Novel Photoactive Nonlinear Optical Polymers for Use in Optical Waveguides

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ABSTRACT: Photoactive polymers were developed for use in waveguide delineation, which affords the opportunity to laterally define a waveguide through lowering the refractive index in optically exposed areas. Synthesis of a series of photosensitive polymers was reported and their photochemical kinetic behavior characterized. The photoactive group was a dinitrostilbene chromophore which was incorporated as a side chain pendant on a methacrylate backbone. Results obtained revealed that, on irradiation, the chromophore electronic absorption maximum underwent both a hypsochromic shift and oscillator strength reduction which was shown to manifest as a refractive index reduction of more than 0.05 at 1.3 μm. A full investigation of the photochemical kinetic behavior was completed along with analysis of both electronic absorption and infrared spectral data of the bleached polymers. As a comparison, the kinetic behavior of current chromophores utilized in nonlinear optical devices, the nitrostilbene and (dicyanovinyl)hexatriene, as well as the *o*-nitro-*p*-cyanostilbene, was also evaluated. For all chromophores, the donor group was an amine. Kinetic experiments confirmed that the dinitrostilbene chromophore was indeed, quantitatively, the most sensitive and that, in solution, a quantum efficiency as high as 0.11 was measured. The polymers synthesized exhibited promising photochemical properties which would make them interesting waveguide cladding materials, either incorporated in the active layer as lateral cladding or imposing a dielectric loading as the upper cladding layer.

Introduction

Current fabrication technology for NLO polymer devices requires improved materials for waveguide definition by laser initiated photochemistry. These materials must be highly sensitive to irradiation, with the resulting structure both maintaining bulk mechanical strength and exhibiting chemical stability. Polymer device fabrication methods employ a variety of technologies to create waveguides in films. Among those utilized are polymer etching[1,2] encompassing eximer laser ablation, reactive ion etching, and other lithographic techniques, as well as photochemical delineation. Etching techniques can create either rib or channel waveguides by polymer removal from unmasked areas. This involves either wet chemistry etching of areas previously degraded, in a manner similar to positive resist lithography, or direct laser ablation. In contrast, photochemical delineation[3-6] requires a chemical reaction which modifies the material spectral properties and hence its refractive index, especially at wavelengths close to electronic absorption. By comparison, this technique requires fewer processing steps, can create graded refractive index boundaries rather than abrupt, and offers the opportunity to laser print the waveguide. This work introduces the synthesis, development, and characterization of a novel photosensitive polymer system which should facilitate high speed photochemical delineation of waveguides. A dinitrostilbene chromophore (shown in Figure 2) was chosen for the investigation, as it had molecular characteristics which were both nonlinear and photochemically active. This moiety undergoes, on irradiation, an intramolecular cyclization, and as the polymer does not undergo a major structural change, there is minimal stress developed in the bulk film. The active chromophore was incorporated as a side chain pendant group on a methacrylate backbone host. The polymer spectral properties were characterized as a function of exposure time, and photochemical kinetic experiments were carried out in both the solid state and solution. This was monitored by changes in both transmittance and refractive index in the solid film, and optical density in solution, with irradiation dose.

Photochemical Delineation and Waveguides

There are several critical requirements involved in the photochemical definition of waveguides by photosensitive polymers. First, there must be complete chemical control and homogeneity of the photochemistry. In most cases the waveguide is masked, allowing the reaction to occur outside this region. The chemistry is designed to reduce the refractive index in the exposed areas which allows lateral confinement in the masked region, facilitating waveguide delineation. This is illustrated in Figure 1.

As most nonlinear optical materials are highly absorbing, the irradiation wavelength must be sufficiently removed from the absorption maximum to obtain light penetration through the 10–15-μm multilayer structure, below the active layer. Sensitivity must be high enough therefore to allow efficient reaction at this wavelength. In order to maintain waveguide stability and confinement, the photochemical process must be completely irreversible, both by thermal means and from irradiation. Irradiated areas must also maintain mechanical strength with minimal volume shrinkage and stress development in the affected region. Also the refractive index change created must be large enough to support the waveguide design geometry and confine the light; i.e. the more extreme the bend, the greater the index change between the guide and lateral cladding.

