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Wei Liu,[1] Soo-Hyuong Lee,[1] Suizhou Yang,[1] Shaoping Bian,[1] Lian Li, [1] Lynne A. Samuelson,[2,*] Jayant Kumar,[1] and Sukant K. Tripathy[1,†]

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Azophenols with various substituents at the para position of the phenyl ring were enzymatically polymerized in the presence of H_2O_2. Structural characterization of the synthesized polymers by FTIR, FT-Raman, and NMR (^1H and ^{13}C) spectroscopy confirms our previous observation that this enzymatically catalyzed coupling reaction occurs primarily at the ortho positions, with some substitution at the meta position of the phenol ring. The strong constraint and poor packing of the azobenzene chromophores in the polymer leads to a significant blue shift of the π-π^* transition absorption and slow photoisomerization and thermal relaxation in comparison to the monomers. Surface relief gratings (SRG) with large surface modulation have been fabricated on these enzymatically synthesized polymer films.

Key Words: Peroxidase; Azopolymer; Enzymatic polymerization; Surface relief gratings

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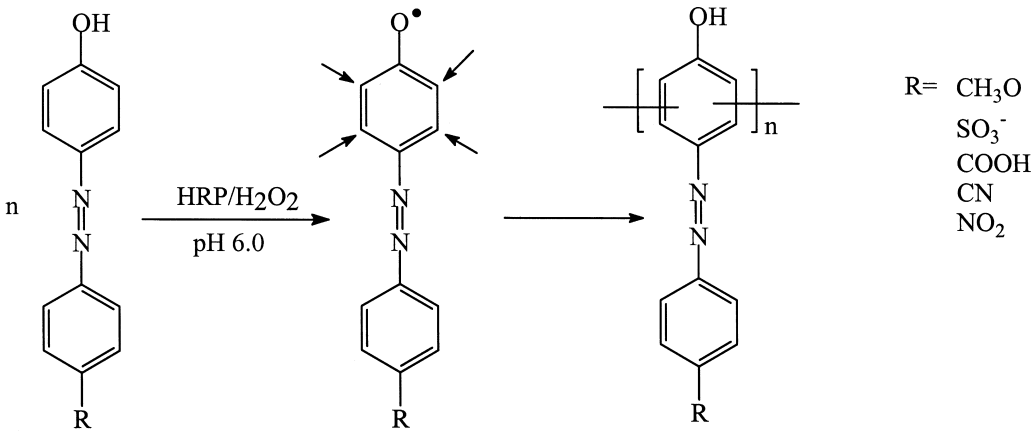
INTRODUCTION

To date, most azobenzene-containing polymers have been chemically synthesized [1] through post-azo-coupling reactions to introduce azobenzene chromophores as a pendant side chain of the polymer [2]. Recently, an alternative class of azobenzene "macrodye" polymers was developed by our research group through peroxidase-catalyzed polymerization of azo chromophore functionalized aniline or phenol monomers [3] Enzymatic polymerization of azo-functionalized anilines and phenols is advantageous compared to traditional chemical methods, in that it allows one to build in substantial chromophore density in the polymers. The final polymers have almost 100% dye content which is significantly higher than those polymers that are chemically post modified with azo groups. Structural characterization of poly(4-phenylazophenol) showed that the peroxidase catalyzed coupling reaction occurs primarily at the ortho positions, with some coupling at the meta positions of the phenol ring of the monomers as well [3b]. This results in the formation of a branched polyphenylene backbone with pendant azo functionalities on every repeat unit of the polymer chain. The articulated structure of the polymer leads to large free volume and poor packing of the azo chromophores. Interesting photochemical and physical properties, such as slow photoisomerization and thermal relaxation rates, were observed in these enzymatically synthesized azo polymers [4]. To further understand the reaction mechanism of this approach, a series of para-substituted azophenol monomers was enzymatically polymerized as shown in Scheme 1. Detailed characterization of the reactions, as well as the structural and photonic properties of the synthesized polymers will be presented.



Scheme 1.

EXPERIMENTAL

Materials

Horseradish peroxidase (HRP) (EC 1.11.1.7) (200 unit/mg) was purchased from Sigma with RZ>2.2. A stock solution of 10 mg/ml in pH 6.0, 0.1M phosphate buffer was prepared. The azophenol monomers with para substitution on the phenyl rings were synthesized according to the procedure described in the following section. All other chemicals and solvents used were commercially available, of analytical grade or better and used as received.

