

NOVEL APPROACHES FOR NOVEL MATERIALS

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ABSTRACT

In our lab we have been actively involved in the design of newer methodologies for the synthesis of novel materials like Dendrimers, Hyperbranched Polymers, Bio-Sensors, Electrochromic Polymers, Liquid Crystalline Polymers, Conducting Polymers and new thermoplastics based on heterocycles. We have designed and synthesized a dibenzyl propylenedioxythiophene (PProDOT-Bz₂) polymer. PProDot-Bz₂ exhibits an extremely high contrast of 89% at λ max (632 nm) with coloration efficiencies of the order of 575 cm²/C, in fact, these are the best reported values to date.¹ We have been successful in the synthesis of 100% sulphonated polyaniline.² We have also designed and fabricated the first Conductimetric Immuno Sensor based on PEDOT.³ We have achieved the successful electrochemical homopolymerization of sulfonated thiophene and pyrrole.⁴ In the case of dendrimers and hyperbranched polymers, we are exploring the potential of carbonyl azide approach for efficient one pot synthesis.^{5,6} In this manuscript we present the above-mentioned results in detail.

RESULTS AND DISCUSSION

Electrochromic Polymers: Electrochromics (ECs) are materials where the color exhibited is a function of applied potential. EC materials, where the color changes from a highly opaque colored state to a highly transmissive bleached state are most desirable as they are potential candidates for applications in display device. In these systems, the change in percentage transmittance ($\Delta\%$ T) between the two states is called the contrast. The higher is the contrast, the better is the utility as a material for display applications. Conjugated polymers based on 3,4-alkylenedioxythiophene have attracted a lot of attention both in academic as well as in industrial labs, as potential candidates for display application because of their high contrast, low oxidation potential, better stability and faster switching speed. We have designed and synthesized various polymers based on 3,4-alkylenedioxythiophene as shown in figure 1. These polymers were studied for their electrochromic properties. The result obtained indicated that, poly (proDOT-Bz₂) gives 89% contrast with the switching time of 200msec. The obtained value is the highest contrast and fastest switching time reported till date.

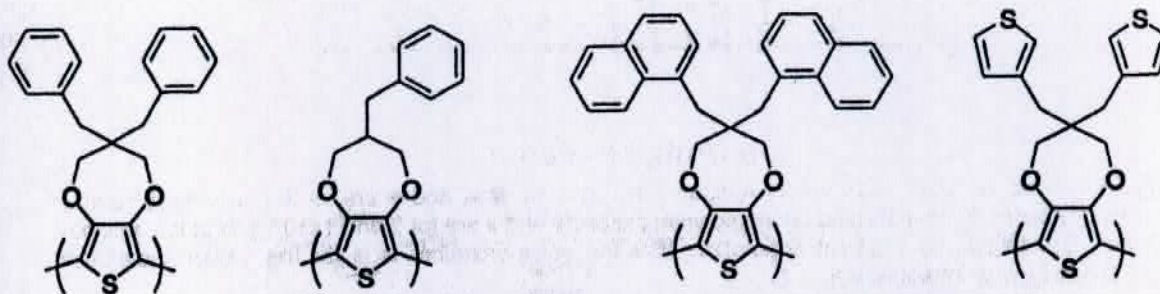


Figure 1: Electrochromic polymers based on 3,4-alkylenedioxythiophenes.

Immunosensors: Immunoassays are based on specific binding reactions that occur between antigen and its complementary antibody. In an immunosensor, either an antibody or an antigen forms the immobilized element and the detection and quantification of the complementary biospecific binding pair is carried out. This can be achieved by measuring turbidity, precipitation reaction or agglutination. Electrochemical

