Enzymatically Synthesized Photodynamic Polyaniline Containing Azobenzene Groups

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A novel polyaniline containing azo groups has been synthesized using horseradish peroxidase catalyzed oxidative free radical coupling of 4,4′-diaminoazobenzene in the presence of hydrogen peroxide. The spectral changes observed indicate polymerization accompanied by trans−cis isomerization, leading to structural constraints in the growing polymer chain. This soluble azo polymer consists of azo groups in the main chain as well as in the side chain. Upon photoexcitation of the polymer in solution, the chromophores undergo structural photoisomerization. The polymer relaxes to a conformation having spectral features identical to those of the conformation prior to photoexcitation if the excitation is carried out within the trans absorption band. Photoexcitation at the cis absorption band or thermal kinetic randomization of the chromophore conformation in the polymer in solution results in relaxation of the structural constraints, which leads to a different constrained conformation.

1. Introduction

Current interest in polymers for photonics technologies has stimulated extensive investigations of azo-containing organic molecular systems. Azobenzene and stilbene derivatives have been synthesized and studied for their linear and nonlinear optical properties, and their potential in optical devices has been explored by introducing these functional molecules in polymer matrixes or as part of the polymer chain.[1,2] Reversible photoisomerization of these functional groups has enabled the writing of holographic images and surface relief gratings on these polymer films, which demonstrate their applicability in optical image processing and data storage.[3] An ultrathin polymer film with azobenzene groups in the side chain has been demonstrated to control the orientation, configuration, and optical properties of liquid crystals acting as a command surface.[4] Though a large number of azobenzene-containing polymers have been chemically synthesized and studied, the main focus has been on polymers containing azo groups in the side chain.[2] Although the synthesis of main chain azo polymers has not been as extensive, there are reports on main chain azopolymers with flexible backbone linkages such as polyesters and polyureas.[5] Conjugated main chain azo polymers are expected to possess interesting luminescent or conducting properties.

Recently there has been much interest in enzyme-catalyzed polymerization as a new methodology for polymer synthesis. Enzymes such as peroxidase, laccase, and lipase among others have been used for the synthesis of polymers and other specialty chemicals.[6,7] Peroxidase-catalyzed polymerization of phenols and anilines has been utilized to produce controlled polymeric structures.[7] We have extended the enzyme-catalyzed polymerization of aromatic amines and phenols with polar functional groups to synthesize water-

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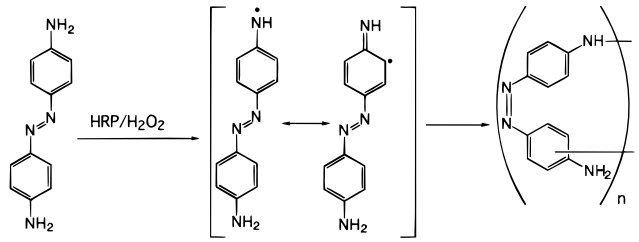
Scheme 1: Polymerization of Diaminoazobenzene by HRP in the Presence of Hydrogen Peroxide[a]



[a] As-synthesized polymer contains azo groups both in cis and trans conformations.

soluble polyanilines and polyphenols.[8] Here, we report the first synthesis of a photodynamic polymer by enzyme-catalyzed polymerization. Horseradish peroxidase catalyzed oxidative free radical coupling of 4,4′-diaminoazobenzene (DAB) led to a polyaniline containing azo groups as part of the main chain as well as the side chain of the polymer. A partial mechanism of the enzyme-catalyzed polymerization of DAB is represented in Scheme 1.[8,9] The azo linkage in the monomers to begin with is predominantly in the trans conformation. Interestingly trans−cis isomerization accompanies polymerization, and completion of the polymerization is indicated by the near complete exhaustion of the trans state. The effect of photoexcitation on the trans−cis−trans isomerization of the chromophores and the resulting conformational changes in the polymer has been compared with the thermally assisted conformational changes of the polymer and its relaxation under ambient conditions. Solvatochromic behavior as well as the effect of changing the solvent properties on the net population of cis and trans isomers is also discussed.