Synthesis of Azophenol Monomers

To synthesize 4-((4-methoxyphenyl)azo)phenol, 0.1 mol (12.3 g) of p-anisidine was first dissolved in 45 ml of concentrated hydrochloric acid and 45 ml of water. The solution was cooled to 5°C and 0.1 mol of sodium nitrite in 40 ml of water was added drop wise while the temperature was maintained below 5°C. The resulting diazonium salt solution was added slowly, with stirring, into a mixed solution of phenol (9.4 g, 0.1 mol), sodium hydroxide (17.4 g) and water (200 ml), and stirring was maintained at 0-5°C for 12 hours. Concentrated hydrochloric acid was then slowly added to the cold mixture with vigorous stirring until it became acidic. The resulting precipitate was filtered with gentle suction and washed with water to isolate the free form acid. The product was dried under vacuum for 24 hours and further purified by recrystallization from an ethanol/water mixture.

Other substituted azophenol monomers were synthesized following a similar procedure as described above with the exception that different para-substituted aniline derivatives were used to form the diazonium salt. The isolated yields for these monomers were approximately 80-90%. The structures of the synthesized monomers were characterized by ^{1}H and ^{13}C NMR spectroscopy and the results are as follows:

(1) 4-((4-methoxyphenyl)azo) phenol, ^{1}H NMR (500 MHz, DMSO-d_6), δ ppm 6.94 (d, 2H); 7.11 (d, 2H); 7.75 (d, 2H); 7.82 (d, 2H); 10.20 (1H from OH). ^{13}C NMR (125.5 MHz, DMSO- d_6), δ ppm 55.5, 115.4, 116.7, 124.7, 124.9, 146.2, 147.2, 161.2, 162.0.

(2) 4-((4-nitrophenyl) azo) phenol, ^{1}H NMR (500 MHz, DMSO-d_6), δ ppm 7.0 (d. 2H), 7.9 (d, 2H), 8.0 (d, 2H), 8.4 (d, 2H). ^{13}C NMR, δ ppm 117.0, 123.5, 125.6, 126.7, 146.4, 148.8, 156.7, 163.7,

(3) 4-((4-carboxylicphenyl)azo) phenol, ^{1}H NMR (500 MHz, DMSO-d_6) δ ppm, 6.5 (d, 2H), 7.3 (d, 2H), 7.4 (d, 2H), 7.7 (d, 2H), ^{13}C NMR (125.5 MHz, DMSO-d_6), δ ppm 120.0, 121.2, 126.8, 130.2, 136.5, 142.1, 154.5, 174.8, 175.6.

(4) 4-((4-sulfonatephenyl)azo)phenol, ^{1}H NMR (500 MHz, DMSO-d_6), δ ppm, 6.6 (d,2H), 7.50 (d, 2H), 7.51 (d, 2H), 7.8 (d, 2H), ^{13}C NMR (125.5 MHz, D_2O), δ ppm 116.6, 122.4, 125.7, 127.5, 146.3, 150.6, 152.8, 162.2.

(5) 4-((4-cyanophenyl)azo) phenol, ^{1}H NMR (500 MHz, DMSO-d_6), δ ppm 7.0, (d, 2H); 7.85 (d, 2H); 7.95 (d, 2H); 8.02 (d, 2H) 10.56 (1H from OH), ^{13}C NMR (125.5 MHz, DMSO-d_6), δ ppm 112.8, 117.0, 119.5, 123.5 126.4, 134.2, 146.1, 155.2, 163.2.

Enzymatic Polymerization

Enzymatic polymerization of the various azophenols was carried out at room temperature following the procedure described previously [3b]. To 100 ml of a 50% acetone and 50% 0.01 M sodium phosphate buffer mixture, 1.0 g of 4-((4-methoxyphenyl)azo) phenol and 2.0 ml of HRP stock solution were added. The reaction was initiated by the addition of H_2O_2. To avoid the inhibition of HRP by H_2O_2 at high concentration, [5] a dilute stoichiometric amount of H_2O_2 (0.2 M) was added incrementally under vigorous stirring over a three hour time period. After the addition of H_2O_2, the reaction was left stirring for one more hour. The yellow precipitate formed during the reaction was then collected with a Buchner funnel, washed thoroughly with a 20% acetone/80% water solution to remove any residual enzyme, phosphate salt, and unreacted monomer and then vacuum dried for 24 hours. Similar experimental conditions were used for the NO_2 and CN substituted azophenols.

Polymerization of the sulfonated and carboxylic substituted monomers was carried out in a mixture of 80% phosphate buffer/20% acetone and the other conditions are similar to that described previously. In these reactions, no precipitates were formed and the resulting polymers were solubilized in the reaction media. The polymer solutions were dialyzed against deionized water for 24 hours using a dialysis bag (SPECTRUM®) with a molecular weight cut off of 3000 D to remove unreacted monomer and phosphate salts. The resulting dialyzed solution was then condensed and dried in a vacuum oven at 50°C.

