Chapter 1

General Introduction

1.1 Light Harvesting in Natural Systems

The conversion of light energy into chemical energy in plants and photosynthetic bacteria, which has been optimized by the process of evolution, is a subject of interest in many areas of research of contemporary science.[1] The ultimate idea of using the light energy absorbed by a molecule to drive endothermic reactions, such as splitting of water to H_2 and O_2 for use as a fuel source, is very appealing, and much effort has been put into understanding of primary events of photosynthesis. In photosynthesis, absorption of light by chlorophyll is followed by a long-distance energy transfer to the reaction center where 'trapping' occurs with generation of a long-lived charge-separated state.[2] As for the energy transfer, the excited-state energy of the chromophore is transmitted, without electron transfer, to the quencher which itself enters an electronically excited state. This is more likely to occur if the quencher has available low energy excited state and does not undergo easy oxidation or reduction (Figure 1.1).

The elegant structure and mechanism of energy transfer in the photosynthetic complex of the purple bacteria was recently clarified[2,3] (Figure 1.2). In the reaction center **RC**, a radical ion (charge-separated) pair is generated. It withdraws and transfers an electron through the membrane. The energy for this process is collected by chlorophyll molecules in light harvesting complexes **LH1** and **LH2**. Most photosynthetic bacteria have two or more light harvesting complexes with distinct

biochemical and spectroscopic properties. **LH2** is referred to as the outer antenna because the energy it collects flows through another, inner antenna complex **LH1**, and then is ultimately transferred to **RC**. In **LH2** nine pairs of two fairly short α-helical polypeptides (not shown) and associated pigment molecules (bacteriochlorophylls **B800** and **B850**) are combined into a ring. **B800** and **B850** are held inside a complex mostly by coordinate bonds between Mg metal centers and amino-acid polar groups. There are hydrophobic interactions between **B850** and peptide side-chains, and hydrogen bonds between **B800**'s acetyl carbonyl oxygen and the side chains of the neighboring aminoacids of the β-proteins.[2] Eighteen **B850** chromophores are held near the membrane surface, arranged as a wheel of a turbine, and nine **B800** are in the middle of the membrane and parallel to the surface. The chemical environments of **B800** and **B850** are different, so they absorb at different wavelengths, 800 nm and 850 nm, respectively. The **LH1** ring contains sixteen units of **B875** and thus it is wider and is capable of accommodating the reaction center **RC**.

Interestingly, the plant light harvesting center is quite different from the described bacterial one, having one long protein chain of 232 aminoacids that is folded into four helixes, with twelve chlorophyll molecules between them. It lacks the repetitive simplicity of **LH2**. Nevertheless, some of the principles of construction are the same.[4]

When a photon hits one of the chlorophylls **B800** (Figure 1.2), the absorbed energy spreads extremely rapidly (in less than 1 ps) to **B850** where it delocalizes

between all eighteen **B850** in 0.2-0.4 ps due to their favorable orientation. Where the rings touch, the energy can 'jump' the short distance to another complex where it again spreads out. **B875** absorbs at lower energy, so **LH1** serves as an energy funnel for the reaction center **RC** for which absorption maximum is the most red-shifted. Thus, the energy of photons is conducted and collected in a very short time with minimal loss.[5]

1.2 Experimental Modeling of Light Harvesting Processes

From the example above, it is seen that nature relies on non-covalent (supramolecular) methods of assembly. Nevertheless, to understand the interactions between chromophore and quencher under controlled conditions covalently bound model assemblies are particularly useful. Studies on covalently bound complexes where light-absorbing part and quencher are linked by a covalent bond have contributed a great deal to our understanding of the photosynthetical processes.[6] This method allows precise knowledge of the distance between two groups, their relative orientation and the nature of the pathway linking the two components. Luminescent complexes are particularly useful in the area of photosynthesis studies and modeling because they tend to have long-lived excited states, and loss of luminescence (quenching) is an obvious sign that excited-state complex is reacting with another group rather than undergoing radiative decay. The porphyrin-quinone system is one of the most commonly studied because of its relevance to naturally occurring photosynthesis.