2. Experimental Section

2.1. Materials. Horseradish peroxidase was purchased from Sigma Chemicals Co., St. Louis, MO. Diaminoazobenzene was synthesized in the laboratory following the chemistry described below. All other chemicals used were of analytical grade or better and were used as obtained.

The spectral properties of the polymer and the polymerization reaction were studied using a Perkin-Elmer Lambda 9 UV−vis near-IR spectrometer. The structural characterization of the monomer and polymer were carried out using a Perkin-Elmer 1760X FTIR spectrophotometer and a Bruker 250 MHz NMR spectrometer. Elemental analysis was performed at Robertson Microlit Laboratories, Inc., Madison, NJ. Thermal degradation patterns of the polymers were studied using a TA Instruments TGA-2950 thermogravimetric analyzer. The samples were heated at a rate of 20 °C/min under a nitrogen atmosphere. The molecular weight was determined using gel permeation chromatography (GPC) utilizing Waters model 510 pump and Waters model 410 refractive index detector with Jordi columns relative to polystyrene standards. Dimethylformamide (DMF) containing 1% LiBr was used as the eluent. The photoexcitation of the polymer solution in DMF was achieved using a UV lamp with emission at 254 and 360 nm, and a continuous wave Argon ion laser at 488 nm. The laser beam was expanded to excite a larger volume of the sample.

2.2. Methods. 2.2.1. Synthesis of Diaminoazobenzene. The reaction scheme for the synthesis of 4,4′-diaminoazobenzene is given in Scheme 2. 4-Aminoacetanilide (14.5 g, 0.095 mol), sodium perborate (20 g, 0.13 mol), boric acid (5 g, 0.08 mol), and 250 mL of glacial acetic acid were placed in a flask, and the mixture was kept at 56 °C for 6 h. After the violet color of the reaction mixture turned brown, the reaction mixture was cooled to room temperature. The yellow precipitate was filtered and washed with water until the washings were neutral.

4,4′-Bis(acetamido)azobenzene from the above reaction was mixed with 75 mL of methanol and 75 mL of 6 N HCl. The blackish-red solution at an elevated temperature was refluxed for 90 min. The solution was subsequently cooled to obtain a violet-colored precipitate, which was later filtered off. This product was dissolved in 250 mL of water and neutralized with 2.5 N sodium hydroxide solution, which resulted in the precipitation of 4,4′-diaminoazobenzene as a yellow-colored solid. The precipitate was filtered, washed with water, and then purified by column chromatography with silica gel using a mixture of ethyl acetate and *n*-hexane (1:1 v/v) as the eluent. The proton NMR spectrum of the purified diaminoazobenzene in dimethylsulfoxide-d_6 (DMSO-d_6) gives two doublets of equal intensity at 6.65 and 7.55 ppm corresponding to the 3, 3′, 5, and 5′ protons and 2, 2′, 6, and 6′ protons, respectively. The ^{13}C spectrum of the compound shows four peaks: 114.55 (3, 3′, 5, and 5′), 124.62 (2, 2′, 6, and 6′), 144.19 (1, 1′), and 151.64 (4, 4′) ppm. The N−H and aromatic C−H stretching frequencies appear in the range 3100−3450 cm^{-1} as multiplets. The C═C and NH_2 deformation bands appear around 1600 cm^{-1}. The bands at 1370 and 1150 cm^{-1} are due to the para-substituted azobenzene.

2.2.2. Enzymatic Polymerization of Diaminoazobenzene. The enzymatic polymerization of diaminoazobenzene (0.1 g) was carried out in 200 mL of 20% ethanol solution in 0.1 M Tris-HCl buffer, pH 6.0. Horseradish peroxidase (about 300 units) was dissolved in the reaction medium, and the reaction was initiated by the addition of 100 μL of 30% hydrogen peroxide. The reaction starts instantaneously and is over in less than 1 h. The reaction mixture was filtered, and the precipitate was washed with 20% ethanol and subsequently with deionized water to remove unreacted monomers and the enzyme. The yield of the polymer was about 70%. The isolated polymer is soluble in common polar organic solvents such as DMSO and DMF. The GPC analysis estimates a molecular weight of the order of 80 000 (M_w) with a polydispersity of 4.8.