The refractive index is dominated by the electronic absorption spectra of the principal chromophore. This is described in the single oscillator approximation Sellmeier equation,[7] as illustrated in eq 1,

$$n^2 - 1 = \frac{A}{(\lambda_0^{-2} - \lambda^{-2})} + B \qquad (1)$$

where λ_0 is the absorption maximum wavelength, λ is the wavelength at which the refractive index is to be determined, A is a constant proportional to the chromophore oscillator strength, and B accounts for all other absorption contributions. Thus it can be seen that both a lowering

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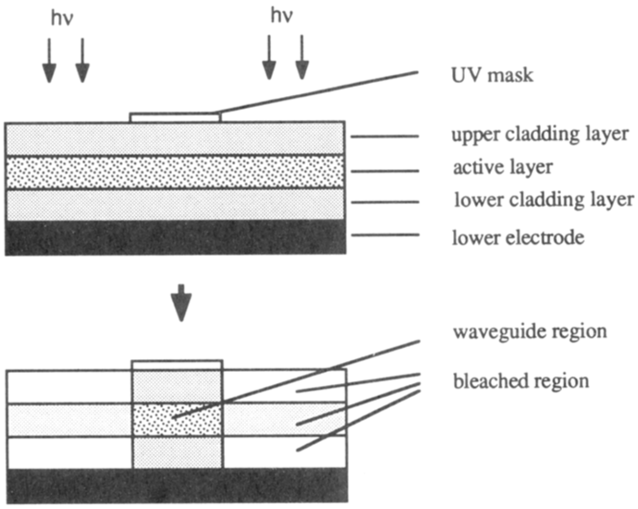


Figure 1. Polymer multilayer waveguide fabrication process by photobleaching.

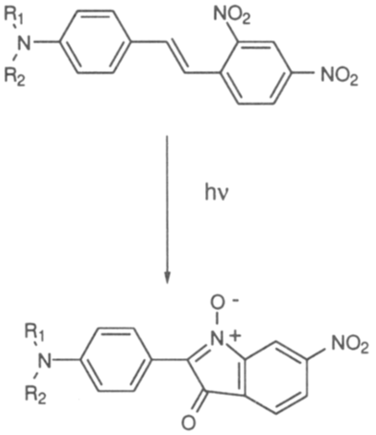


Figure 2. Formation of substituted isatogens on photochemical reaction of dinitrostilbene.

of the chromophores oscillator strength and a hypsochromic shift of its absorption maximum wavelength will effectively reduce the resultant refractive index. This has the potential therefore to laterally define a waveguide if the photochemistry can be tailored to result in either of the above criteria on irradiation outside the guiding region.

Photoactive Methacrylate Polymers

The system chosen for an initial investigation was a copolymer containing a chromophore which had both photochemical and nonlinear optical activity. The chromophore, a dinitrostilbene, shown in Figure 2 along with its subsequent photoproduct, has a suitable molecular structure to enhance its second order nonlinear effects. Previous research[8,9] has developed structure–property relationships designed to optimize nonlinear susceptibility, and this molecular engineering approach was used for chromophore conception. As can be seen, there is π orbital conjugation throughout the length of the molecule, with donor–acceptor functionalities at both ends. This allows an asymmetric electronic charge distribution of the delocalized π orbitals which has been shown to maximize the molecular hyperpolarizability β, an intrinsic factor in enhancing nonlinear activity.

Research has previously shown[10] that *o*-nitrostilbenes, on irradiation, undergo an irreversible intramolecular cyclization to form isatogens. This is believed to occur through a series of pericyclic transformations, with the kinetics of subsequent steps after photon absorption being thermally controlled. These experiments have shown that among the most sensitive of this class of compounds is the 2,4-dinitro-4′-(dimethylamino)stilbene. On irradiation, this was shown to form primarily the 2-(4-(dimethylamino)phenyl)-6-nitroisatogen as well as other byproducts. Solution quantum efficiencies at wavelengths close to λ_{max} were reported to be of the order of 5%.[10] This represents a considerable improvement on data obtained from the (dimethylamino)-4-nitrostilbene chromophore.[11]

A methacrylate polymer backbone was chosen to host the chromophores as pendant side groups. This was selected due to its ease of monomer synthesis, transparency, and suitable polymer properties such as T_g. Due to the intractability of the homopolymer, methyl methacrylate was introduced as a comonomer to improve solubility.