A typical example is presented in Figure 1.3 where it was found that the rate of electron transfer exponentially decreases with increasing chromophore-quencher distance.[7]

Recent interest in modeling of natural light-harvesting complexes was accompanied by simultaneous increase of interest in synthetic light-harvesting polymers.[8] A polymer antenna usually consists of a number of light absorbing chromophores (donors) and energy traps (acceptors). In the field of polymer physics and chemistry, singlet energy migration and excimer formation have been extensively studied for homopolymers and copolymers in solution and in low temperature glasses (rigid environment).[9] Fluorescence techniques have been demonstrated to be powerful method for obtaining detailed information on the molecular structure of polymers and energy transfer processes within or between macromolecules. As an example, in a covalently bound donor-acceptor (D-A) system (Figure 1.4) it was found that the quantum efficiency of energy transfer was very high: 1.00 for D-D and 0.70 for D-A transfer. In addition, it was stated that cross-chain (as opposed to down-chain) energy transfer occurs because of the large Förster radius R_0 (the distance at which energy transfer occurs with 50% probability) for D-A in this system, around 25 Å. The relationship between these two modes of energy transfer had yet to be solved.[10]

1.3 Macrocyclic Vinylaromatic Polymers as Promising Light Harvesting Models

Design and preparation of suitable organic molecules consisting of donors, bridges and acceptors is important. It has the advantage that specific properties of the

complex natural processes can be tuned and will provide new details of energy and electron transfer in nature. Macrocyclic vinylaromatic polymers are of interest as a platform for the construction of antenna polymers for several reasons. First, the synthesis by anionic polymerization and end-to-end coupling of polymer dianions with bifunctional electrophiles under conditions of high dilution[11] is convenient and flexible allowing insertion of up to four different types of chromophores into a single polymeric macrocycle with excelent control of their relative positions (Figure 1.5) and overall polymer characteristics, such as molecular weight and polydispersity. Second, in the rings a more efficient energy transfer between the chromophores compared to the corresponding linear polymers is anticipated. For instance, molecular modeling (Sybyl, MM1, AM1) of atactic or isotactic macrocyclic polystyrene and poly(2-vinylnaphthalene) with degrees of polymerization between 10 and 40 has indicated that these structures are largely flat ellipsoids measuring about 30-40 and 10-20 Å in length and width, respectively. Because of a conformational preference for a pseudo-equatorial orientation of the pendent groups, there is a clear tendency for roughly parallel and partially eclipsed alignments of these groups along the periphery of a largely planar ring (Figure 1.6). The calculated distances between neighboring chromophores are between 3.2 and 4.2 Å, far smaller than calculated for linear polystyrene (PS).[9] Both of these factors are expected to lead to a faster energy transfer between the transition dipoles in macrocyclic polymers compared to that expected for an atactic linear chains. It was recently found that macrocyclic polymers, such as macrocyclic polystyrene[12] and poly(9,9-

dimethyl-2-vinylfluorene),[13] exhibit an increase in photoluminescence compared to their linear analogues.

1.4 Synthetic Methodologies for Preparation of Macrocyclic Polymers

Several approaches have been utilized in preparation of macrocyclic polymers. An intramolecular coupling of α,ω-heterobifunctional polymers at high dilution has been successfully used to synthesize well-defined macrocyclic polymers and block-copolymers. While achieving the target, this method has practical limitations as it involves tedious multistep synthesis with protection – deprotection processes.[14-18] An interesting and original method of an "electrostatic self-assembly and covalent fixation" has been introduced recently and used in preparation of polystyrene (PS) and polytetrahydrofuran (PTHF) of complex architectures, including macrocyclic polymers.[19,20] However, involvement of complex chemistry, inherent side reactions (although minimized to as low as 10%), low yield of isolated macrocycles (52%) and the presence of a large heteroatom-containing linking unit may also limit practical application of the method and the materials prepared by this method. In addition, an ATRP or nitroxide mediated approach to macrocyclic architecture construction[21] does not seem to have a serious potential due to poor control of polymer characteristics and low yields of rings that are in the mixture with non-separable linear chains.