2.2.3. Photoisomerization Studies. The polymer solution in DMF (0.1 mg/mL) in a sealed quartz cuvette was exposed to a UV lamp (254 or 360 nm) for 5 min or to an expanded argon ion laser beam at 488 nm for 15 min. The exposure time was sufficient to produce absorption changes of about 4−5% of the peak absorption. The absorption spectra were recorded immediately after shutting the light source off with a scan speed of 960 nm/min to minimize the change in the absorption characteristics due to relaxation of the polymer during the scan period. The scanning was repeated after every minute until the difference in absorbance between the two scans was minimal. The absorption spectra were subtracted from the spectrum before photoexcitation to get the differential absorption spectra.

2.2.4. Thermal Studies. The polymer solution in DMF was heated to the desired temperature using a water bath in a sealed cuvette and was allowed to equilibrate for 10 min. The absorption spectrum was recorded immediately after removing the sample from the water bath. The spectrum was scanned at a scan speed of 960 nm/min, until the difference between the two successive scans was minimal. The absorption spectra were subtracted from that at the room temperature to get the differential absorption spectra.

3. Results and Discussion

3.1. Kinetic Studies. The polymerization reaction has been followed spectroscopically. Figure 1 gives the spectral changes during the polymerization in an aque-

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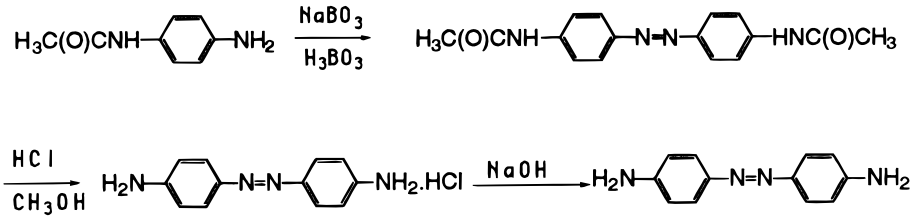
Scheme 2



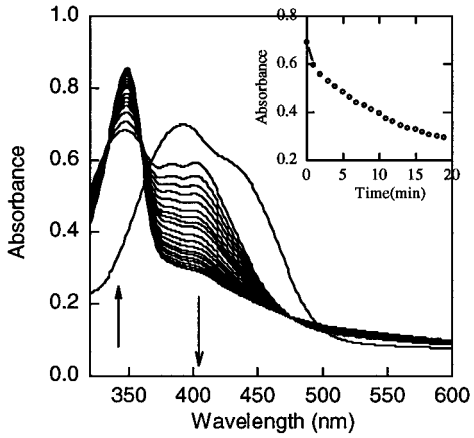


Figure 1. Change in absorbance during the horseradish peroxidase catalyzed polymerization of diaminoazobenzene in Tris-HCl buffer at pH 6.0. Inset is the decrease in absorbance measured at 400 nm as a function of time during the polymerization of diaminoazobenzene.

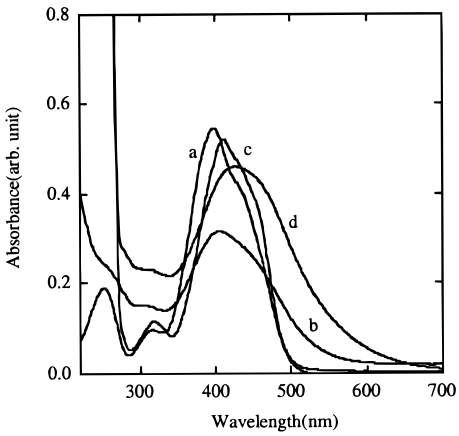


Figure 2. Absorption spectra of the (a) monomer and (b) polymer in methanol and the (c) monomer and (d) polymer in DMF.

