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Photo-fabrication of Electroactive Polymers for Photonics.

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Abstract:

Novel azo chromophore containing polymers have been synthesized both chemically and enzymatically. Surface initiated mechanism for relief structure form ation on the azo polymer films have been studied for a high molecular weight azo functionalized poly(acrylic acid) by restricting the free surface in a controlled manner. Enzyme catalyzed poly(phenol) and polyaniline containing azo functional groups have also been synthesized and for the first time the feasibility of these biologically derived electroactive polymers for surface relief grating applications are undertaken.

Keywords: Spin casting, Self-assembly using surface chemistry, Amorphous thin films, Polyaniline and derivatives, Other conjugated and conducting polymers.

1. Introduction:

Development of new polymeric materials for practical applications requires novel synthetic approaches to prepare and to optimize specifically designed polymers for desired properties. Azobenzene functionalized polymers have received extensive interest over recent years as potential materials for reversible optical storage media [1], formation of holographic grating [2], optical switching [3] and electro-optic modulation [4] applications. Reversible photoisomerization of azo containing organic molecular systems have been extensively investigated for linear and nonlinear optical properties in the context of photonics technologies.

A large number of azobenzene containing polymers have been chemically synthesized and studied, with the main focus on polymers containing azo groups in the side chain [5]. A versatile post-azo coupling reaction has been used to synthesize a series of novel epoxy [6] and acrylate [7] based azo containing NLO polymers by our group. Enzyme catalyzed polymerization is a new methodology which is only recently been utilized to prepare structurally diverse electroactive polymers. As an extension of our earlier work [8], we have synthesized novel photodynamic polymers such as polyaniline and polyphenol containing azo chromophore by enzyme catalyzed polymerization. The effect of photoexcitation of the *trans* ⇒ *cis* ⇒ *trans* isomerization of the chromophores and the photofabrication of surface relief structures using these different azo functionalised electroactive polymer materials will be presented. This is the first example of direct physical manipulation, transport and patterning of conducting polymers employing light beams.

2. Azo functionalized poly(acrylic acid):

Azobenzene chromophore functionalized poly(acrylic acid) (PAA) copolymers were synthesized through modification of the high molecular weight (250,000 g/mol) poly(acrylic acid). Commercially available PAA was partially esterified (50%) with N-ethylanilinoethanol to yield the anilino functional copolymer. The para position of the aniline moiety can be readily functionalized through a post-azo coupling reaction [6]. Upon reaction with the diazonium salt of 4-aminobenzoic acid this polymer resulted in HPAA-CA and reaction with the diazonium salt of 4-nitroaniline yielded HPAA-NO_2. The average molecular weight increased to about 500,000 upon esterification, followed by a further increase after azo functionalization. The HPAA-CA and HPAA-NO_2 are both highly soluble in polar organic solvents such as DMF and DMSO and have T_g's of 85 and 91 °C respectively. Optical quality films of both polymers were obtained by spin coating solutions of 100 mg of polymer in 1 mL of DMF onto processed glass slides then vacuum drying. The refractive index and thickness of these films are measured using a prism coupler (Metricon 2010). The average thickness of the spin-coated films is 0.6 μm.

Surface relief grating (SRG) on the azo-functionalized polymer films can be formed using a simple, two-beam interferometer setup. The experimental arrangement is discussed and demonstrated in detail in an earlier publication [9]. The grating formation behavior for these very high molecular weight poly(acrylic acid) based azo polymer films, monitored through the diffracted beam intensity, is found to be similar, though somewhat less efficient than that observed previously [2,9] for low molecular weight azo-polymer films. Entanglements believed to be present in high molecular weight polymers such as HPAA-CA and HPAA-NO_2 is a possible reason for the less efficient SRG formation. The modulation depth of the SRG formed on the free surface of the sample, measured using an atomic force microscope (AFM, cp, Park Scientific, Sunnyvale, CA) is shown in Figure 1.

Recently, we reported the significance of having a free, unrestricted surface to establish the surface-initiated mechanism and to form efficient SRG's on azo-polymer film [7]. The dipolar interaction of the azo chromophore with the optically induced electric field gradient leads to macroscopic movement of the polymer and hence grating formation [10]. A novel technique of forming ultra-thin polymer layers using an

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alternate layer-by-layer electrostatic deposition of oppositely charged polyelectrolytes [11] has been used by our group to

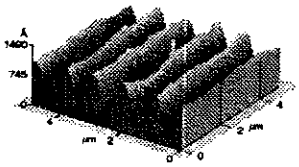

Figure 1: A typical AFM image of the SRG formed in high molecular weight azo polymer, HPAA-CA.

precisely control the free surface. These azo-polymers which contain free acid groups, under proper pH conditions behave like polyelectrolytes. Therefore, alternate polyion layering with the polycation poly-(allylamine hydrochloride) (PAH) with poly(acrylic acid) PAA (each dissolved in 30 mL Milli-Q water at 10 mM concentration, pH = 3.0 ± 0.1) was carried out on top of the spin coated azo polymer substrate. Restricting the surface of the high molecular weight azo-polymer HPAA-NO_2 with 5 bilayers (maximum thickness of 75 Å) of PAH : PAA polyions was found to completely stop the surface-initiated grating formation as shown in Figure 2.