The most extensively studied method of preparation of macrocyclic polymers is an intramolecular alkylation of α,ω-difunctional polymer anions at the conditions of high dilution.[12,22-27] This versatile method, even though bimolecular in nature, is

fast as it involves highly reactive carbanions. The stoichiometric balance is easily achieved under proper experimental conditions, allowing yields of unfractionated macrocycles of 90% and higher. The polymerization allows preparation of predictable molecular weight polymers with narrow polydispersities. In addition, it is the only method that allows synthesis of macrocycles without the presence of heteroatoms or irregularities in the main chain. The synthesis involves initiation by a direct electron transfer from an alkali metal naphthalide or by an addition to a symmetrical dianion (**2**) containing two chromophores and formed by electron transfer to a sterically hindered non-polymerizable vinyl derivative (Scheme 1.1).[28] A second chromophore is incorporated upon polymerization of a monomer (**3**), the molar ratio of which over dianion allows control of the degree of polymerization. The use of low temperatures (-78 ºC and below) avoids inadvertent protonation of precursor (**4**) by solvent and allows separation of its solution into several final aliquots, one of which is protonated or alkylated to give a linear polymer (**6**) having two Ar^3 chromophores at the chain ends. Another aliquot is reacted with a bifunctional coupling reagent under high dilution conditions. This allows predominantly intramolecular coupling to give macrocyclic polymer (**5**). A wide variety of chromophores is possible here for incorporation into the macrocycle, subject only to chemical compatibility with the polymer dianion intermediates. The synthesis has a number of advantages outlined above. In addition, the possibility of preparation of matching (same degree of polymerization) linear and macrocyclic

polymers having identical chromophores is appealing since comparison of properties may directly give valuable and easier to interpret information.

As intermolecular coupling proceeds to some extent, the fractionation of macrocyclic polymer from higher molecular weight polycondensation product is necessary. The fractionation involves selective precipitation of higher MW linear and cyclic polymers by incremental addition of a non-solvent to a solution of the reaction polymer mixture and the analysis of the supernatant solution by SEC in order to monitor the selective precipitation of the higher MW side products.[29] Further fractionation of purified cycles into very narrow MW distribution fractions is possible and desirable using preparative size exclusion chromatography. These narrow MW distribution fractions may allow correlation of ring size with photophysical, thermal and other properties.

A number of macrocyclic polymers, such as polystyrene (PS),[12,27] poly(2-vinylpyridine) (P2VP),[26,27] poly(α-methylstyrene) (PAMS)[30] and macrocyclic polystyrene-*b*-polydimethylsiloxane,[31] have been successfully prepared and characterized. However, macrocyclic poly(2-vinylnaphthalene) (P2VN) has not been synthesized to-date. P2VN has recently received considerable attention, especially in modeling of energy transfer in complex systems.[8,9] There are reports describing radical, cationic and anionic polymerization techniques to prepare P2VN and P2VN block-copolymers.[10,32,33] While most of these reports involved the synthesis of P2VN by radical polymerizations, there is a smaller number of papers dealing with anionic polymerization of this interesting monomer. The reasons for this include difficulties

controlling the polymerization of this monomer, tedious purifications that include typically one or more sublimations and the occurrence of an inadvertent thermal polymerization at ambient temperatures. Thus, it is of practical and academic interest to investigate anionic polymerization of 2-vinylnaphthalene and its potential for the living (absence of spontaneous polymer chain end deactivation) polymerization and preparation of macrocyclic polymers.

