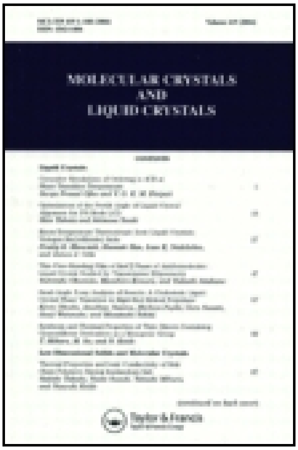

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Control of Optical Properties using Various Nanostructured Materials: Dendrimers, Phase-Separating Block Copolymers, and Polymer Microspheres

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Control of Optical Properties using Various Nanostructured Materials: Dendrimers, Phase-Separating Block Copolymers, and Polymer Microspheres

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Control of the spatial arrangement of atoms over nanoscale dimensions can be used to achieve electronic isolation of chromophores, to control electronic delocalization, to control the spatial variation of material indices of refraction, and to achieve spatially controlled energy transfer. Such control can, in turn, be exploited to avoid quenching of luminescence, to control optical absorption and emission characteristics, to achieve morphological resonances and photonic bandgap phenomena, and to achieve light harvesting and transfer to an active center. Examples of control of optical properties using nanostructured dendimers, block copolymers, and polymer microspheres are given.

Keywords: Nanostructured Materials; Optical Properties; Dendrimers; Block Copolymers; Polymer Microspheres; Electro-Optic Dendrimers

INTRODUCTION

While nano and mesoscale organization lies at the very heart of the function of biological systems, chemists have, until recently, focused largely upon molecular (sub-nanometer scale) organization. The assembly of biological structures makes extensive use of hydrogen-bonding intermolecular interactions and molecular partitioning between hydrophobic and hydrophilic phases. Although the structures arising for phase-separating block copolymer materials, those synthesized using micellar templates, and the spherical structures of polymeric microspheres exploit phase incompatibility [1], chemists have largely achieved nanoscale organization via chemical coupling to form directional bonds, i.e., simple application of standard molecular synthesis concepts on a larger scale. An important exception to this statement is the use of ionic interactions to form multilayer materials by Langmuir-Blodgett deposition. Despite these notable exceptions, it is clear that chemists have only begun to exploit the potential for systematic preparation of materials with nanoscale organization.

Nanostructured materials have most frequently been prepared for application as catalysts, size- and shape-selective sieves and absorbents, sensors, biomimetics, thermal insulators, and templates for synthesis [1,2]. More recently, interest has developed in utilizing such materials for high-density electronic memories and other electronic applications [3].

Nanostructured materials afford the possibility of preparing new materials with unique optical properties. Such properties derive from one or more of the four following features of nanostructured materials: (1) Electronic confinement, (2) electronic isolation, (3) directed energy transfer, and (4) optical (electromagnetic wave) confinement. Quantum well (dot) semiconductor materials provide an example of the influence of electronic confinement upon optical properties. The optical absorption and emission characteristics of a material can be controlled by spatially controlling electron delocalization. The simple particle-in-a-box model of quantum mechanics illustrates some features of such confinement. Obviously, the spacing of the energy levels depend on the dimensions of the box; thus, the absorption and emission spectra are correspondingly influenced.

The utility of electronic isolation is well illustrated by the dependence of luminescence quenching on the nanostructural organization of emitting chromophores. Consider the role of nanostructural control in the development of improved fiber optical amplifiers based on trivalent rare earth ion luminescence. When rare earth ions are doped into silica to form fiber optical amplifiers, self- and ligand-quenching of the rare earth luminescence results in substantial attenuation of the rare earth ion luminescence. Indeed, about 20 meters of rare earth doped silica fiber must be optical pumped to achieve acceptable amplification of an optical communication signal. Such quenching can be avoided by spatially separating rare ions by incorporating them into organized nanoscale structures and by exploiting coordination saturation of the rare earth ions. The former effectively eliminates self-quenching of luminescence while the latter eliminates ligand quenching. As part of the research program of the Department of Defense Multidisciplinary University Research Initiative Center on Nanostructured Materials, Professors Frechet [4] and Harper [5] have incorporated rare earth ions into the cores of dendrimers. The size of the dendrimer was systematically varied by synthesis of successive dendrimer generations. The size necessary to eliminate self-quenching of luminescence was readily identified.