ous solution at pH 6.0. The spectral features change drastically upon the initiation of polymerization. The monomer spectrum has a characteristic broad absorption with a peak maximum at 390 nm, with a shoulder at around 440 nm. Upon the initiation of polymerization, these peaks shift to 380 and 400 nm with the appearance of a new peak at 330 nm. With the progress of the polymerization reaction, the absorbance at 330 nm increased with a concomitant decrease in the absorbance at longer wavelengths, which finally merge to give a broad peak at around 400 nm. The inset in Figure 1 gives the change in absorbance measured at 400 nm as a function of time during the course of the polymerization. It can be observed from the time profile that the polymerization proceeds rapidly in the initial 10 min and slowly thereafter. However, bulk polymerization was carried out in 20% ethanolic solution to increase the solubility of the monomer in the reaction medium, and the reaction was allowed to continue for at least 1 h before the filtration of the precipitated polymer. The absorption features of the monomer in Figure 1 indicate the existence of monomer predominantly in the trans form. Upon initiation of the polymerization reaction, monomer addition is accompanied by trans to cis isomerization. As the reaction proceeds in the aqueous medium, the cis conformation begins to predominate. The polymer must adopt an overall collapsed conformation. This indicates that the resulting polymer will have significant conformational constraints. The absorption spectra of the polymer and the monomer in methanol and DMF are given in Figure 2. The absorption band at wavelengths around 330 nm arise from the cis form and at 400 nm are due to the trans form of the chromophore. The monomer again is predominantly in the trans form. The absorption band of the polymer is broad with contributions from the chromophores and their effective conjugation lengths. There is a large solvatochromic transition going from a thermodynamically poor solvent (water) to DMF. Clearly significant cis to trans isomerization has occurred in the solvation process. For the polymer solution in DMF when water (poor solvent) is gradually added back, the spectral changes are not as dramatic. The polymer absorption maximum (trans) changes by about 25 nm on changing the solvent from 100% DMF to 10% DMF in water. A similar observation was also made while changing the solvent from DMF to methanol. However, we recall that these absorption maxima do have contributions from the effective conjugation lengths, pushing the actual cis and trans absorption maxima to lower wavelengths than reported here. The dynamics of the macromolecule stemming from the contributions of the azo functional groups in the side chain and the backbone of the polymer are further explored by photoexcitation and thermal perturbation of the polymer.

3.2. Characterization. Elemental analysis (experimental values C = 68.79%, N = 20.13%, H = 4.61%; theoretical values C = 68.57%, N = 26.6%, H = 4.76%) suggests that there is an average of two oxidative couplings per molecule. Though there are four possible sites for oxidative coupling, steric hindrance is expected to limit this to fewer bonds per molecule, although branching is possible. Structural characterization of the polymer was carried out by NMR and FTIR spectroscopies. The polymer ^{1}H spectrum in DMSO is broad and featureless as compared to the monomer spectrum. The peaks at 6.55 and 7.5 ppm become very broad, having a multiplet structure, with additional peaks at 6.9, 7.0, 7.9, and 8.0 ppm. The complexity in the proton spectrum indicates the complex nature of the polymer structure. We recall that the oxidative free radical coupling reaction can occur at the ortho and para

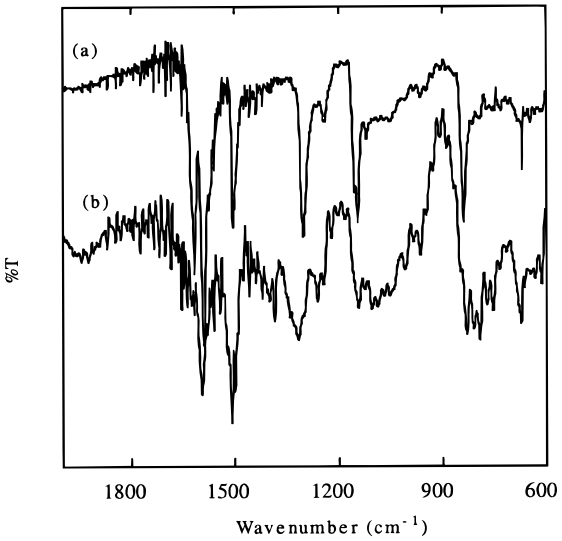


Figure 3. Selected region of the FTIR spectra of (a) monomer and (b) polymer of diaminoazobenzene in KBr.