1.5 References

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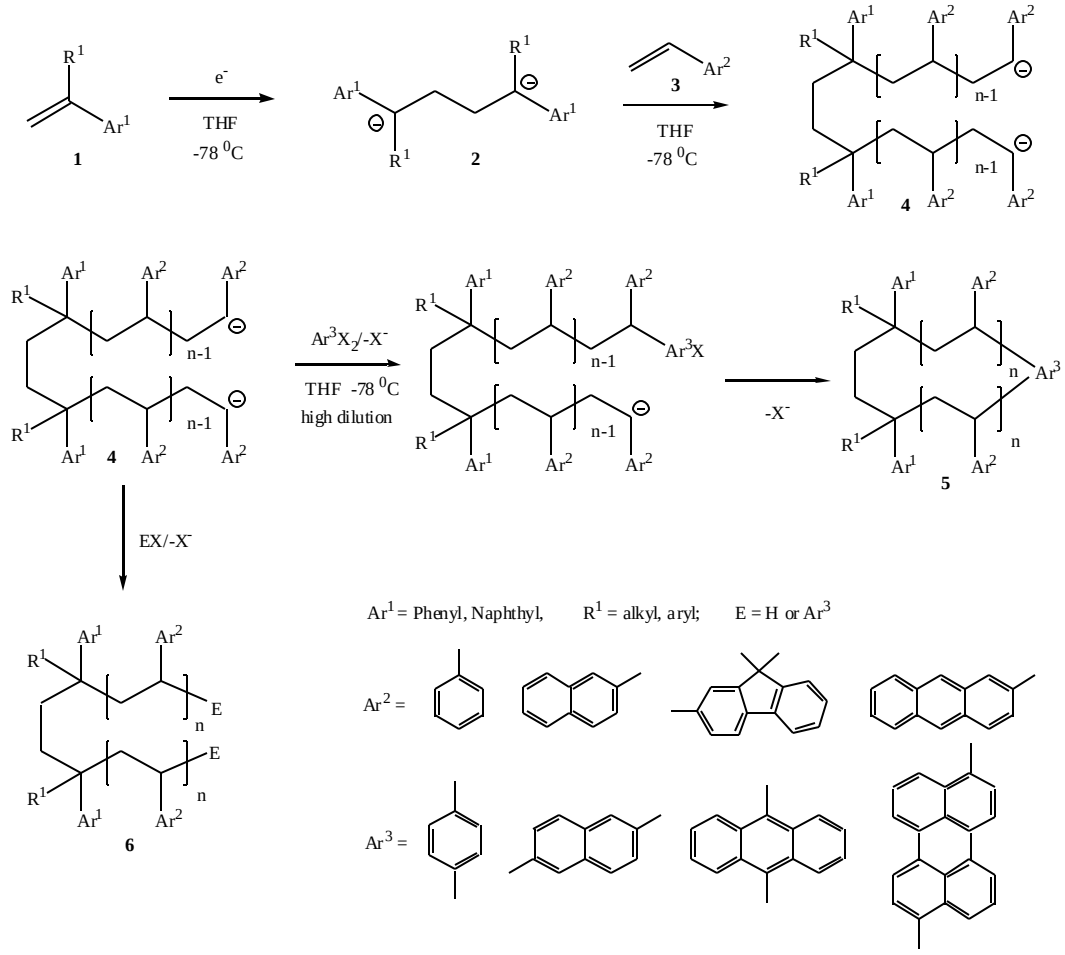

Scheme 1.1. Synthesis of macrocyclic vinylaromatic polymers with variations of chromophores at initiator site, in repeating unit and in coupling group.

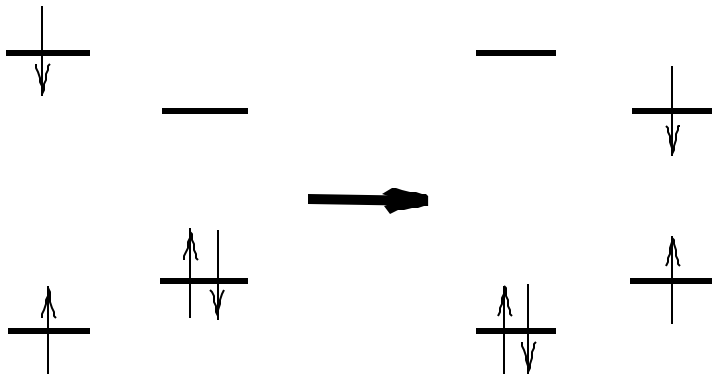

Figure 1.1. Energy transfer upon quenching of a chromophore excited state.