Characterization

Infrared spectra for the polymers were measured on a Perkin-Elmer 1720 FT-IR spectrometer. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra of the monomers and polymers were obtained on a Bruker ARX-500 MHz FT-NMR spectrometer. Raman spectra of the monomers and polymers in powder form were recorded on a Perkin-Elmer 1760 FT-Raman spectrometer. The UV-vis absorption spectra were recorded with a Perkin-Elmer Lambda 9 spectrophotometer. The thermal properties of the polymers were measured with a DuPont thermal analyzer, TGA 2950 (TA Instrument Inc.) and DSC 2910 (TA Instruments Inc.).

Optical Quality Polymer Film Preparation

The CN, NO_2, and CH_3O substituted azophenol polymers were soluble in most polar organic solvents. These polymers were dissolved in spectroscopic

grade dioxane, and then filtered through a 0.45 μm membrane. The solutions were then spin-coated onto glass slides. The film thickness was controlled to 0.2-2.0 μm by adjusting the solution concentration and spin speed. The spin-coated films were then dried under vacuum for 24 hours at 40-50°C and stored in a desiccator until further studies. Since the sulfonated and carboxylic substituted polyazophenols were water-soluble, deionized water was used as the solvent to dissolve these polymers (pH 11 water was used for the carboxylic substituted polyazophenol). The solutions were also filtered through a 0.45 μm membrane and the films were fabricated under heating. The thickness of all spin-coated films was measured by using a Dektak IIA surface profilometer.

Photoisomerization and Thermal Relaxation

The photoisomerization behavior of the monomer and polymer was carried out by irradiation with UV light at 360 nm in DMSO. The azophenol monomer or polymer was dissolved in DMSO, and then 3 ml of this solution was sealed in a 1X1 cm quartz cuvette. UV-vis absorption spectra of these solutions were recorded before and after 5 minutes of exposure to the UV light. The changes in the absorption spectra during the process of thermal relaxation at room temperature were sequentially recorded at intervals of 20 minutes, immediately following the irradiation by UV light at 360 nm for 5 minutes. To minimize the change in the absorption characteristics due to the relaxation of the polymer during the scan period, a scan speed of 480 nm/min was usually used in these measurements.

Surface Relief Grafting Formation

Surface relief gratings (SRG) were holographically recorded by a simple two-beam interference apparatus at 488 nm from an argon ion laser under ambient conditions with a typical laser intensity of 300 mW/cm^2 [6]. The formation process of the grating was probed by monitoring the first order diffraction of a lower power He/Ne laser beam at 633 nm, at which the absorption is negligible. After the holographic gratings were recorded, the surface relief structures of the gratings on the polymer films were imaged by atomic force microscopy (AFM, Autoprobe Cp, Park Scientific Instruments) under ambient conditions. A 100 μm scanner in the contact mode under a scan rate of 1 Hz was used in these measurements.

RESULTS AND DISCUSSION

Enzymatic Polymerization

The data for the enzymatic polymerization of these para substituted azophenols is summarized in Table 1. All enzymatic polymerization reactions were car-

Table 1. HRP-Catalyzed Polymerization of Azophenol Derivatives

Entry	Substitutes	Solvents	Isolated Yield %	Polymer Solubility
1	H	50% Acetone	81.5	*P*
2	CH_3O	50% Acetone	82.2	P
3	SO_3^-	20% Acetone	53.4	W
4	COO^-	20% Acetone	64.5	W
5	CN	50% Acetone	73.2	P
6	NO_2	50% Acetone	68.2	P

ried out at pH 6.0 (pH of the phosphate buffer used), which is the optimal pH for HRP catalysis. The reaction media were formulated based on the properties of the monomers. Azophenol monomers with CN, CH_3O and NO_2 substituted groups are soluble in organic solvents such as dioxane, acetone and DMF. The polymerization of these monomers was carried out in 50% acetone/50% buffer mixtures, similar to that used previously in the synthesis of 4-phenylazophenol. During the enzymatic polymerization, the polymers were formed as precipitates. The resulting products were then collected by filtration and purified by washing with a 20% acetone/80% water mixture.

The azophenol monomers with charged substitutes such as SO_3^- and COO^-, show better solubility in organic solvents than in pure water. Therefore, to improve the solubility of these monomers, a mixed solution of 80% phosphate buffer/20% acetone was used as the reaction media in the enzymatic polymerization. However, the synthesized polymers show better solubility in water than that of the monomers. In contrast to the polymerization of other monomers as mentioned above, no precipitates were produced in these cases and the final polymers were soluble in the reaction media. The synthesized polymers were purified by dialyzing against deionized water to remove the phosphate salt, oligomer and unreacted monomer.

The isolated yields of 70-80% for the solvent soluble azo polymers was comparable to that obtained in the previous enzymatic polymerization of other phenols [9].The yields for the synthesis of the water-soluble sulfonated and carboxylic polyazophenols was around 60%, slightly lower than that of the organic soluble polymers. This may be due to the removal of the low molecular weight species during dialization.