Frechet and Harper have also independently demonstrated that dendrimer structures can be exploited to achieve effective light harvesting and directed energy transfer. The critical design principle is to chose the chromophore structure of an outer shell (higher generation dendron) so that the emission from that structure overlaps the absorption of the chromophore contained in the adjacent lower generation dendron shell. Thus, energy is efficiently transferred from the outer regions of the dendrimer to the core. Ideally, the outer most shell absorbs in the UV while successively more interior shells absorb in the visible, and near infrared regions of the spectrum. The core might for example emit in the infrared. The close proximity of chromophores in various shells of a dendrimer structure insures effective energy transfer by either dipolar or exchange interactions.

Dendrimer structures have also been used to fabricate more efficient organic light emitting materials [6].

Dendrimer structures cannot be made large enough to support morphological resonances. However, polymer microspheres grown to precisely controlled mesoscale sizes (a few hundreds nanometers to many microns) and when chromophores are covalently coupled to the surface of such polymer microspheres morphological resonances can be observed. Such morphological resonances can exist either as whispering gallery modes or as waveguided modes depending on the thickness of the chromophore layer. Dalton and coworkers [7] have shown that such morphological resonances can be exploited to achieve room temperature spectral hole burning of approximately 1-2 nanometer holes in the resonance spectrum of the chromophore. Thus, the spectral dimension, as well as the spatial dimension, can be exploited in the development of high density optical (write once and read many times or write-read-erase) memories. Polymer microspheres have also been recently employed as templates for the synthesis of photonic bandgap materials. Xie has shown that microspheres can be processed into highly regular three-dimensional close packed lattices [8]. Such lattices can be used as a template for synthesis of a lattice characterized by a high index of refraction materials filling the spaces between the close packed spheres. The original polymer microspheres can, in some cases, be dissolved by reagents such as hydrofluoric acid leaving the high index reciprocal lattice. This latter lattice may exhibit photonic bandgap behavior if a clean etch is achieved and the index of refraction of the reciprocal lattice material is sufficiently high.

Phase-separating block copolymer can exhibit a range of interesting nanoscale structures [9]. Such materials may afford potential for the synthesis of electro-optic materials, light emitting diode materials, of semiconductor quantum dots with improved dimensional control, waveguiding materials, and photonic bandgap materials. An obvious use of diblock copolymers that phase separate into lamellae is to develop improved light emitting diode materials by incorporating a hole transporting material into one block and an electron transporting material into the other block. The lumophore could be position at the junction of these blocks. Another application would be to develop electro-optic materials by using the force of phase separation to align an interior block (consisting of head-to-tail coupled second order nonlinear optical chromophores) of a tri- or tetrablock copolymer that separates into lamellae. In this manner, a phase separated block copolymer is similar to a Langmuir-Blodgett fabricated thin film in that surface forces can be exploited to achieve acentric alignment of chromophores.