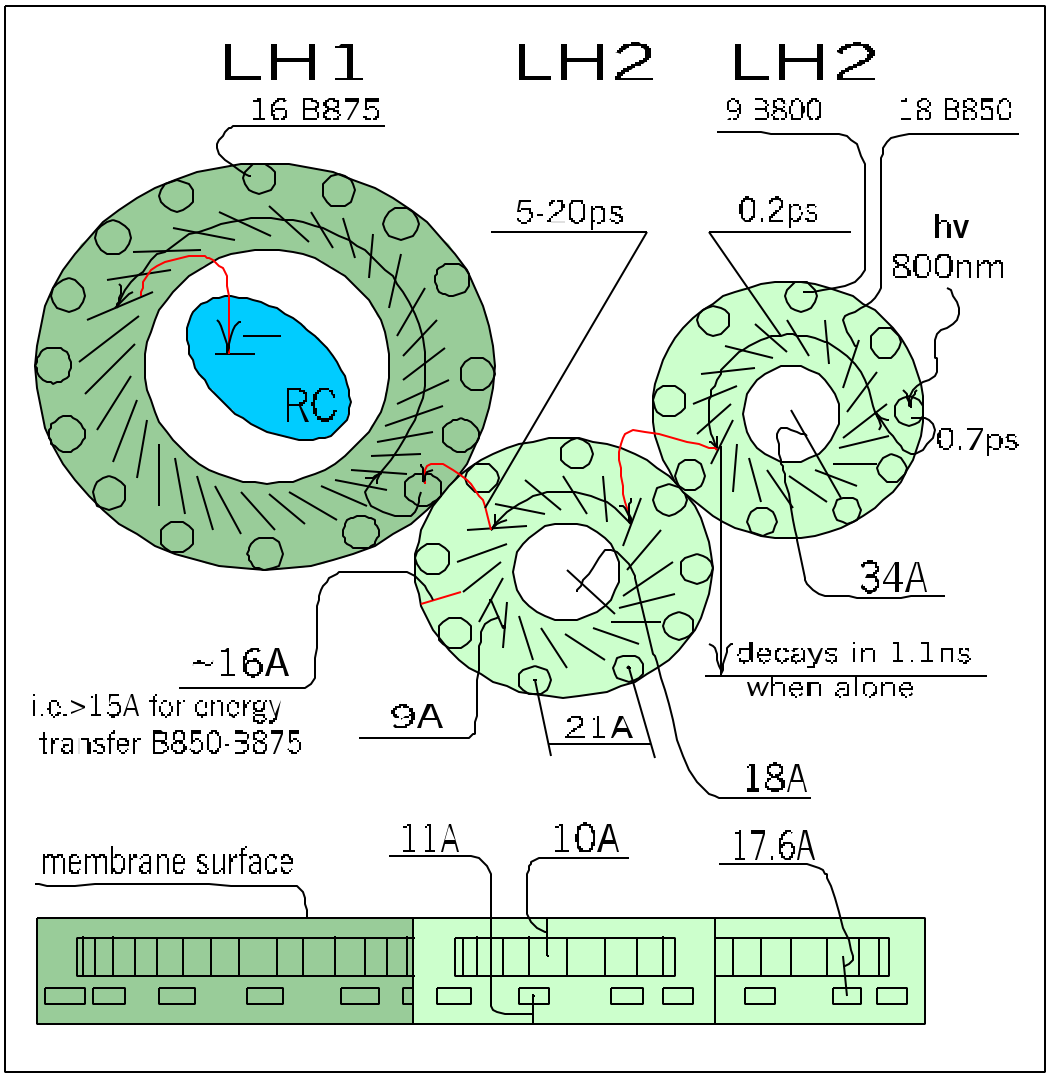

Figure 1.2. Structure of light-harvesting system in photosynthetic bacteria and the path for energy transfer from LH1 to a special pair of bacteriochlorophylls in RC.

