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ULTRASTRUCTURE SYNTHESIS AND NONLINEAR SPECTROSCOPY OF PHOTONIC MATERIALS

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Abstract A brief progress report is provided on (1) the fabrication and integration with high speed VLSI circuitry of high frequency organic electro-optic modulators and (2) preparation of polymer microspheres, containing one or more layers of covalently coupled chromophores, capable of supporting morphological resonances.

INTRODUCTION

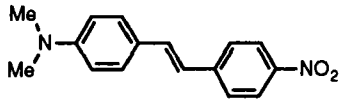
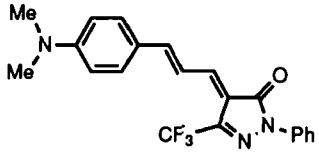
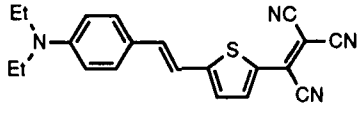
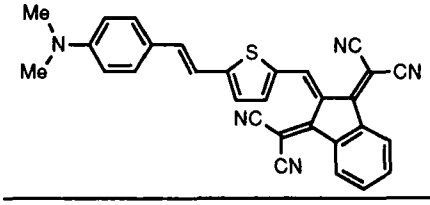
The fabrication and systems integration of high frequency electro-optic modulators based on the incorporation of chromophores with large first hyperpolarizability into polymer matrices requires that many conflicting requirements be simultaneously satisfied.[1-10] The following tasks must be accomplished with the end result of devices characterized by low drive voltage requirements, broad bandwidth, low optical loss, and long device lifetime: (1) design[1,2,9,11] and synthesis of chromophores of adequate molecular first hyperpolarizability (β) which also exhibit good thermal and chemical stability; (2) incorporation of these chromophores in reasonable number density into polymer materials which can be cast into optical quality thin films, poled to induce noncentrosymmetric order, and hardened to lock-in the poling-induced order;[1,2,8,9] (3) processing of nonlinear optical polymeric thin films into low loss buried channel waveguides;[8,9] (4) integration of polymeric waveguides with high speed drive electronics including the deposition of metal electrodes of appropriate design;[8-10] and (5) coupling to silica fiber optic transmission lines.[5,8,9] In a collaborative research effort with Alex Jen of ROITech and Seth Marder of CalTech, we have synthesized a number of chromophores characterized by $\mu\beta$ values of greater than 10^{-45} esu.[9,11,12] These chromophores are (donor)-(π-electron connective segment)-(acceptor) type dipolar molecules where donor groups include alkyl and aryl amines and ketene dithioacetals; connective segments typically are polyene, azo, or heteroaromatic moieties; and acceptor groups include thiobarbituric acids, isoxazolones, pyrazolones, sulfoximines, cyanovinyls, bis(dicyanomethylene) indanes, and cyanosulfone (Sandoz-type) functionalities. These chromophores are functionalized at both donor and acceptor ends to permit covalent coupling of both ends to the polymer lattice. Three approaches have been followed for the realization of materials which can be

efficiently poled and processed into hardened polymer lattices.[9] These include use of asymmetrically functionalized chromophores (which we refer to as DEC chromophores) that are prepared as soluble and processable precursor polymers which can, after poling, be hardened by thermally-induced crosslinking reactions; thermosetting materials where poling and hardening steps are not cleanly separated; and polyamic acid/polyimide-like materials where lattice hardening is effected exploiting intramolecular condensation reactions. High $\mu\beta$ chromophores present several challenges including the fact that high dipole moments can result in centrosymmetric crystallization at high chromophore loading (e.g., greater than 20%) and the strong electron withdrawing groups of these chromophores can influence chemical reactivity including thermosetting reaction rates. Following poling and lattice hardening, materials are processed by reactive ion etching or mutli-color photolithography techniques[8,9] into buried channel waveguides. Reactive ion etching techniques are also used to etch v-grooves in silicon substrates to effect coupling of buried channel polymer waveguides to silica optical fibers.[8,9] Using simple birefringent modulator electrode designs, prototype electro-optic modulators have been fabricated and evaluated over the frequency range from DC to 60 GHz.[14] Using a variety of stripline electrode designs modulator performance evaluation is being extended to 94 GHz. By depositing a planarizing polymer layer on top of a VLSI wafer, vertical integration of electronic and electro-optic modulator circuitry has been accomplished without the degradation in performance of either circuit.