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immunoassays are based on modifications of enzyme immunoassays with the enzyme activities being determined potentiometrically or amperometrically or optically. Till date, there is no report where change in the conformation of conjugated polymer, as a consequence of antibody:antigen binding, has been used for the design of immunosensors. Swager and co workers have suggested that this approach may not succeed because there may not be a significant conformational change in the conjugated polymer upon antigen binding to the surface entrapped antibody. However, in the present work, we have developed a conductimetric reagentless immunosensor using the biospecific binding pair of goat antirabbit IgG and rabbit IgG. Another feature of the present work is the easy fabrication of the immunosensor by physical entrapment of the antibody or the antigen during the polymerization. The concept of the present immunosensor is based on the change in the conformation of the polymer due to the formation of antigen-antibody adduct. This is manifested macroscopically in terms of change in the conductivity of the polymer. The immunosensor devices were fabricated by immobilizing different concentration of goat antirabbit IgG on the polymer matrix. The immobilization was done in two ways; (a) by physical adsorption on to the polymer matrix after polymerization, and (b) by immobilization of the antibody in the polymer.

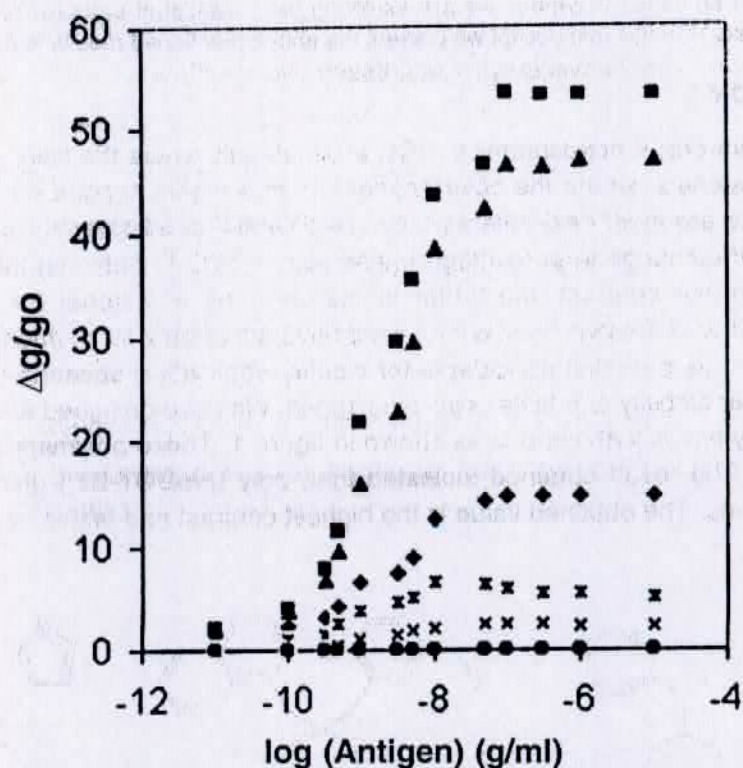
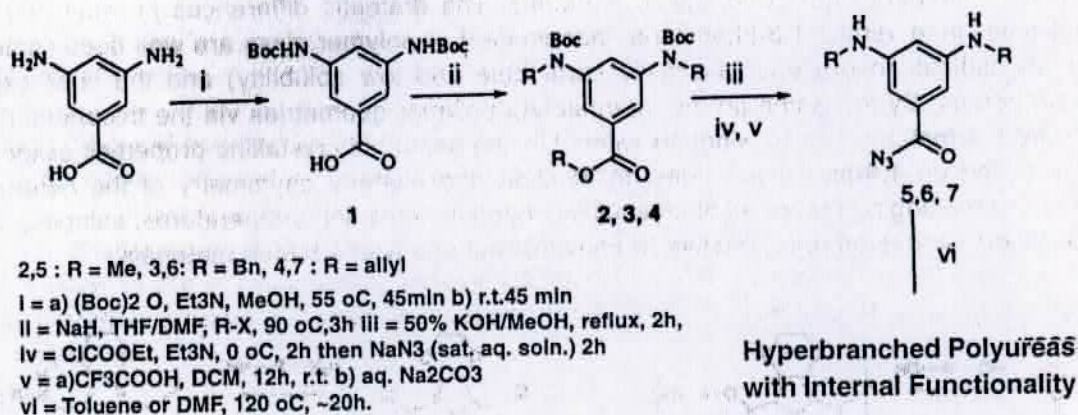


Figure 2: Sensor response as a function of Antigen concentration (■ ▲ and ◆ are for 3, 5, and 1×10^{-5} g/ml of the antibody, respectively, immobilized during polymerization. ★ and × are for 3 and 1×10^{-5} g/ml of the antibody, respectively, immobilized by physical adsorption after the polymerization. ● is for the control experiment where no antibody was immobilized).