The solubility of the synthesized polymers is strongly substituent dependent. The polymers with CN, CH_3O and NO_2 substitutes are soluble in most polar organic solvents such as dioxane, DMSO and THF. In fact, the synthesized polymers with SO_3^- and COO^- substitutes are polyelectrolytes and soluble in water. Due to the different dissociation behaviors of the sulfonated and carboxylic groups, the sulfonated polyazophenol is water soluble in the entire pH range, while the carboxylic substituted polyazophenol shows only good solubility in basic water solutions.

POLYMER CHARACTERIZATION

UV-vis Absorption

Figure 1 shows a comparison of the UV-vis absorption spectra of the monomer and polymer solutions for the various substituted azophenols. The substituted azophenol monomer spectra are similar to that of 4-phenylazophenol with a strong absorption peak around 355-400 nm due to π-π* transition and a weak broad peak at about 440-600 nm due to n-π* [7]. The absorption peaks for both the π-π* and n-π transitions shift to longer wavelength compared to the 4-phenylazophenol because of the presence of the substituent at the para position of the phenyl ring. In the case of CN and NO_2 azo monomers, the absorption peaks of the n-π* are observed at 550 and 600 nm, respectively. Upon polymerization, the

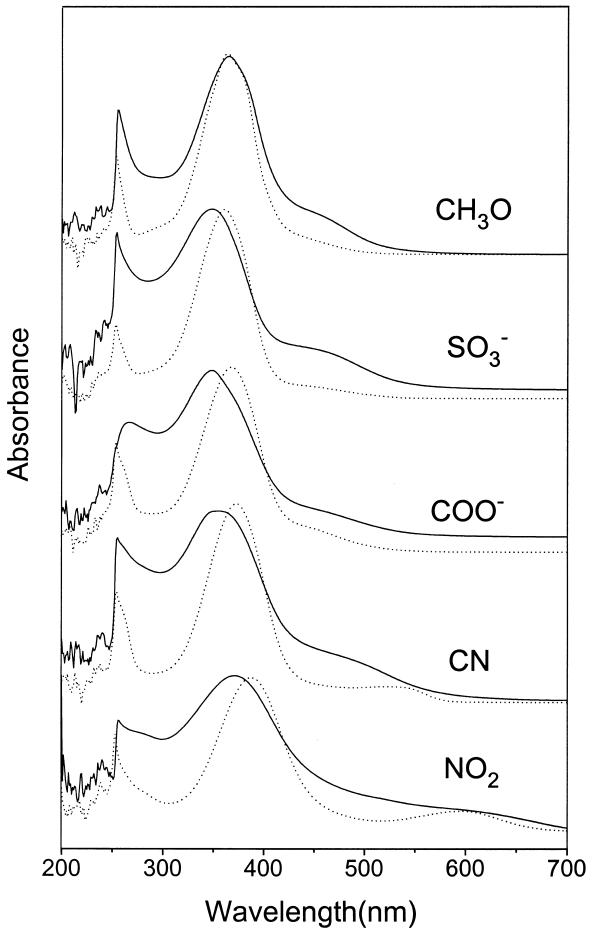


Figure 1. UV-Vis absorption spectra of (—) monomer and (···) polymer of substituted azophenol in DMSO.

absorption spectra of the polymer changed significantly compared to that of the monomers. The peak assigned to the π-π* transition shifts significantly to shorter wavelength. For example, a 20-30 nm blue shift is observed for the π-π* transition for the sulfonated and carboxylic substituted polyazophenols. The blue shift in these substituted polyazophenol systems is more remarkable than that previously observed in the synthesis of poly (4-phenylazophenol).

Usually, the enzymatic polymerization of phenol and aniline may lead to a red shift of the π-π* transition in the polymer, as previously observed in napthol and phenylphenol and other monomer systems [8]. This unusual blue shift of the π-π* transition was first observed in the enzymatic polymerization of diaminoazobenzene and 4-phenylazophenol. It may arise from the strong steric hindrance and conformational constraint that occurs during the incorporation of the monomer into the polymer chain. This in turn disrupts the conjugation of the phenol and the phenyl ring in the polymer and results in a shift in absorption. This is discussed in more detail later in the paper.

FTIR Spectroscopy

Structural characterization of enzymatically synthesized azophenol polymers has been carried out in previous work [3b]. The peroxidase-catalyzed polymerization of phenolic compounds usually produces polymer with a complicated structure. Typically a mixture of polymers with different structures is produced, as Akkara *et al*. observed in the enzymatic synthesis of polyphenylphenol and polybenzidine [9]. The precise structure for these enzymatic polymers is extremely hard to determine. However, the major coupling mechanisms of the polymer may be characterized by FTIR, NMR and FT Raman spectroscopy, to help in determining the general structural properties of the synthesized polymers.