Experimental Section

Materials. Solvents and starting materials were purchased from Aldrich and used without further purification.

Apparatus. Refractive index measurements were carried out using a Metricon prism coupler and YAG laser. A Spectra Physics argon ion laser with a coherent digital photodetector was used for photochemistry kinetics experiments.

Synthesis of *N*-[4-(*N*-(2-Hydroxyethyl)-*N*-methylamino)benzylidene]aniline (1). Into a three necked flask fitted with a condenser and Dean Stark trap was added 4-[*N*-(2-hydroxyethyl)-*N*-methylamino]benzaldehyde (100 g, 0.56 mol) and toluene (600 mL). The mixture was stirred and warmed to 60 °C until all the aldehyde had dissolved. To this was added a slight excess of aniline (57 g, 0.62 mol) and the resultant solution heated to reflux. The reaction was monitored by observing the volume of water produced, which was collected in the Dean Stark trap. When no more water was observed to be condensing, the solution was cooled and about half the solvent removed under reduced pressure. To this concentrated solution was added an equivolume amount of hexane and the mixture stirred then cooled in an ice bath. Crystallization of the product occurred, which was collected by filtration and then dried. Purification was carried out by recrystallization from a 1:1 volume mixture of ethanol and ethyl acetate. Yield: 117 g, 86%. Mp: 121 °C.

Synthesis of 4-[*N*-(2-Hydroxyethyl)-*N*-methylamino]-2′,4′-dinitrostilbene (2). 2,4-Dinitrophenylacetic acid (135 g, 0.6 mol) was added to toluene (1000 mL); then the mixture was stirred for about 15 min in a three necked light shielded flask fitted with Dean Stark trap and condenser. The Schiff base (1) (120 g, 0.47 mol) was then slowly added and the mixture allowed to stir overnight during which the formation of the slightly darker carboxylate intermediate occurred. Acetic acid (60 g, 1 mol) was slowly added and the solution heated to reflux for 2 h. Evolution of CO_2 indicated that decarboxylation had occurred. The solution was cooled and half the solvent removed under reduced pressure. An equivolume equivalent of hexane was then added and the solution cooled in ice. The crude solid product formed on crystallization was collected by filtration and dried. This was then recrystallied from a 1:1 2-propanol–ethyl acetate mixture. Yield: 121 g, 74%. Mp: 189 °C. ^1H NMR ($CDCl_3$), δ: 3.29 (s, 3H), N—CH_3; 3.74 (t, 2H), –CH_2–; 4.12 (t, 2H), –CH_2—O–; 6.94 (d, 2H) Ar H's ortho to NR_2; 7.67 (m, 4H) $CH{=}CH$, Ar H's meta to NR_2; 8.08 (d, 1H) Ar H para to NO_2; 8.44 (d, 1H) Ar H meta to NO_2; 8.87 (s, 1H) Ar H ortho to NO_2.