positions of the amine group due to the resonance stabilization of the free radical.[4,9] In the present case, the para positions are not available for the reaction. There are four possible sites for the oxidative coupling in the monomer, which if accessed will result in a very branched structure. This branching in the polymer may assist in the solubilization in polar organic solvents. As the NMR spectrum was not very useful in any structural evaluation, we used the fraction soluble in chloroform (oligomers) for evaluating the possible type of bonds involved in the oxidative coupling. The monomer ^{1}H NMR spectrum (in chloroform-*d*) shows two doublets at 6.75 and 7.8 ppm corresponding to the 3, 3′, 5, and 5′ protons and 2, 2′, 6, and 6′ protons, respectively. The oligomer spectrum is still very complex, but the peak structures are clearer. A first look at the spectrum shows multiple additional peaks (both singlets and doublets) downfield of each of the peaks of the monomer due to the additional aromatic ring deshielding. The chemical shift positions of these peaks range from 6.8 to 7.2 ppm and 7.9 to 8.3 ppm. These additional doublet peaks have coupling constants identical to the monomer peak, indicating that they arise from the same pair of protons as in the monomer. The singlet peaks are arising from the protons ortho to the coupled carbons. The shifts in their position arise from the change in the chemical environment of the protons due to chemical coupling.

A selected region of the FTIR spectrum of the (a) monomer and (b) polymer of diaminoazobenzene in KBr is given in Figure 3. The monomer absorption bands are sharper as compared to those of the polymer. At a higher energy region (3600−3200 cm^{-1}), the multiplicity in the NH and CH stretching frequencies disappear due to the broadening of the peaks upon polymerization. The sharp peaks of the monomer at wavenumbers 3480, 3380, 3340, and 3210 cm^{-1} disappear with the appearance of a broad peak at around 3400 cm^{-1} for the polymer. There are no peaks pertaining to the NH groups (around 2800 cm^{-1}) in the polymer. In the lower energy region, the bands around the 1100−800 cm^{-1} wavenumber region are more complex in the polymer as compared to those in the monomer. This is indicative of the increased substitution in the benzene ring.[10]

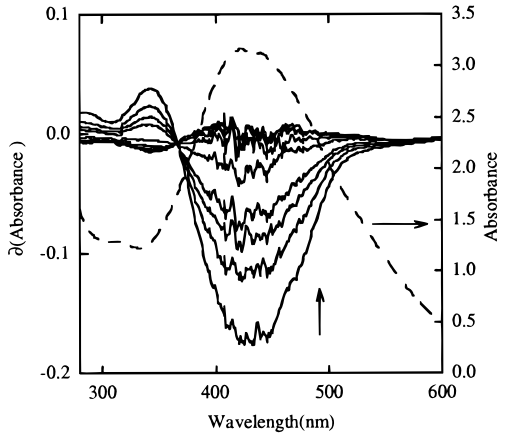


Figure 4. Change in the absorbance upon exposure to UV light (360 nm). The solution was excited with UV light for 5 min, and then the absorbance was recorded at every minute; the difference of the absorbance with that before radiation is plotted as a function of wavelength. For clarity, data presented here are the spectra recorded every minute for 4 min and subsequently every 4 min following irradiation. The arrow represents the direction of time increment. The dotted line is the absorption spectrum of the polymer before irradiation.

Thermal stability of the polymer was studied by thermogravimetric analysis. The weight loss onset temperature is 241 °C. At 249 °C, about 5% weight loss was observed with 20% weight loss at 436 °C. The polymer appears to be fairly thermally stable. The characteristic spectral features of the polymer were unchanged even after heating to weight loss onset temperatures (∼250 °C).