ELECTRO-OPTIC DENDRIMERS

We report here the use of dendrimer structures to prepare electro-optic materials with improved electro-optic coefficients. The central idea behind the development of electro-optic dendrimers is to minimize unwanted intermolecular electrostatic interactions that oppose the realization of finite acentric (or noncentrosymmetric) order that is necessary for non-zero macroscopic electro-optic activity [10]. Intermolecular electrostatic interactions are very spatially anisotropic for molecules exhibiting large dipole moments. These interactions particularly favor centric ordering for molecules of prolate ellipsoidal shape (The most common shape of second order nonlinear optical chromophores). Side by side approach of chromophores along their minor ellipsoidal axes strongly favors centric ordering of the chromophores. The closer the molecules can approach each other the more serious the problem with unwanted intermolecular interactions increasing with an R^6 dependence (where R is the separation of chromophores). Such intermolecular electrostatic interactions account for the fact that it is extremely difficult to grow crystals of second order nonlinear optical chromophores with acentric space groups. Practical organic electro-optic materials are typically prepared by electric field poling of second order nonlinear optical chromophores in a polymeric matrix (near the glass transition temperature). The poling-induced order is subsequently locked-in by induction of crosslinking reactions that coupled the chromophores to a three-dimensional crosslinked polymer matrix. The electro-optic activity that is observed results is the result of the competition of three forces: (1) The chromophore dipole-applied field force that attempts to induced acentric order, (2) chromophore-chromophore intermolecular electrostatic forces that typically attempt to induce centric order, and (3) thermal collisions that randomize chromophore order. One would anticipate from the competition of these three forces that a maximum would be observed in the plot of electro-optic activity versus chromophore loading (chromophore-chromophore intermolecular separation) in the polymer matrix. The position of the maximum and (hence the maximum obtainable electro-optic activity) should vary with chromophore shape. That this is indeed the case is illustrated in Figure 1. The data shown in Figure 1 are for a chromophore that we refer to as FTC (the structure of this chromophore is shown in Figure 2). Only the π-electron portion of the chromophore contributes significantly to optical nonlinearity. When this chromophore is not incorporated into a dendrimer structure that significantly modifies its shape, the chromophore is essentially a prolate ellipsoid. Theory [10] correctly predicts that close approach along the minor axes of the chromophores dramatically attenuates electro-optic activity at high chromophore concentrations. Theory also predicts that improved electro-optic activity can be achieved by modifying chromophore structure to inhibit close approach along the minor axes of the chromophores. The most practical approach for chromophores such as FTC is to attempt to make the chromophores as spherical as possible. A dendritic synthetic scheme affords a systematic approach to this

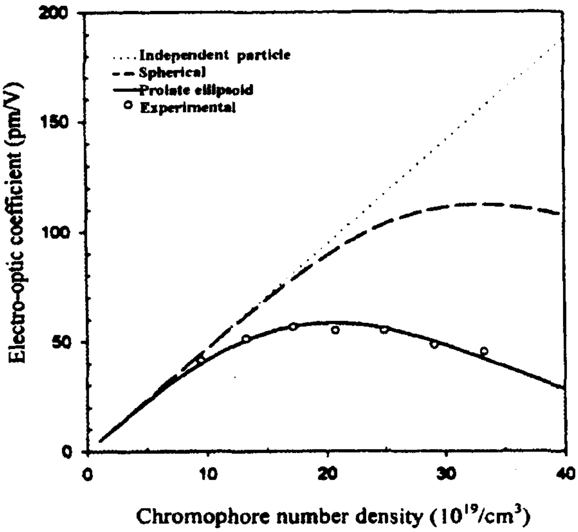

Figure 1. Experimental (circles) and theoretically predicted (lines) variation of electro-optic coefficient with loading of FTC (see Figure 2) is shown as a function of chromophore loading in a polymer matrix. Theory predicts a dependence on chromophore shape. Independent particle refers to no intermolecular electrostatic interactions.

goal. Practically, one might anticipate an approximate doubling in the maximum realizable optical nonlinearity if optimum shape can be achieved. In preliminary studies, we observe an increase in maximum achievable electro-optic activity that is approximately consistent with theoretical predictions.

An electro-optic dendrimer material offers other advantages. Most notably positioning a π-electron chromophore at the core of a dendrimer structure can lead to improved chemical and photochemical stability. Such stability is critically important for the utilization of electro-optic materials to fabricate devices such as electrical-to-optical signal transducers, optical switches, electromagnetic sensors, phase-shifters, etc. Materials must survive temperature excursions encountered in device fabrication and operation. They must also survive in the presence of constant optical power of 10-300 mW.

