical behavior in the solid state. If two or more monomers are copolymerized, several arrangements are possible in the polymer structure. If the structural units alternate in a linear fashion, the product is called an alternating copolymer. Usually the properties of an alternating copolymer are a combination of the properties of the two monomers along with structural regularity. If the distribution of structural units are random, the polymer is called a random copolymer whose properties are an average of the properties of monomers. A third arrangement is where homopolymers jointed end-to-end. Such an arrangement is referred to as a block copolymer. Block copolymers frequently exhibit phase separation which typically gives rise to a dispersed phase consisting of one block type in a continuous matrix consisting of the second block type [4]. In many applications, the dispersed phase consists of hard domains which are crystalline or glassy and amorphous, and the matrix is soft and rubber-like. A block copolymer can act as an emulsifier for a system of two immicible homopolymers [5]. Block polymers exhibiting phase separation show

two transitions where the modulus changes markedly over a narrow temperature range. Elasticity is a general property of block copolymers containing a combination of incompatible hard and soft blocks. The hard blocks in the domains serve as tie-points, or thermolabile crosslinking sites [6]. These physical crosslinks are reversible.

Long-chain branched polymers, including star-shaped, comb-like, and randomly branched polymers, are a class of polymers between the linear polymers and polymer networks. The properties of the polymers are influenced by their overall dimensions and long-chain branching. The presence of long-chain branched molecules causes different properties compared to a pure linear polymers such as narrow molecular weight distribution [7], smaller radius of gyration [8], and different properties in solid state governed by the overall dimensions of polymer chains.

Dendrimers are monodispersed macromolecules with radially symmetric branching. Dendrimers consist of three architectural components: a core; interior layers (generations) attached to the core; and an exterior of terminal functionality connected to the outmost generation. Due to their special architectures, dendrimers show interesting properties such as controllable size, compartmentalization, solubilization, preorientation, and cage location [9].

Graft polymers are macromolecules with a 'backbone' of one polymeric species attached to which are one or more side chains of another polymeric species. Graft polymers may have comblike or random graft structures. Because of

thermodynamic incompatibility of the backbone and side chain, most graft polymers show microphase separation behavior in solid state (4, 10). These polymers exhibit many unique thermal and mechanical properties including thermoplastic elasticity. Generally property differences between linear and branched polymers apply to graft copolymers.

Crosslinked polymers are insoluble and infusible three-dimensional networks in which polymer chains are joined together. Crosslinked polymers exhibit many special properties compared to linear and branched polymers. Improvement of physical properties by cross-linking are most significant. For example, modulus increases with degree of crosslinking. Crosslinked polymers behave like soft elastic solids at elevated temperature [11]. Other special behavior include improved creep, compression set, and stress relaxation; lower thermal expansion and heat capacity; higher heat distortion temperature, tensile strength and reflective index. Glass transition temperature increases as crosslink density increases [12].

An economic way to meet the needs for new materials is to make polymer blends, the mixtures of at least two polymers or copolymers, including homologous, miscible, immiscible, and compatible polymers [13]. From the economic point of view, this approach has many advantages over others such as extending engineering resin performance by diluting it with a low cost polymers; developing materials with expected properties; forming a high performance blend from synergistically interacting polymers, etc. However, The development of polymer blends is limited by the fact that many polymers are

immisible to each other and the microphase separation occurs in immisible blends, resulting in poor elongation and impact-strength properties.

II. POLYMERS WITH SUPRAMOLECULAR TOPOLOGIES

In contrast to molecular chemistry, supramolecular chemistry, the chemistry beyond molecules, is concerned with the organized entities of high complexity resulting from the association of at least two chemical species by intermolecular (noncovalent) interactions [14].

Interpenetrating polymer networks (IPN) are a combination of at least two polymers in a network which are synthesized in juxtaposition (Figure 2) [15].

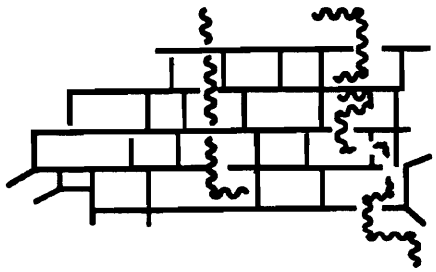


Figure 2. Interpenetrating polymer network

For IPN, if mixing takes place at the early stage of the polymerization and the polymerization proceeds simultaneously with crosslinking, phase separation may be controlled. Therefore, polymer mixtures with limited phase separation

can be produced via interpenetration polymerization. IPN are a special example of topological isomerism of polymers [16]. Some permanent entanglements between two crosslinked polymers are inevitable in any intimate mixture of crosslinked polymers.