Arnold and coworkers[15] have demonstrated that irreversible room temperature spectral hole burning could be achieved by exploiting morphological resonances in chromophores physically absorbed on the surface of polymer microspheres. We have extended that observation by covalently coupling photo-reversible chromphores to the surface of polymer microspheres where the size of the polymer microsphere is systematically varied to investigate the excitation of various order morphological resonances.

RESULTS AND DISCUSSION

Of the choromphores which we have investigated, those most resistant to electric field-catalyzed decomposition and photo-induced decomposition were the trifluoromethylpyrazolones and the bis(dicyanomethylene) indanes (see the following table).

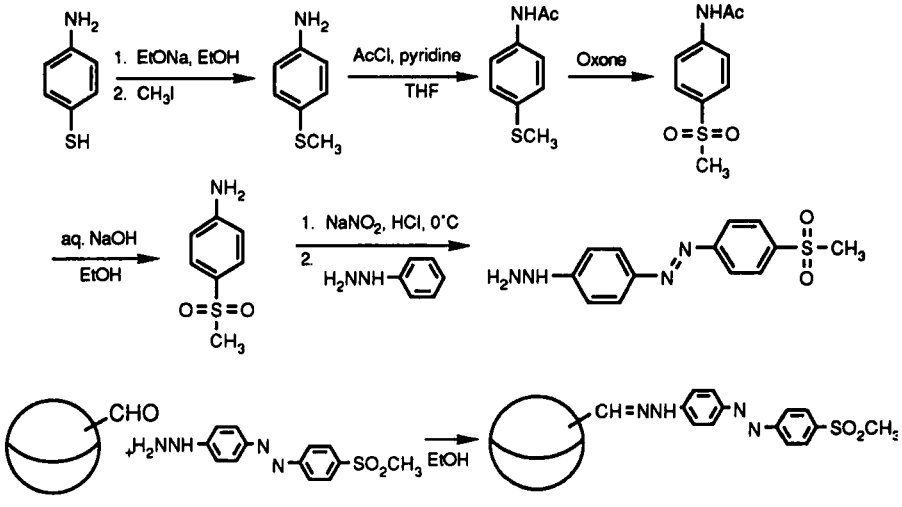
NLO Chromophore	$\mu\beta$ (x10^{-48} esu) at 1.907 μm	Reference
	482	a
	1380	b
	6200	c
	6144	b

a Marder, S.R., et al., *Science* **263**, 511(1994)
b Unpublished results
c Wong, K.Y., et al., *J. Appl. Phys.* **75**, 3308(1994)

These chromophores yield poled nonlinear optical materials exhibiting an improvement in electro-optic coefficient of 2-3 over conventional azobenzene and DANS type chromophores. As observed for all of the high dipole moment chromophores, realization of large electro-optic coefficients depends upon avoiding crystallization at high chromophore number density. Stable tricyanovinyl materials are obtained only by covalent coupling of the tricyanovinyl group to the polymer backbone at the last step of synthesis. We are now in the process of carrying out waveguide fabrication using these chromophore-containing polymers and final assessment of their utililty as nonlinear optical materials depends upon factors such as optical loss which has not been assessed at this time.

We have carried out functionalization of polymer bead surfaces both by modifying the monomer feed to incorporate monomers containing active functional groups and by derivatization of preformed beads using chemical reagents developed by Olah and coworkers.[16] The labeling of polystyrene microspheres with a fluorescent azobenzene dye is shown below. Utilizing this material, we have demonstrated multiple room temperature spectral hole burning (9 holes per 20 nm with hole widths on the order of 0.7 nm);

photoreversible spectral hole burning; and hole burning effected for mean bead diameters ranging from 500 nm to 24 microns.



Using chromophores functionalized at both ends, polymer microspheres coated with multiple chromophores layers have been fabricated and the dependence of the characteristics of morphological resonances upon the thickness and refractive index characteristics of chromophore coatings have been evaluated. Expected variation, based upon MIE scattering theory[17,18], in morphological resonance characteristics have been observed.

Current research efforts focus upon exploration of the attachment of a variety of chromophores to polymer microsphere surfaces. Included in this group are 1,2-diarylethenes.

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