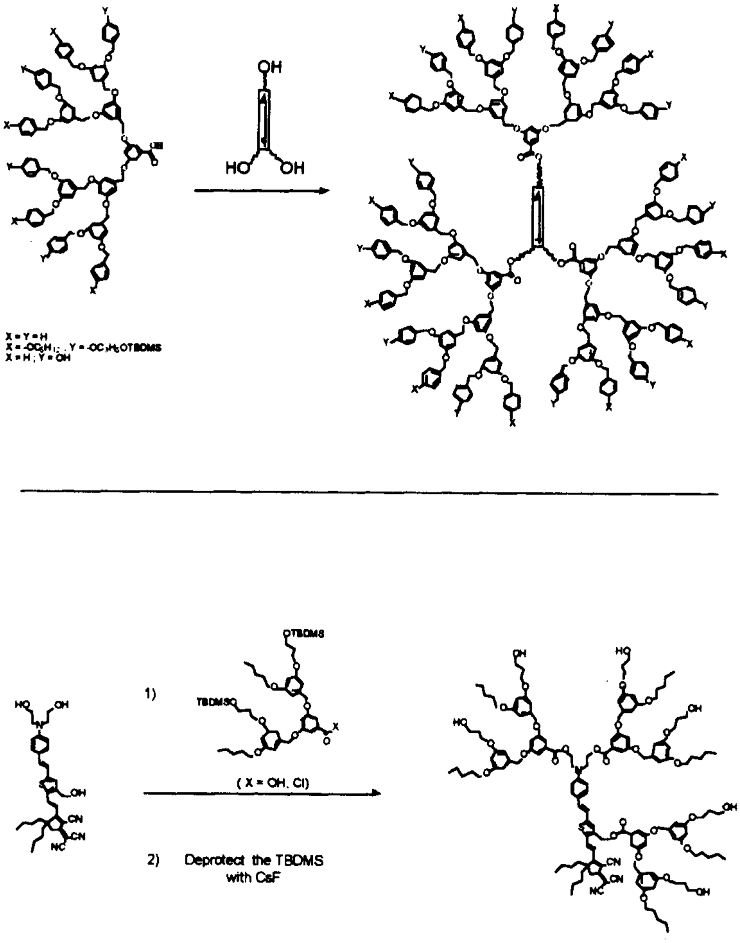

Figure 2. The general structure of an electro-optic dendrimer is shown above (top) while the specific structure of the FTC-dendrimer is shown below (bottom). The size of the electro-optic dendrimer can be systematically increased one generation at a time.

An electro-optic dendrimer structure is also suited for lattice hardening to lock-in poling-induced acentric order. For the structure shown in

Figure 2, lattice hardening is accomplished by a thermosetting reaction involving the peripheral hydroxyl groups.

ELECTRO-OPTIC TETRABLOCK COPOLYMERS

We have prepared tetrablock copolymers of the form: ABCD (i.e., poly-(4-vinylpyridine)-b-PNLO-b-polystyrene-b-poly-(4-vinylphenol) abbreviated as P4VP-b-PNLO-b-PS-b-PVPh). PNLO stands for a polymer of nonlinear optical chromophores (4,4'-aminosulfone-azobenzenes) assembled in a head-to-tail manner (see Figure 3).

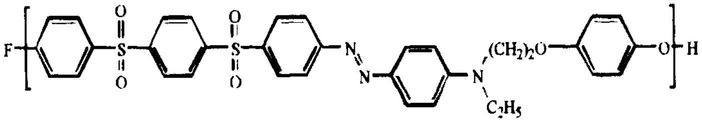

Figure 3. The structure of the monomer used to form the PNLO block is shown. Note that this is a dipolar second order nonlinear optical chromophore. Assembly of these chromophores into an acentric lattice will give rise to macroscopic electro-optic activity.