The modulation depth of the SRG written for 30 min on the free surface of the sample, measured using AFM is 220 Å. The grating formed on the free surface is consistent with previous results however, a saturated behavior was observed when the free surface is restricted with five bilayers. This saturated behavior, due to the bulk birefringence grating, is confirmed by an observed decrease of about 60% in the diffracted signal when the writing beam is turned off and shows no surface features under AFM. The photostationary equilibrium of the diffracted beam intensity and the subsequent decrease due to randomizing of the chromophores confirm the bulk orientation grating formed in the material. Study of high molecular weight azo polymers with ultra thin transparent

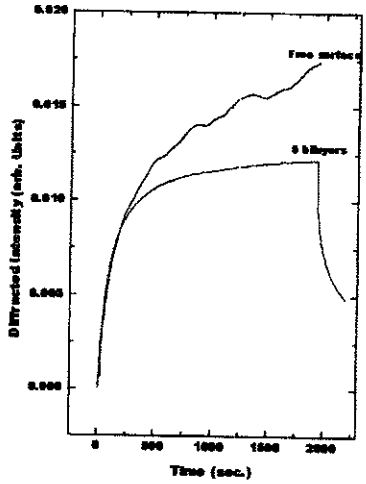

Figure 2: The grating formation on the free surface and on the restricted portion (5 bilayers of PAH : PAA) of the azo polymer film HPAA-NO_2.

polymer overlayer clearly establishes the surface driven mechanism for the surface deformation process. This understanding of the surface fabrication process allows us to explore photopatterning of conjugated polymers like poly(phenol) and polyaniline, containing azo chromophore.

3. Azo-functionalised poly(phenol):

Horseradish peroxidase (EC 1.11.1.7) (200unit/mg) was purchased from Sigma Chemicals Co., St. Louis, Mo., with Rz>2.2. A stock solution of 10 mg/ml in pH 6.0, 0.1M phosphate buffer was prepared. 4-phenylazophenol was obtained from Aldrich Chemical Co. Inc., Milwaukee, WI and used as received. All other chemicals and solvents used were also commercially available, of analytical grade or better and used as received.

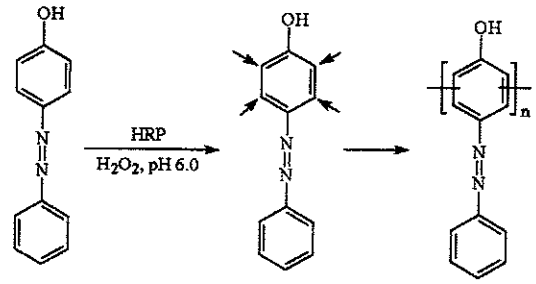

Figure 3: Reaction scheme for the enzymatic polymerization of poly(phenol).

The enzymatic polymerization of azo-phenol was carried out at room temperature in a 100 ml of 50% acetone and 50% 0.1M sodium phosphate buffer mixture, which contained 2 g azo-phenol monomer. To the solution, 1 ml of HRP stock solution was added. The reaction was initiated by the addition of a stoichiometric amount of H_2O_2 under vigorous stirring. To avoid the inhibition of HRP due to excess H_2O_2, diluted H_2O_2 (0.2M) was added incrementally using a peristaltic pump for over 3 hours. After the addition of H_2O_2, the reaction was left stirring for at least 1 hour. The precipitate formed during the reaction was then collected with a Buchner funnel, washed thoroughly with 40% acetone to remove any residual enzyme, phosphate salts and un-reacted monomer and then vacuum dried for 24 hours. 10 wt% of the polymer was then dissolved in dioxane and spin coated onto a glass slide to obtain optical quality films. Figure 3 shows a schematic of this polymerization reaction.

Surface relief deformation characteristic on this azo polymer film was carried out using a single laser beam [12]. The 544 nm He-Ne laser beam with Gaussian intensity profile and linear polarization is focused using a 10X spherical lens. The horizontally polarized, circular Gaussian beam has a radius [illegible] at the focal plane and the peak intensity is 1 W/cm^2. It is seen from the Figure 4 that dramatic surface deformation is produced that is photo and thermo reversible. The transport occurs only along the polarization direction and the lateral size of the induced surface deformation is approximately equal to the diameter of the Gaussian beam.

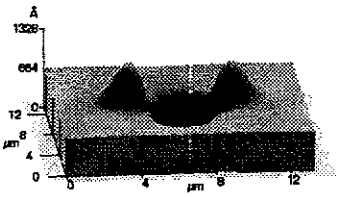

Figure 4: AFM image of the azo poly(phenol) exposed to horizontally polarized single Gaussian laser beam.