Synthesis of 4-[*N*-(2-Methacryloylethyl)-*N*-methylamino]-2′,4′-dinitrostilbene (3). To a solution of the stilbene alcohol (2) (50 g, 0.15 mol) in ethyl acetate (250 mL) was added (dimethylamino)pyridine catalyst (1.8 g, 15 mmol), methacrylic anhydride (27 g, 0.18 mol), and pyridine (40 g, 0.44 mol). The reaction mixture was allowed to warm to 50 °C, protected from light, and stirred overnight. The solvent was then reduced by half by vacuum rotoevaporation and hexane (1000 mL) added. On cooling, the product crystallized out and was collected by filtration. This was then purified by recrystallization from a 2:1 ethyl acetate–2-propanol volume mixture. Yield: 49 g, 82%. Mp: 133 °C. ^1H NMR ($CDCl_3$), δ: 2.11 (s, 3H), –CH_3; 3.32 (s, 3H), N—CH_3; 3.75 (t, 2H), –CH_2–; 4.56 (t, 2H), –CH_2—O–; 5.69 (s, 1H), =CH–; 6.28 (s, 1H), =CH–; 6.98 (d, 2H), Ar H's ortho to NR_2; 7.79 (m, 4H), $CH{=}CH$, Ar H's meta to NR_2; 8.15 (d, 1H), Ar H para to NO$_2$; 8.50 (d, 1H), Ar H meta to NO$_2$; 8.93 (s, 1H), Ar H ortho to NO$_2$.

Synthesis of Polymer 4. A solution of dinitrostilbene monomer (**3**) (30 g, 75 mmol) in γ-butyrolactone (150 g, 25 wt % total monomer concentration) was warmed to 64 °C and degassed by vigorously bubbling argon through the mixture for 2 h. Previously degassed methyl methacrylate (7.54 g, 75 mmol) was then injected through a rubber septum into the reaction mixture. After an additional 20 min, an aliquot from a solution of AIBN (0.369 g, 1.5 mol % total monomers) in γ-butyrolactone (2 mL) was also injected. (In total, four aliquots (0.5 mL each) were injected at intervals of approximately 2.5 h.) It was found experimentally that such high levels of initiator were necessary to afford good polymer yield. Both inlet and outlet needles were then removed and the contents of the sealed vessel allowed to stir at 64 °C for 18 h. This resultant solution was diluted to 3 times its original volume with dichloromethane and then precipitated into a 5-fold excess of ethyl acetate. The product was collected by filtration, then redissolved in THF, and precipitated into 2-propanol. Purification was further carried out by successive reprecipitation of the polymer solution in dichloromethane into ethyl acetate until no monomer was observed to be present in the polymer by either HPLC or TLC. For reprecipitations, the polymer solution was made as dilute as possible. This improved the quantity of monomer which remains in solution after precipitation and facilitates the purification process.

Preparation of 2-Nitro-4-cyano-4′-(dimethylamino)stilbene. A solution of *p*-tolunitrile (40 g, 0.342 mol) in H$_2$SO$_4$ (50 mL) was slowly added to a chilled 3:1 volume mixture of H$_2$SO$_4$ (100 mL) and HNO$_3$ (33 mL). The temperature was maintained at under 10 °C throughout. The *o*-nitro-*p*-tolunitrile product formed as crystals and was collected by filtration, rinsed in water, and then recrystallized from 2-propanol. Yield: 87%.

o-Nitro-*p*-tolunitrile (25.1 g, 0.155 mol) was mixed with (dimethylamino)benzaldehyde (23.9 g, 0.160 mol) and piperidine (5 g, 55.8 mmol); then the mixture was heated to 120 °C with stirring. This afforded a dark red product which was collected and then recrystallized from a 4:1 volume equivalent of ethyl acetate and 2-propanol. Mp: 189 °C. Yield: 68%. ^{1}H NMR (CDCl$_3$), δ: 3.05 (s, 6H), N—CH_3; 6.69 (d, 2H), Ar H's ortho to NR$_2$; 7.42 (m, 4H), CH=CH, Ar H's meta to NR$_2$; 7.70 (d, 1H), Ar H para to NO$_2$; 7.88 (d, 1H), Ar H meta to NO$_2$; 8.14 (s, 1H), Ar H ortho to NO$_2$ and CN.