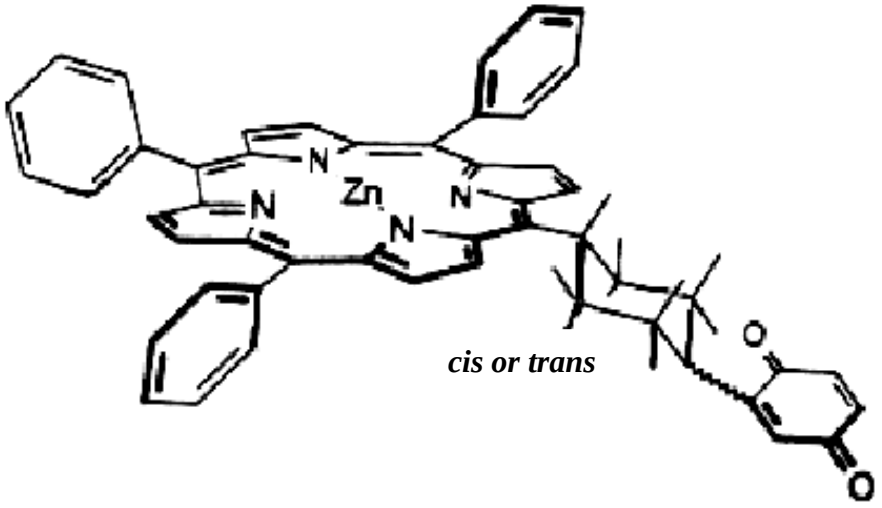

Figure 1.3. An example of covalently linked chromophore-quencher assembly.

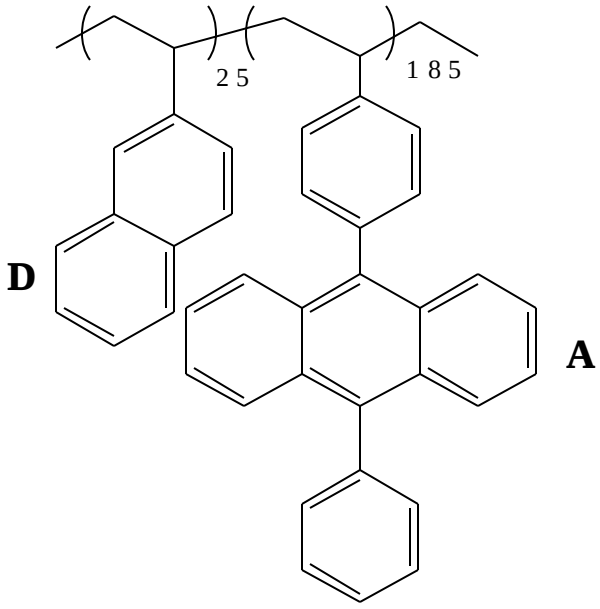

Figure 1.4. Covalently bound polymer system of donor (**D**) and acceptor (**A**).