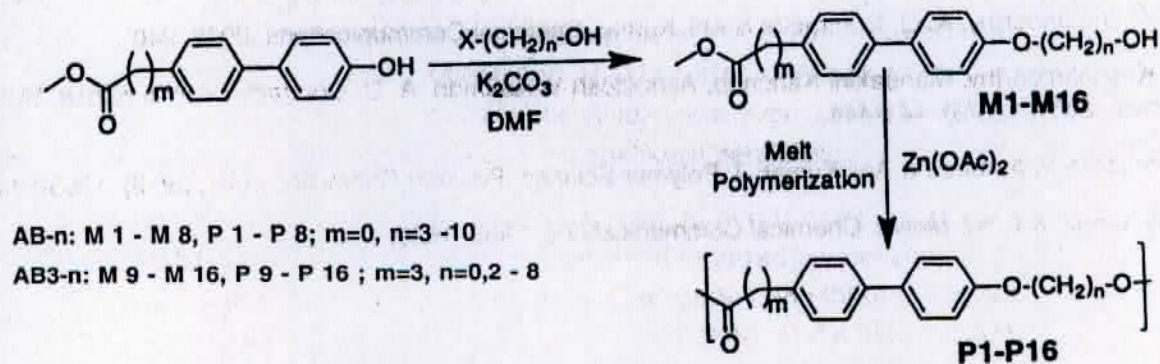
Internally Functionalized Hyperbranched Polyureas: The characteristic features of a dendritic molecule are core, surface and internal cavities formed by the highly branched structure. A growing interest in the field of dendritic molecules is to have specific latent or reactive sites either on the surface or in the interior for further manipulation. Such a specific site, especially in the interior, is a very useful tool to perform selective chemistry inside the dendrimer. Recently, we have reported on synthesis of unsubstituted hyperbranched polyurea from 3,5 diamino benzoyl azide[5]. If amine group in this monomer is alkylated and if alkyl group is a masked functional group like allyl or nitro group then polymerization will lead to internally functionalized hyperbranched polymers. The internal functional groups can then be modified to make a variety of dendritic structures suitable for various

applications. Based on these facts, N-substituted hyperbranched polyurea with methyl, benzyl and allyl substituents have been synthesized using *in situ* generation of isocyanate by decomposition of carbonyl azide. These polymers were characterized by ^1H NMR, IR and SEC techniques. The degree of branching was calculated from ^1H NMR spectra and was found to be 0.5. The N-alkylated benzoyl azides required for synthesis of hyperbranched polyurea were synthesized starting from 3,5-diaminobenzoic acid as shown in Scheme 1.



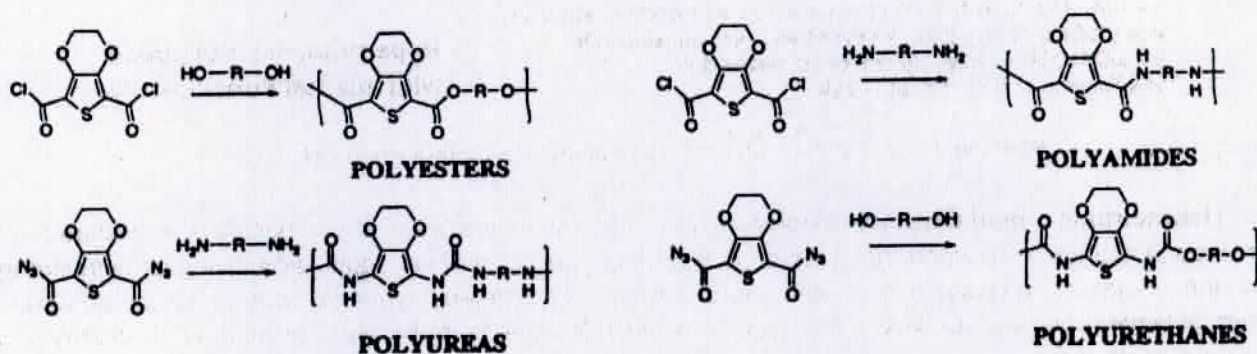
Scheme 1: Synthesis of internally functionalized hyperbranched polyureas