Results. The synthesis of a series of polymers containing the photoactive chromophore as a pendant side chain group was completed, and an example is shown in Scheme 1. Table 1 shows experimental, physical, and molecular weight data for the polymers synthesized, while Chart 1 gives a summary of the polymer molecular structures. Solution studies were carried out using the dimethylamino model compounds of the side chain chromophores as well as the *p*-cyano-*o*-nitrostilbene moiety, which should exhibit reaction kinetics and sensitivity similar to those of the dinitrostilbene. These are shown in Tables 3 and 4. Terpolymers containing the photochemically less sensitive but nonlinearly active aminonitrostilbene were also targeted to examine whether selective photobleaching of the dinitro chromophore can be achieved. The synthesis of the aminonitrostilbene and (dicyanovinyl)hexatriene monomers and polymers has been previously described.[12]

Discussion. Preparation of the dinitrostilbene alcohol was facilitated through the Schiff base intermediate (**1**). In this case the Schiff base was isolated to improve purity of the final product. On addition of the benzenecarboxylic acid, a Knoevenagel condensation occurs, affording an intermediate which, on addition of the acetic acid, undergoes decarboxylation to give the stilbene alcohol (**2**) in good yield.[12] The monomer (**3**) is then formed on nucleophilic substitution of the anhydride by the alcohol (**2**) with pyridine as base in the standard way. Again, a good yield was obtained. It was necessary to exhaustively purify the monomer by both recrystallization and chromatography in order to ensure a high yield of polymer. However even with the pure monomer, free radical polymerization using AIBN catalyst was inefficient unless high levels (1–2 mol %) of initiator were used. This was felt at least in part due to the intrinsic chain transferability of the dinitrostilbene moiety with its reductive potential. In all cases the resultant polymer was of low molecular weight. This was confirmed by size exclusion GPC using the universal calibration method to calculate the number average molecular weight (M_n). It was also observed from this that as the nitro group concentration in the polymer increased, the molecular weight decreased.

Scheme 1

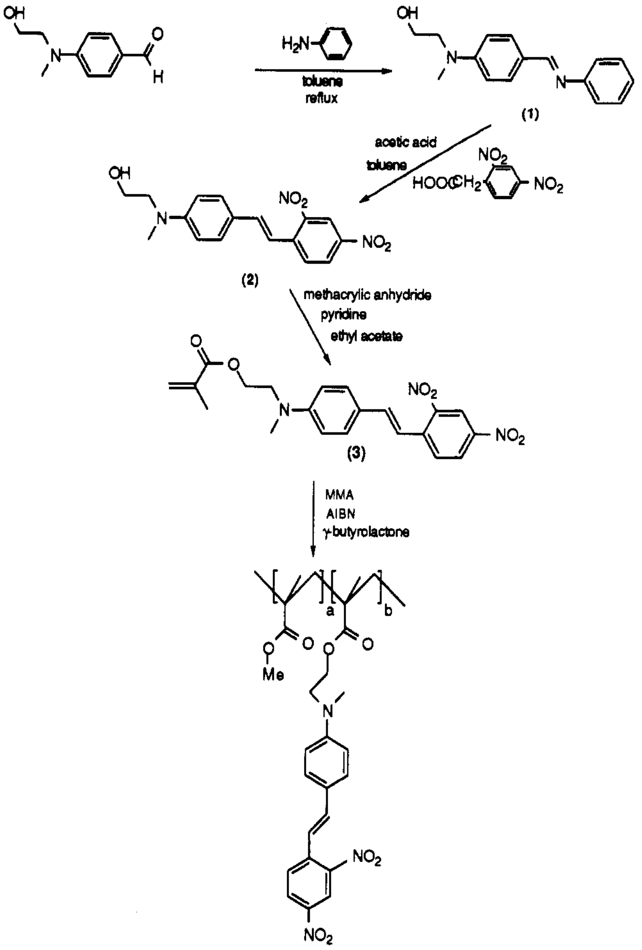
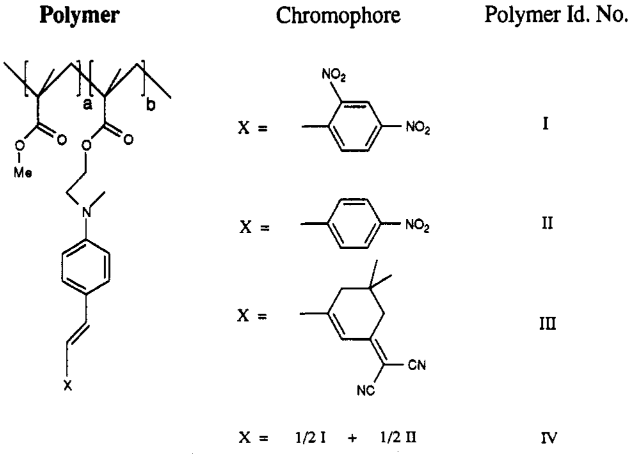