Polycatenanes are extended interlocking ring systems without covalent bonds between the rings. The term "catenane" comes from the Latin word catene meaning chains. However, since Frisch et al. first suggested the existence and possible syntheses of polycatenanes in 1953 [17], no pure polycatenanes have been isolated and characterized. Some subclasses of polycatenanes are shown in Figure 3.

Polyrotaxanes are supramolecular assemblies consisting of linear molecules onto which are threaded cyclic species (Figure 4). The term 'rotaxane' is derived from the Latin words for wheel and axle [18]. Bulky groups are attached to the linear molecules, either at the ends or in the middle of the chain, to prevent diffusion loss of the molecules, dethreading. If there exist strongly attractive forces between cyclic and linear species, blocking groups may not be necessary. Polyrotaxanes can be classified as main chain and side chain polyrotaxanes, depending on the differences in the location of the covalent and physical linkages. Polyrotaxanes can also be divided into two types, homopolyrotaxanes and heteropolyrotaxanes, based on the chemical structures of cyclic and linear species. Homopolyrotaxanes consist of chemically equivalent macrocycles and polymer chains. Heteropolyrotaxanes are comprised of chemically different cyclic and linear components.

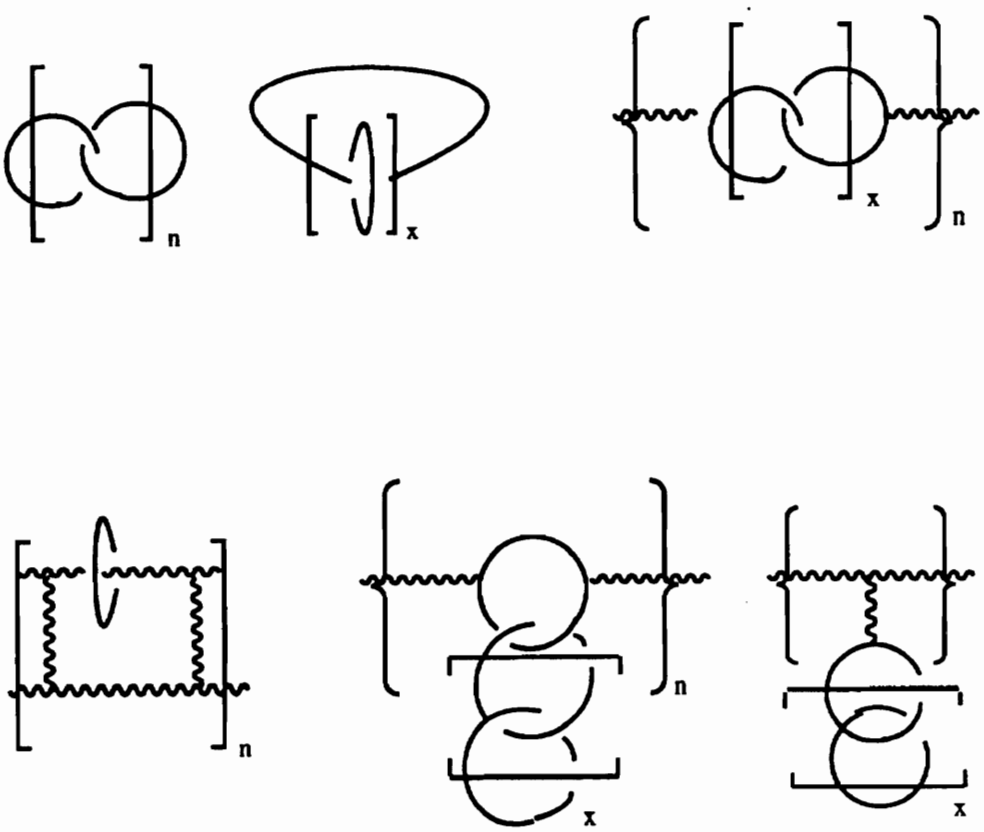


Figure 3. Some subclasses of polycatenanes

Similarly to conventional copolymers and polymer blends, a wide range of physical properties can result from judicious combination of cyclic and linear components of polyrotaxanes. If the macrocycles and linear polymer chains are compatible, the crystallinity of polyrotaxanes can be changed by adjusting the macrocycle contents in polymers. The toughness of the polymers can be