3.3. Photoisomerization. In the photoexcitation experiments, the solution of the polymer in DMF was excited with UV light (360 nm) for 5 min and immediately after that the spectra were recorded every minute for 15 min. The difference of these spectra with the spectrum before photoexcitation is plotted in Figure 4. The absorption spectrum of the polymer in DMF before photoexcitation is given in dotted line for comparison. The differential absorption spectra show a decrease in absorbance at the peak positions in the absorption spectrum (320 and 420 nm) and increase in absorbance at the minimum in the absorption band (340 nm). We may ascribe these to the trans and the cis forms of the azo groups in the polymer.[2b] It is anticipated that during the relaxation of the polymer after photoexcitation the polymer will undergo a series of cis−trans isomerizations due to the structural constraints in the polymer. It can be observed from the figure that the polymer relaxes to a conformation that has the spectral features identical to those of the one before irradiation. The time taken to completely relax to the original conformation is about 10 min. A significantly shorter cis−trans isomerization time scale has been reported for isolated azo chromophores or azo chromophores in the side chain polymers in solution.[1b] The long time needed for relaxation in this case can be ascribed to the conformational changes associated with the isomerization in a constrained geometry.

The above experiment was repeated with the excitation at 488 nm using an Ar$^+$ laser. The excitation beam

(10) *The Aldrich Library of Infrared Spectra*, 3rd ed.; Pouchert, C. J., Ed.; Aldrich Chemical Co.: Milwaukee, WI.

was expanded to about 1 cm^2 to excite as large an area of the sample as possible. The time series difference spectra were identical to those observed in the case of 360 nm irradiation. Therefore, one can conclude that the exposure of the molecules to pump beams within the trans absorption envelope causes similar kinds of perturbations in the molecular conformation. The molecules undergo conformational changes upon photoexcitation, due to the trans−cis isomerization, and return to a conformation that has the ground-state absorption spectrum of the polymer conformation before photoexcitation in about 10 min. The bulk thermal properties (TGA) of the polymer before and after photoexcitation were also identical, further ensuring that no photodegradation occurred during the photoexcitation. Both pump beams were within the trans absorption envelope but significantly in the wings.

The excitation of the polymer solution in DMF with UV light at 254 nm presents quite a different picture. Upon solvation in DMF the as-synthesized polymer, where the chromophores were predominantly in the cis state, has relaxed to a conformation with strong absorption in the trans band. We conjecture that structurally unconstrained regions (including short side chains) have relaxed to the trans state. Upon excitation at 254 nm we expect an increase in the net population of the trans isomer, given that we are predominately exciting the chromophores in the polymer in the constrained cis state. As expected, we observe an increase in the absorbance at 420 nm after photoexcitation at 254 nm, indicating this increase in the trans population. If the relaxation of the chromophores in solution followed the pattern observed in the photoexcitation within the trans absorption envelope, we would expect the absorption spectrum after relaxation to be identical to the one before photoexcitation. The absorbance at 420 nm decreases with time to first reach the levels before photoexcitation as expected. However, it continues to decrease further such that in about 15 min we achieve a net decrease in the trans population which is equivalent to the increase we achieved by photoexcitation in the first place. Correspondingly we achieve an increase in the absorbance at 340 nm, indicating an increase in the total cis population. The constrained regions with cis conformation upon photoexcitation and subsequent relaxation have undergone a geometry transformation that is even further constrained.

3.4. Thermal Effects. We have observed that there are two classes of azo linkages in the polymer, relatively flexible and significantly constrained (for example mostly in the side chain and in the backbone). Conformational transition from trans to cis to trans is completely reversible upon photoexcitation in the trans absorption band. Photoexcitation in the cis band associated with constrained geometries has established irreversible complex chain dynamics. We clearly expect that the constrained and flexible regions would have different trans−cis−trans isomerization characteristics and relaxation dynamics. This is further substantiated by bringing about polymer chain perturbation by elevating the solution temperature and following the dynamics by UV−vis spectroscopy. Figure 5 gives the difference absorption spectra of the polymer solution heated to various temperatures with respect to the spectrum at

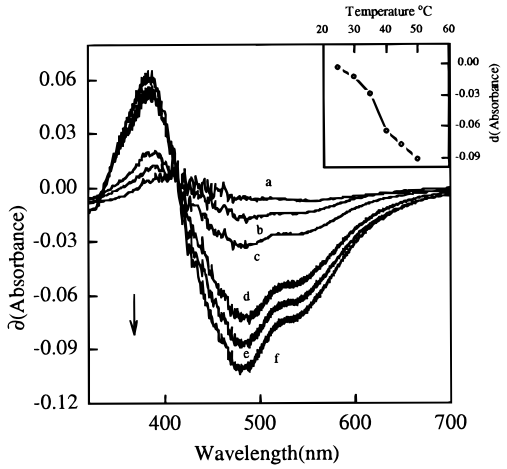


Figure 5. Difference absorption spectra of the polymer in DMF heated to various temperatures with respect to the polymer at 20 °C. The polymer solution was equilibrated at temperatures (a) 25, (b) 30, (c) 35, (d) 40, (e) 45, and (f) 50 °C, and the absorption spectra were recorded at 960 nm/min. Inset is the plot of absolute change in absorbance measured at 470 nm as a function of temperature.