As previously observed in the polyazophenol without any substitution, the FTIR spectra of the polymers show broad peaks around 3300-3600 cm^{-1}, that are due to OH stretch and internal hydrogen bond formation [10]. The retention of a strong OH stretch region in the polymer suggests that most of the OH groups in the monomer are not involved in the coupling reaction and that the resulting polymer has significant phenol functionality. Due to the presence of the para substituted group at the phenyl ring, the vibration bands from 1700-600 cm^{-1} become more complicated and it is difficult to obtain more structural information from these FTIR spectra of the polymers.

NMR Spectroscopy

Direct information on the coupling mechanism may be provided by the comparison of the ^{1}H and ^{13}C NMR spectra of the monomers and polymers of these substituted azophenols. The ^{1}H NMR spectra of the monomers show very sharp peaks. After polymerization, however, the peaks become very broad. This broad-

ening of the proton NMR resonance peaks is attributed to polymerization and has been previously observed with other enzymatically prepared polyphenol systems [8]. The ^{1}H NMR spectra of the polyazophenol with sulfonated and carboxylic substituents are featureless with a broad peak ranging from 6.6 ppm to 8 ppm due to the aromatic protons. This unusual broadening may be caused by either the high molecular weight or the broad distribution of the resulting polymer as proposed by John and coworkers [8]. Further inspection shows that the resonance peak for the ortho proton of the phenol ring decreased significantly and almost disappeared in the spectrum of the polymer. These results are consistent with our previous observation in the enzymatic synthesis of poly(4-phenylazophenol) and confirm that the ortho positions of the phenolic ring are the most favored for coupling in the enzymatic polymerization of azophenol derivatives.

The ^{13}C NMR spectra of the polymers are more resolved and more informative than the ^{1}H NMR polymer spectra. Figure 2 shows the ^{13}C NMR spectra of the monomers and polymers of the different substituted azophenols. The peaks of the monomer spectra are assigned as shown. Several interesting features are worth noting. First, the strong broad peaks in these polymer spectra are assigned to the carbons of the phenyl ring. The chemical shifts of these peaks in the polymer spectrum show little change, other than broadening, when compared to that of the monomer. This suggests that coupling is not occurring on the phenyl ring. It may, therefore be concluded from these ^{13}C NMR spectra, that the phenyl ring of the monomers remains primarily intact during the enzymatic polymerization. Secondly, the resonance peaks of the carbons from the phenol ring are weakened significantly in the polymer spectra. This is especially true for the peaks of the ortho carbons of the phenol ring, which decreased dramatically and almost disappeared in each of the polymer spectra. These results are concordant with the data obtained from the ^{1}H NMR spectroscopy and supports a preferable ortho coupling of the phenolic ring in these reactions. Also, the peak from the meta carbon of the phenolic ring shows a significant decrease in intensity, indicating that some meta coupling may also be occurring. The significant weakness of the resonance peaks for carbons 1 and 4 of the phenol ring may be explained by the phenol ring being coupled to form a rigid backbone, leading to the longer relaxation time of these carbons in the NMR pulse.

The NMR editing technique, DEPT 90 was used to further characterize the structure of the polymers and the coupling mechanism. In the DEPT 90 spectrum, only the protonated aromatic carbons are observed. The disappearance of the upfield peaks, with chemical shifts over 135 ppm, in the DEPT 90 spectra suggests that these peaks are from the non protonated aromatic carbons (corresponding to carbons 1, 4, and 8 in the monomer structure). The major spectral features of DEPT 90 in the downfield region from 110-130 ppm are quite similar to that of the normal ^{13}C NMR spectrum. Two strong resonance peaks (corresponding to carbon 6 and 7 in the monomer structure) appear in DEPT 90 spectra. However, the changes of some broad peaks in DEPT 90 spectra may not be neglected. For example, in the DEPT 90 spectrum of the SO_3- substituted polyazophenol, the peaks around 118