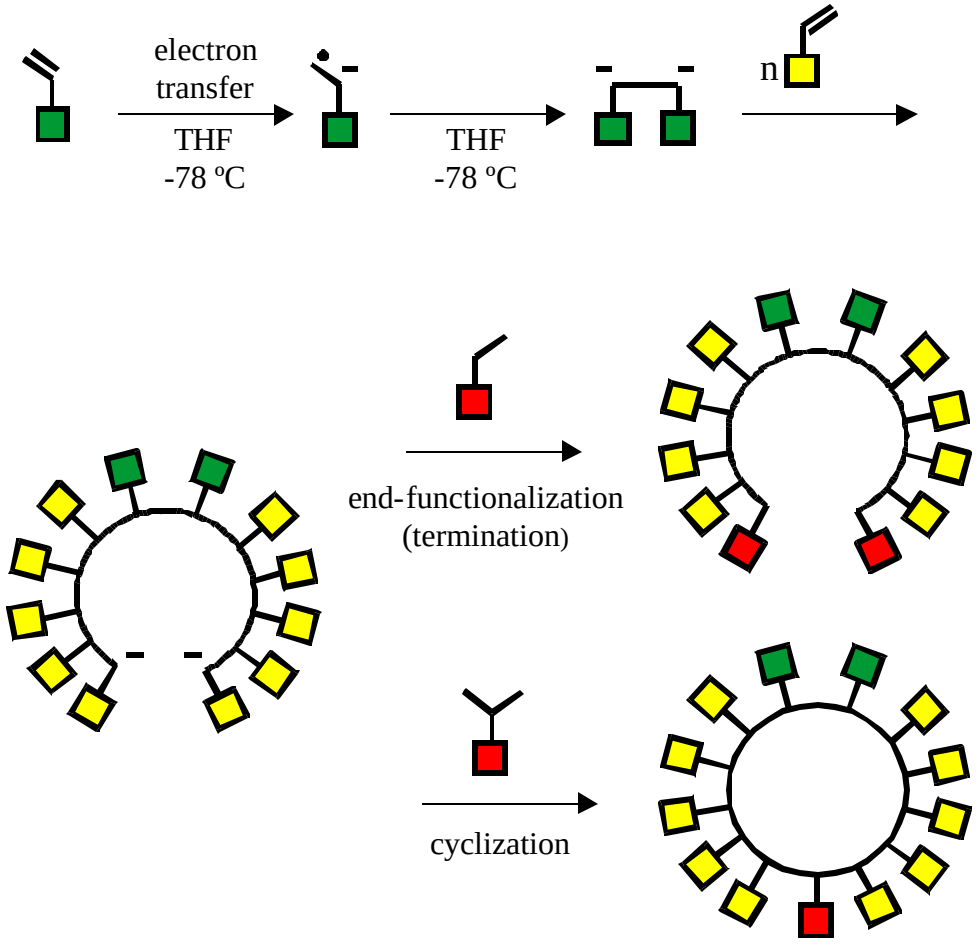

Figure 1.5. Simplified representation of the synthesis of macrocyclic polymers by anionic polymerization and end-to-end coupling of polymer dianions with bifunctional electrophiles.

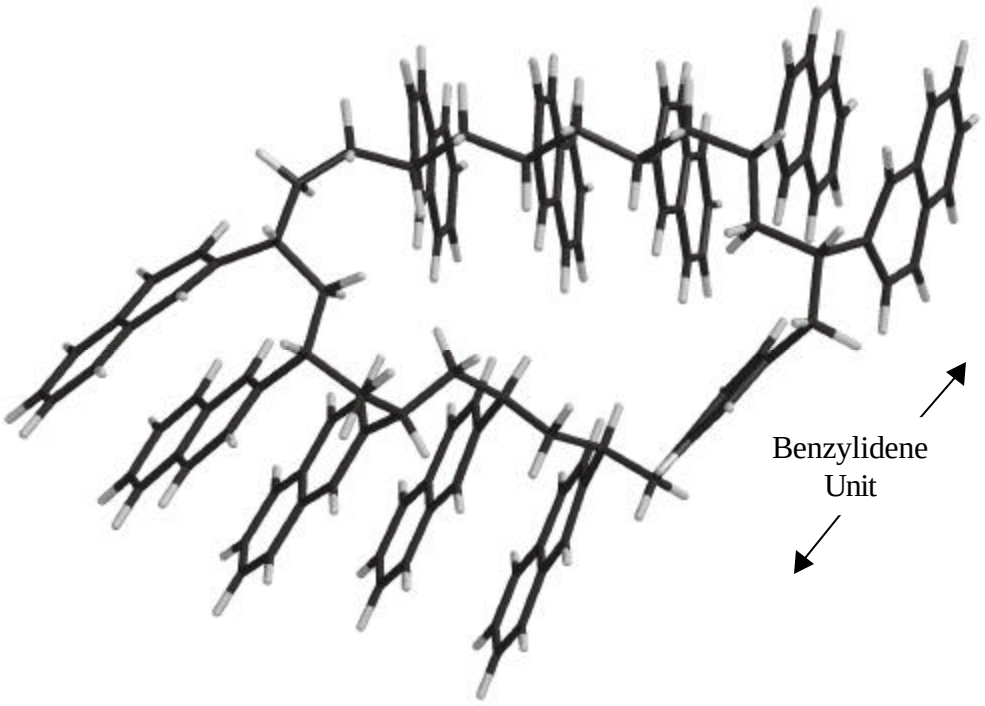

Figure 1.6. Sybyl calculated minimized structure of isotactic poly(2-vinylnaphthalene) with $DP_n = 10$.