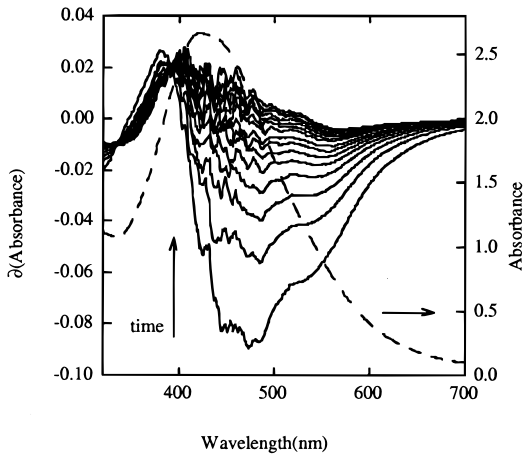


Figure 6. Relaxation of absorbance under ambient conditions after heating to 50 °C. The difference of the spectra with that before heating is plotted as a function of wavelength. The dotted line is the absorption spectrum of the polymer at room temperature.

20 °C. It can be observed that heating the solution causes characteristic changes in absorption features of the polymer. As the temperature is increased more and more constrained cis regions are expected to transform to the flexible trans state. However, it is observed that there is an increase in the constrained cis population immediately after heating the solution with a corresponding decrease in the trans state. This transition is superlinear to 40 °C and continues to increase to 50 °C linearly with somewhat smaller slope (see inset to Figure 5). Both cis and trans bands recovered or depleted upon heating have their characteristic absorption maxima red-shifted by about 60 nm as compared to the photoexcitation scenario. It appears that the change in the conformation caused by heating results in a redistribution of the effective conjugation lengths of the chromophores in the polymer.

Figure 6 gives a series of difference spectra caused by the thermal perturbation, induced by heating the solution to 50 °C, as it cools to room temperature. It can be observed that the macromolecular conformations

do relax but irreversibly. Upon heating to an elevated temperature, constrained cis regions convert to expanded trans forms and vice versa, leading to a modified geometry for the polymer chain. Upon cooling, the trans and cis populations redistribute but the polymer does not relax to the original low-temperature conformation as new constrained regions are generated. The structural constraints are perturbed, resulting in the change in the local minima of various constrained conformations. The relaxation to a conformation with a changed absorption spectrum implies that the polymer now has a different population of the cis and trans states of the azo group, resulting in a different distribution of conjugation lengths. Through many heating and cooling cycles this excitation−relaxation behavior (rate) is reproducible. However through each cycle the polymer relaxes to a conformation with a different ground-state spectral signature (slightly different cis−trans ratios).

4. Conclusions

A photodynamic polyaniline containing azo functional groups has been synthesized by enzyme-catalyzed polymerization. A unique feature of this polymerization is that isomerization (trans to cis) of the chromophore accompanies the polymerization process. Photodynamic properties of this polymer in a good solvent, such as DMF, is defined by the photoselection of the chromophores in the polymer in their relaxed or constrained conformations. The polymer undergoes photoisomerization upon photoexcitation in the trans band, which relaxes back with a slow kinetics to a conformation having spectral characteristics identical to those before photoexcitation. Upon photoexcitation in the cis band (254 nm), whose presence indicate constrained geometries, or upon thermal perturbation, the macromolecules undergo dynamic conformational changes that are quite different. Upon relaxation the excited polymers return to a final conformation with spectral properties quite different from those before excitation. Through each heating and cooling cycle or excitation in the cis band, a different relaxed conformation is realized.

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