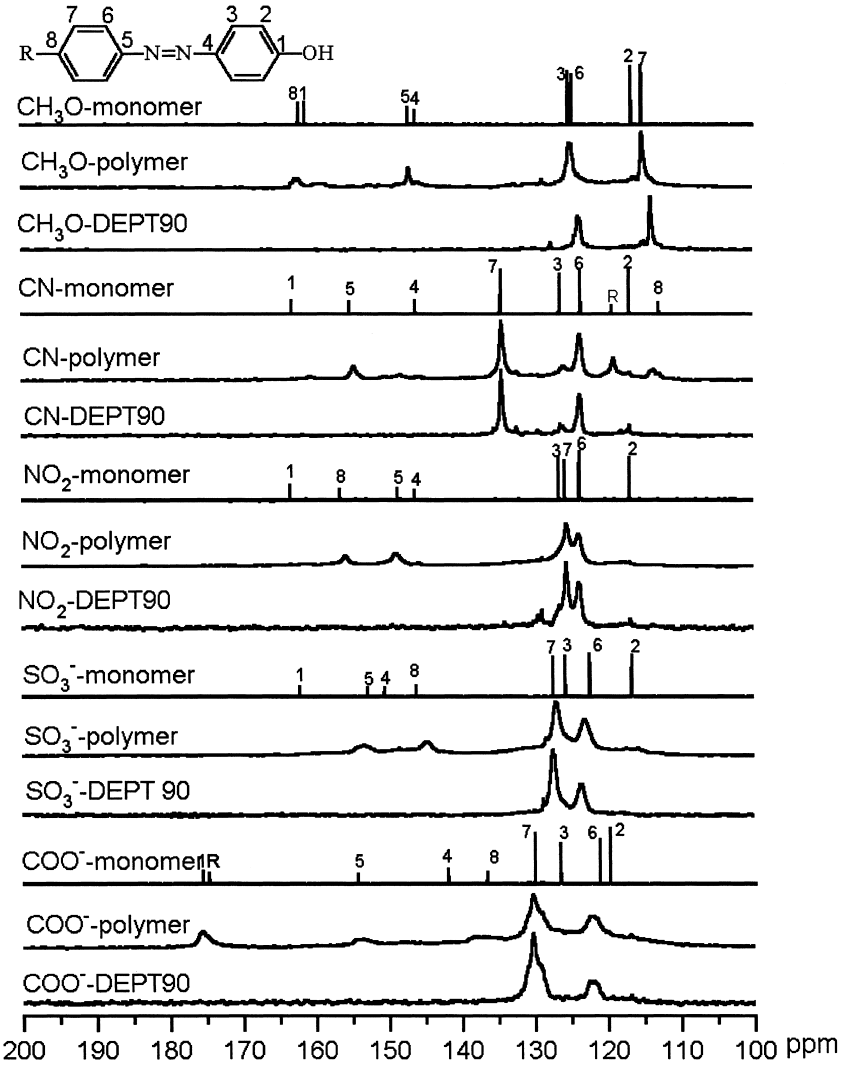


Figure 2. ^{13}C NMR of monomer and polymer of substituted azophenol in DMSO– d_6. The assignments for the monomer are made as shown.

ppm and 132 ppm are decreased compared to the normal ^{13}C NMR spectra. A similar peak decrease at 116 and 128 ppm is also observed in the spectrum of the NO_2 substituted polymer. These peaks are most likely due to the non-protonated aromatic carbons formed by C-C coupling during the enzymatic polymerization [11].

FT-Raman Spectroscopy

Interesting conformational and structural information on the synthesized polyazophenols is also provided by FT-Raman spectroscopy. The FT-Raman spec-

tra of the monomers and polymers are shown in Figure 3. The absence of the C-H in-plane bending vibration of mono-substituted benzene at 1006 cm^{-1}, previously observed in the 4-phenylazophenol spectrum, is a signature of the presence of the para substitution of the phenyl ring in these spectra. The ring vibration bands at around 1191 cm^{-1} for the para-disubstituted benzene (phenol ring) decrease in these polymer spectra due to the coupling reaction occurring on the phenolic aromatic ring, as was supported in the previous NMR studies.

The vibrations of the azo bond, (N=N), are strongly Raman active. The two Raman vibrations of the N=N are assigned as shown in the monomer spectra. The strong band at around 1420 cm^{-1} is due to the trans form of azophenol and the weak band at around 1472 cm^{-1} is due to the cis form [12]. As expected, the trans form is dominated over the cis form in the monomers. After polymerization however, the vibration feature of the N=N changes significantly. The band due to the trans form of the azo bond, at around 1420 cm^{-1}, decreases dramatically in the polymer spectra, while the band at around 1470 cm^{-1} becomes dominant. This