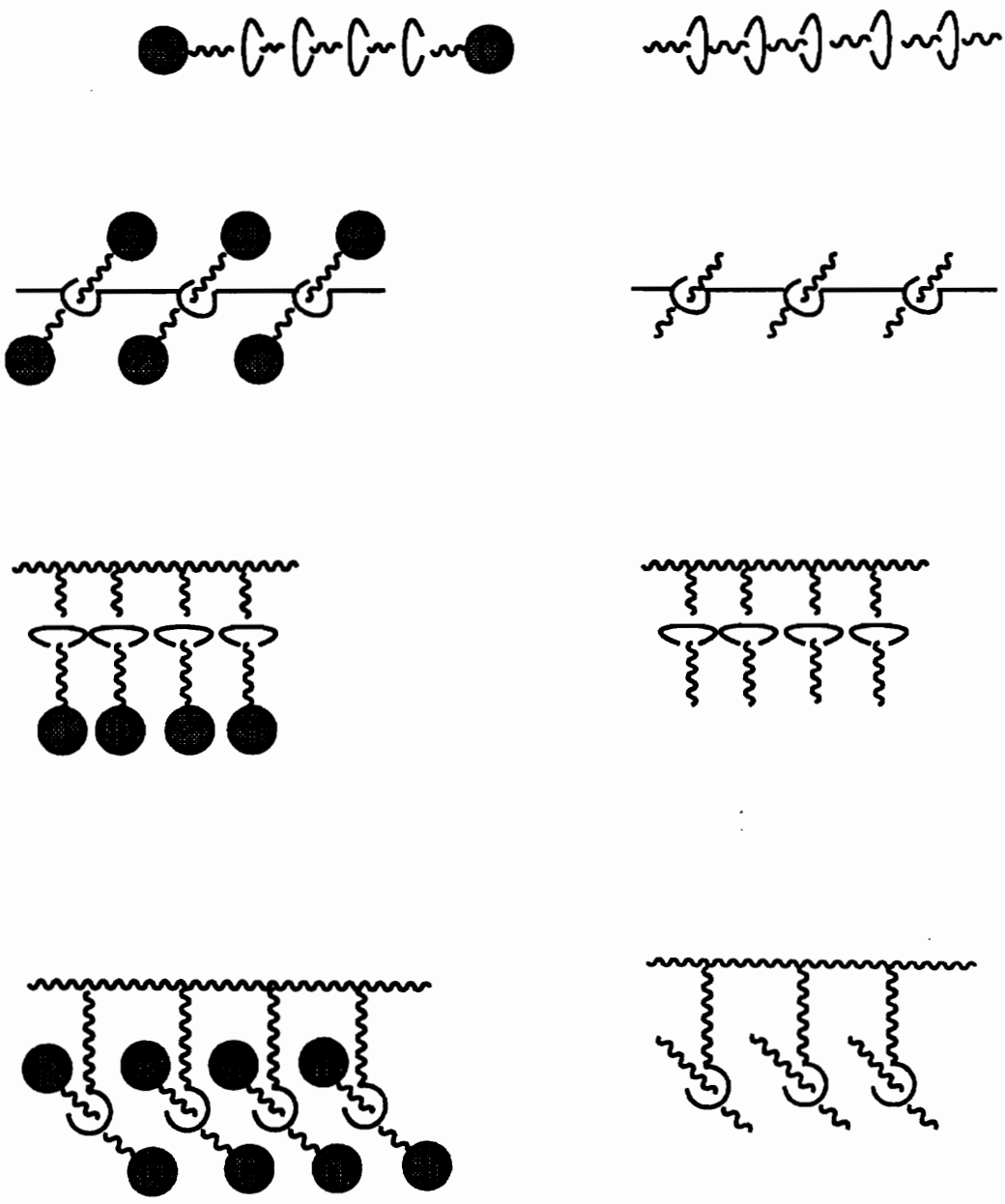


Figure 4. Polyrotaxane structures