The concept is to use the phase-incompatibility of the blocks together with highly preferential hydrogen bonding involving the A and D blocks to achieve acentric assembly of the form ABCDABCD.... This will result in macroscopic electro-optic activity if the A block exhibits strong binding to a substrate surface and the copolymer blocks phase separate into lamellae of the form |A|B|C|DA|B|C|DA|.... We believe that this presents one of the few attempts (if not the first attempt) to achieve a quasi-crystalline lattice of acentrically order second order NLO chromophores by systematic design exploiting enthalpic considerations (and most particularly the stabilization of structures by hydrogen bonding).

The synthesis was carried out by reaction of a P4VP-b-PNLO-Ph-NH_2 block copolymer containing an aniline end group with a poly-4-(tert-butyldimethylsiloxy)styrene-b-PS-CO_2H (PBDMSS-b-PS-COOH) diblock copolymer containing a t-butyldimethylsilyl-protected polyvinylphenol endowed with a carboxylic end group in the presence of diphenylphosphoryl azide (DPPA) in N,N-dimethylacetamide. After the formation of the P4VP-b-PNLO-PhNH-CO-PS-b-PBBDMSS tetrablock copolymer the PVPh block was obtained by deprotection of t-butyldimethylsilyl group of the PBDMSS block with tetrabutylammonium fluoride in THF. The PBDMSS-b-PS-COOH precursor was synthesized by initiation of 4-(t-butyldimethylsiloxy)styrene by t-butyllithium in THF at -78°C followed by the addition of styrene and end-functionalized with carbon dioxide. The end-functionalized P4VP-b-PNLO-Ph-NH_2 block copolymer was synthesized by step polymerization of 4-(4-(4-fluorophenylsulfonyl)-phenyl)sulfonyl-4'-N-ethyl-N-2-(4-hydroxyphenol)-ethyl-azobenzene and coupling of the resulting polymer to P4VP end-functionalized with a phenolic end group.

The structures of the individual polymer blocks and the subsequent copolymers (including the final tetrablock copolymer) have been confirmed by NMR, FT-IR, and Size Exclusion Chromatography. Although we had not completed characterization of the tetrablock copolymer morphologies by electron microscopy and by second order nonlinear optical measurements, some evidence for selective interaction of the chromophore blocks has been obtained by binding studies. The interactions of the P4VP-b-PNLO diblock with the polystyrene-b-polyvinyl-phenol (PS-b-PVPh) diblock and with polymethyl-methacrylate-b-poly-(2-hydroxyethyl methacrylate) (PMMA-b-PHEMA) diblock copolymers have been studied. This process was studied by measurement of the increased solubility of the P4VP-b-PNLO copolymer in toluene/CH_2Cl_2 (99/1,V/V) or in ethylacetate due to the formation of the more soluble complexes with the PS-b-PVPH and the PMMA-b-PHEMA block copolymers. The increases in solubility were monitored through increases in visible absorption at 452 nm., the absorption maximum of the PNLO segment. The apparent binding constants of the PS-b-PVPh and the PMMA-b-PHEMA block copolymers in toluene/CH2Cl2 (99/1,V/V) and in ethylacetate were on the order of 10^5 and 10^3 M^{-1} respectively.

CONCLUSIONS

It is clear that nanostructured materials can give rise to new and novel optical propreties. Structures that show particular promise included dendrimers, phase-separating block copolymers, and polymer microspheres. Clearly, these structures are only beginning to be explored and interesting new properties should arise with increasing sophistication in the preparation of these materials.

A word of caution is appropriate concerning anticipating the technological impact of nanostructured optical materials. Take the example of improved optical amplification materials developed from rare earth core dendrimers. Such materials dramatically improve luminescence efficiency by suppressing self- and ligand quenching of the rare earth ion luminescence. However, fiber optical communication is based on high temperature processed silica and organic materials will simply not survive the processing temperatures. Rare earth core dendrimers would have to be used with sol-gel processed glass or with polymer fibers. Such implementation cannot be anticipated on the based on scientific considerations.

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