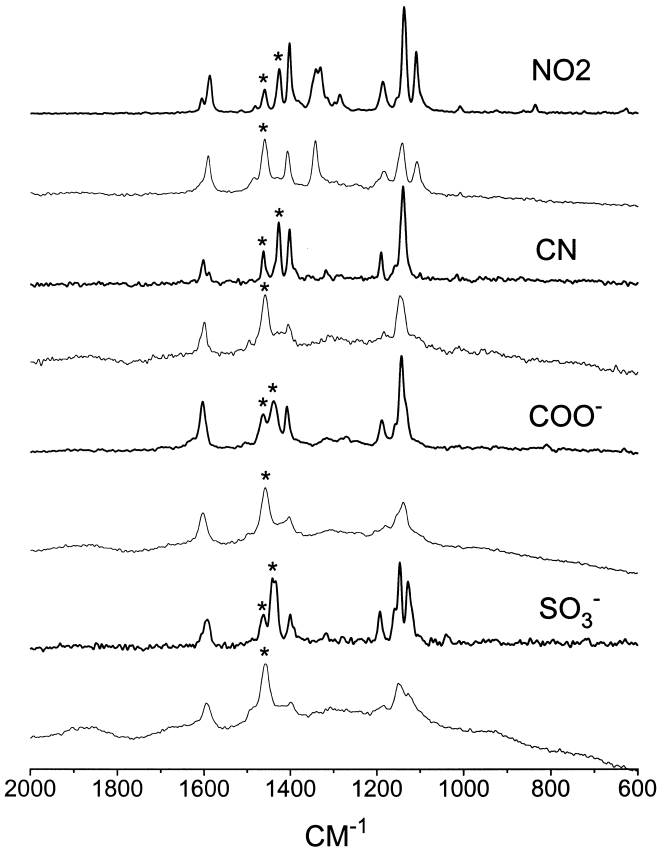


Figure 3. FT-Raman Spectra of monomer and polymer of substituted azophenol in powder form. The spectra were recorded in the region of 2000-600 cm^{-1}. *Peak assigned to (N=N).

band may be explained by either the *cis* form vibration or another unknown conformational azo bond.

The FTIR and NMR spectroscopic studies on these substituted polyazophenols show that the coupling reaction occurs at the ortho as well as some meta positions of the phenol ring. This leads to the formation of a branched phenylene polymer backbone with a pendant azo-phenyl ring on every repeat unit. Strong steric hindrance and conformational constraint may be incurred during these reactions to form highly articulated polymer structures. As a result, some of the *trans* azophenol units may be driven to adopt a *cis* form or perhaps even another unknown conformational structure in the polymer to accommodate a lower overall energy of the molecules. This steric hindrance and conformational constraint may become more dramatic when substituent groups such as SO^{3-} and COO^{-} are present and may explain the unusual blue shift of the π-π^* transition and change of the N=N vibration in the polymer spectra.

Thermal Properties

The thermal properties of these enzymatically synthesized polymers were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen. The DSC measurements were run at a scan rate of 10°C/min. The samples were cooled after the first scan and the Tg value was taken to be the inflection position on the second scan trace. These substituted polyazophenols show good thermal stability, similar to that observed previously with the poly (4-phenylazophenol). Typically, the TGA measurements showed a weight loss that started at around 230°C. There is less than a 15% mass loss up to 300°C and less than 40% up to 600°C. However, very different behaviors were observed in the DSC measurements for these substituted polyazophenols. The polymers with CH_3O and CN substitutes showed a T_g at approximately 134°C and 176°C, respectively. No apparent T_gs were observed for the other polymers.

Photochemistry

Figure 4 shows that the absorption spectra of the substituted poly(4-phenylazophenols) in DMSO before and after irradiation by UV light at 360 nm. As expected, the absorption band at around 350 nm, due to the π-π^* transition of the trans form of the azo bond, decreases significantly after irradiation, while the absorption band at 440-600 nm due to the n-π^* transition of the cis form of the azo bond increases. The photoinduced isomerization of the corresponding monomer was also monitored by a similar procedure. However, under the same conditions, the photoisomerization processes for the monomers could not be monitored in DMSO by UV-vis absorption spectroscopy because of the fast thermal relaxation process. Therefore, the photoinduced trans to cis isomerization