4. Enzymatic Polymerization of 4-Phenylazoaniline

The enzymatic polymerization of 4-Phenylazoaniline was carried out in 200 ml of 20% ethanol solution in 0.01M KH_2PO_4 buffer, pH 4.0. Horseradish peroxidase (about 300 units) was dissolved in the reaction medium and the reaction was initiated by addition of 100µl of 50% hydrogen peroxide. After addition of hydrogen peroxide, the reaction was left stirring for an hour. The dark brown precipitate formed is then filtered and washed with 20% ethanol and subsequently with deionized water to remove unreacted monomers and enzyme. The obtained solid was dried and dissolved in chloroform for column chromatography and in DMF for UV-vis absorption studies. The chemical structure of the polymer is shown in Figure 5. Raman spectroscopy of the polymer showed –N=N– stretching indicating preservation of the azo functional during the polymerization process.

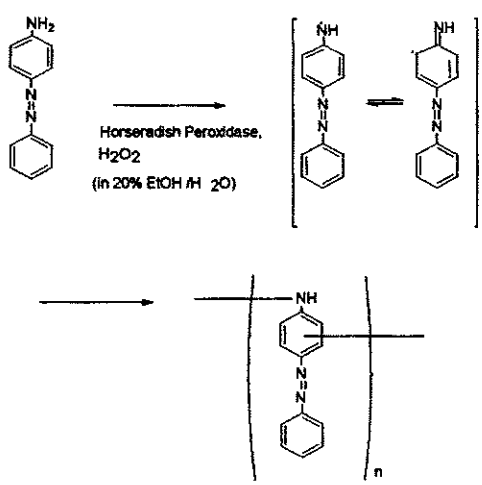

Figure 5: Synthesis of azo functionalized polyaniline.

The polymer dissolved in DMF is sealed in a quartz cuvette and exposed to an expanded argon ion laser at 488 nm for 15 min. The absorption spectra were recorded immediately after removing from the laser source with a scan speed of 960 nm/min to minimize the change in absorption characteristics due to relaxation of the polymer during the scan period. The absorption spectra were subtracted from the spectrum before photoexcitation to obtain the difference absorption spectra (Figure 6). The polymer molecules in the solution showed conformational changes upon exposure to the light as shown in Figure 6. This is due to the *trans⇒cis⇒trans* photoisomerization of the azobenzene chromophore and further confirmed that the azo functional groups were preserved during the photoisomerization process. What is unusual about this polymer is that the azobenzene groups are both in the side chain as well as in the main chain in an articulated strucutre. Before photoexcitation there is an equilibrium population of trans aa well as cis states in possible constrained conformations. Photoexcitation in the trans band has led to a further build up of cis population and depletion of trans states (fig 6a). What is interesting is that upon relaxation, a net increase in the trans states occurs implying that some of the constrained, predominantly cis segments in the original polymer solution have now relaxed to a trans state (fig 6d) [8].

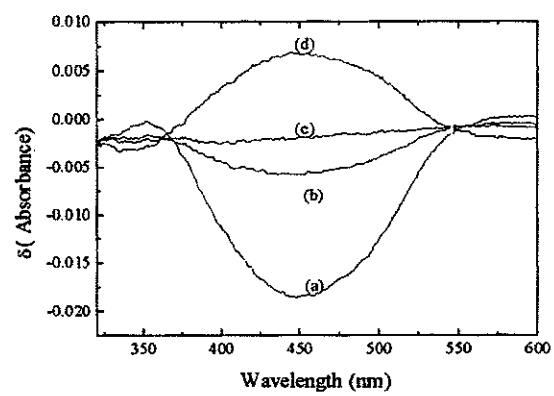

Figure 6: Difference absorption spectra of the polymer in DMF excited with λ=467.5 nm from an Ar^+ laser. (a) immediately after excitation, (b) after 75 min, (c) after 150 min and (d) after 12 hrs.

The DMF polymer solution is then cast into a film on a glass slide and exposed to an interference pattern of an Ar^+ laser beam at 488 nm. An AFM scan of the exposed region showed formation of surface relief grating patterns. In this case, the SRG could be formed with higher writing intensities (> 5W/cm^2 at the peak) than the azo functionalized poly(phenol) described earlier. This is probably due to the articulated chain structure and complex morphology of the polymer film, which showed aggregation upon casting the film.

5 Summary:

Photofabrication of SRG's in high molecular weight azobenzene functionalized polymer was achieved under normal working conditions. The importance of having a free surface for efficient SRG's was demonstrated by restricting the surface of the azo polymer thin film through a layer-by-layer electrostatic deposition of oppositely charged polyions. Study of chain entanglements in high molecular weight azo polymers without

and with restricted surfaces paves way to understand the process of surface relief structures formed in conjugated azo polymers. Azo chromophore containing poly(phenol) and polyaniline were synthesized by enzyme catalyzed polymerization. The photodynamic characteristics of these enzymatically synthesized electroactive conjugated azo polymers are studied by forming single beam or two-beam interference pattern.

Acknowledgements

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