Thermotropic Liquid Crystalline Polyesters: Main chain thermotropic liquid crystalline polyesters belong to an important class of polymers because of their widespread commercial applications such as high-strength fibers, thermoplastics, displays and optical storage devices. The general synthetic strategy for the preparation of such polymers involves an A-A + B-B type of polycondensation. In the case of main chain thermotropic polyesters containing biphenyl mesogens in the backbone, it has been observed that the thermal transitions were sensitive to if the biphenyl unit is a part of diol (**PB-n**) or diacid (**BB-n**). An AB-type self condensation route, apart from possessing an advantage of built-in stoichiometric control for attaining high molecular weight, also permits the generation of novel types of main chain thermotropic liquid crystalline polymers with better control over molecular structural features, such as configurational isomers, well-defined placement of lateral substituents, and the introduction of controlled degree of branching. The synthesis and characterization of two series of polyesters containing spacers were carried out using the novel AB-type self-polycondensation approach and the structure-property relationships in these polymers were studied (Scheme 2). The thermal analysis of these polymers was done by using DSC. These polymers exhibited the odd-even effect in melting and isotropization temperatures. The transition temperatures of the AB-type polymers were found intermediate between the two isomeric A₂+B₂ route polymers reported in the literature indicating the importance of the direction of the linking group.



Scheme 2: Synthesis of AB-n and AB3-n Polyesters

New Processible Thermoplastics: We have designed a synthetic scheme which allows the synthesis of novel and new materials which are useful in various applications like LED's and new processible thermoplastics and fibers containing heterocycles (Scheme 3). The anticipated property enhancements stem from the unique molecular geometry of the aromatic 2,5-thiophene moiety: its nonlinear structure with an exocyclic bond angle of 148° is intermediate between that of 1,4-phenylene (180°) and 1,3-phenylene (120°) commonly used to prepare high performance materials. The dramatic differences between the polymers based on 1,4-phenylene versus 1,3-phenylene, independent of polymer class are well documented. Often, the formers are difficult to process (thermally intractable and low solubility) and the later exhibit poor mechanical properties. By focussing on the intermediate polymer geometries via the thiophene moiety, we anticipate larger thermal processing windows without losing desirable crystalline properties associated with the materials based on 1,4-phenylene units. In addition, the bilateral asymmetry of the heterocycle will certainly influence melting points, rates of crystallization, glass transition temperatures, solubility, miscibility with other polymers, adhesion, etc., relative to conventional phenylene based materials.



Scheme 3: Synthesis of New Processible Thermoplastics.

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REFERENCES

1. K. Krishnamoorthy, Ashootosh V. Ambade, Mandakini Kanungo, A. Q. Contractor & Anil Kumar, *J. Mater. Chem.*, 2001, 11(12) 2909-12.
2. Mandakini Kanungo, Divesh. N. Srivastava, Anil Kumar, A. Q. Contractor, *Chemical Communications*, 2002, 680.
3. K. Krishnamoorthy, A. Q. Contractor & Anil Kumar, *Chemical Communications*, 2002, 240.
4. K. Krishnamoorthy, Mandakini Kanungo, Ashootosh V. Ambade, A. Q. Contractor & Anil Kumar, *Synthetic Metals*, 2001, 125(3), 441-444.
5. Ashootosh V. Ambade & Anil Kumar, *J. Polymer Science, Polymer Chemistry*, 2001, 39 (9), 1295-1304.
6. Anil Kumar, & E. W. Meijer, *Chemical Communications*, 1998, 1629.