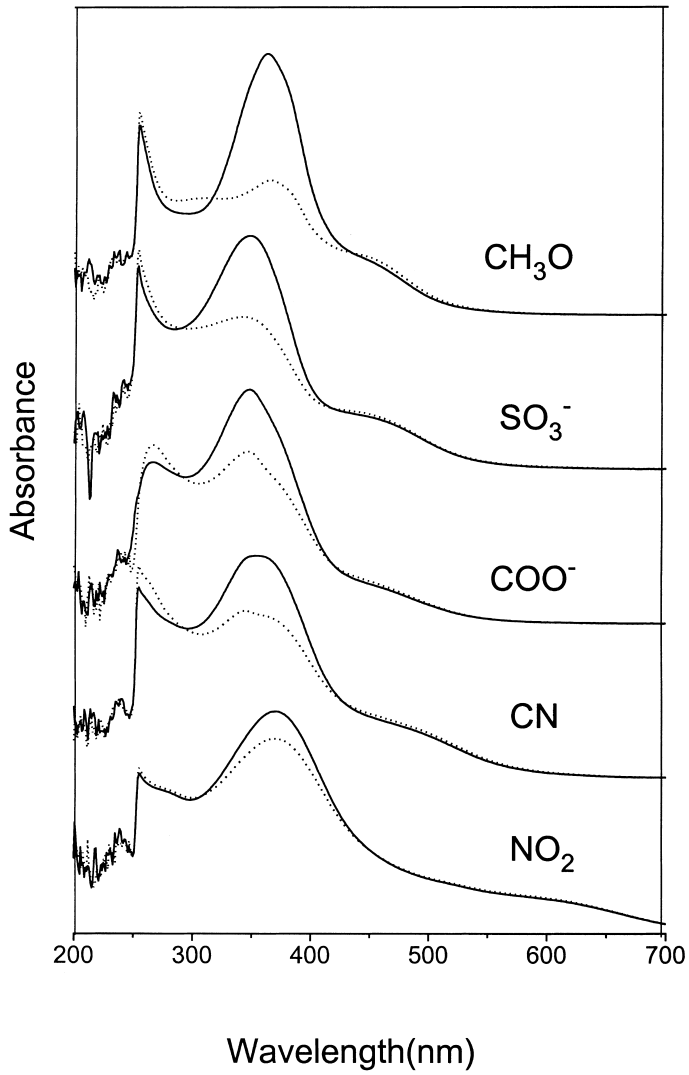


Figure 4. UV-vis absorption spectra of substituted polyazophenols in DMSO before and after irradiation by UV light at 360 nm for 5 minutes.

processes of these substituted azophenol monomers had to be monitored at very low temperature [13].

The observed trans to cis photoisomerization process in these polymers is reversible. However, the cis to trans thermal relaxation process of these polymers is very slow (data not shown), and similar to that observed with the poly(4-phenylazophenol). The differences in the photochemical behaviors between the polymer and monomer may be attributed to the articulated polymer structure in a constrained geometry as was previously discussed.

Photofabrication of Surface Relief Gratings

One of the important applications of these enzymatically synthesized macromolecular dyes is in the photoinduced fabrication of SRG's. Taking advantage of the good solubility of these polymers, optical quality films may be fabricated by spin coating the polymer solution onto glass slides. Surface relief gratings were optically inscribed on these polymer films at room temperature. This photofabrication process of surface relief gratings features is a simple, one step process that doesn't require any subsequent post processing [14]. As an example, a three-dimensional view of the SRG written on the methoxy substituted polyazophenol film is shown on the top of Figure 5. A SRG with surface modulation around 0.4 μm was formed on this film. The surface modulations on different polymer films, under the same writing conditions, were measured and are comparatively shown in the bottom of Figure 5. SRG's with large surface modulation (around 3000-4000 Å) were fabricated on the films of the organic soluble polymers. However, the writing efficiencies were found to be very low on the polymer films with the

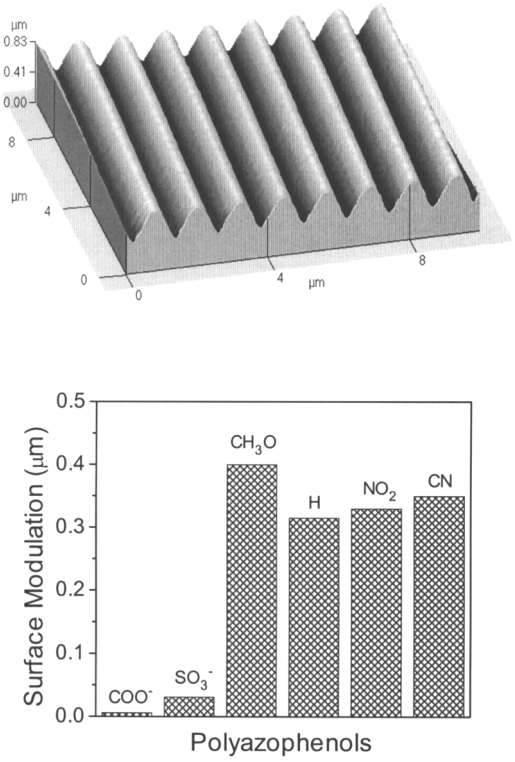


Figure 5. 3D view of the SRG patterns formed on methoxy substituted polyazophenol film (top). Comparison of the surface modulation of the SRG formed on different substituted polyazophenol films (bottom).

charged, sulfonated and carboxylic substituted groups. Explanations for this difference in behavior are currently under investigation.

CONCLUSION

A series of polyazophenol "macrodyes" with various substituents at the para position of the phenyl ring have been synthesized using an enzymatic approach. Structural characterization by FTIR, NMR and FT-Raman further confirms our previous observation in the synthesis of poly(4-phenylazophenol) that the coupling reaction occurs at the ortho as well as meta positions on the phenol ring of the monomer. These biologically derived azo polymers show interesting photochemical behavior due to the strong constraints of the azo chromophores in an articulated polymer structure. SRG's with surface modulation of around 3000-4000 Å can be fabricated on the optical quality thin films of these polymers. This new class of macromolecular dyes demonstrates new opportunities regarding the design and synthesis of processable, optically active polymer systems for photofabrication.

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This paper is dedicated to the memory of Sukant Tripathy, our dear friend and colleague, whose inspiration, creativity and achievements in science will always live on.

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