Table 1. Properties of Synthesized Polymers

polymer ID no.	polymer composition X/MMA	yield (%)	T_g (°C)	M_n
I	5050	87	151	415 000
II	50/50	91	142	622 000
III	49/51	82	126	152 000
IV	24/26/50	74	133	62 000

Chart 1



Photoactivity

Reaction Kinetics. A detailed understanding of the kinetics of the photochemistry process is necessary to determine both the concentration and refractive index profiles through the plane during irradiation. As the intrinsic absorption of the chromophore is so high, even thin films will show an irradiation intensity gradient between the front and rear planes normal to the incident light. A concentration gradient through the film which manifests as a refractive index profile is created. In the experimental setup, the transmission of argon ion laser irradiation at both 488 and 514 nm through a thin polymer film was measured with time. However, as this was both the irradiation and analyzing wavelength, there was observable photoproduct absorption (see Figure 6) which had to be accounted for in the kinetics analysis. For the case where the photoproducts have measurable absorption at the analyzing wavelength, an approximate solution[13] has been derived for short reaction times. Let the absorbing species have an initial concentration of C_0 and after time t of C. The irradiation intensity at the film surface is I_0 and at depth x through the film is I. The initial material absorption coefficient is $a = \sigma(N/V)$ where σ is the absorption cross section and (N/V) is the number density of the absorbing species. The absorption coefficient of the sum of all products is b. The quantum yield for the photochemical reaction is Φ.

$$\mathrm{d}L/\mathrm{d}x = -(a-b)CI - bC_0I \tag{2}$$

$$\mathrm{d}C/\mathrm{d}t = -\Phi aCI \tag{3}$$

Equation 2 is a modification of the Beer–Lambert law, and eq 3 is the photochemical reaction rate expression. For small reaction times (when $C/C_0 \approx 1$), solving for both C and I, these become

$$I = I_0\left[\frac{\mathrm{e}^{-aC_0x}}{\mathrm{e}^{-\Phi(a-b)I_0t}(1-\mathrm{e}^{-aC_0x}) + \mathrm{e}^{-aC_0x}}\right] \tag{4}$$

$$C \cong C_0\left[1 + \left(\frac{a}{a-b}\right)\frac{\mathrm{e}^{-\Phi(a-b)I_0t}e^{-aC_0x} - \mathrm{e}^{-aC_0x}}{\mathrm{e}^{-\Phi(a-b)I_0t}(1-\mathrm{e}^{-aC_0x}) + \mathrm{e}^{-aC_0x}}\right] \tag{5}$$

Assuming transmittance through the film $T = I/I_0$ and that $T_0 = \mathrm{e}^{-aC_0d}$ where d is the thickness, then it can be shown that

$$\ln\left[\frac{(1-T)T_0}{(1-T_0)T}\right] \cong -\Phi(a-b)I_0t \tag{6}$$

The quantum yield for a photochemical reaction can thus be determined from a plot of $\ln[(1-T)/T]$ versus time. At short reaction times, the tangent to the curve should have a slope $\Phi(a-b)I_0$. Electronic absorption spectrometry was used to determine both starting and final absorption coefficients.

In solution, it is assumed that the mobility of both reactants and products is sufficient to prevent a concentration gradient from forming through the plane of irradiation. The quantum yield can then be expressed as shown.

$$\Phi = \frac{\mathrm{d}[A_0]/\mathrm{d}t}{I_{\mathrm{abs}}} \tag{7}$$

where $\mathrm{d}[A_0]/\mathrm{d}t$ is the initial rate of reaction and I_{abs} is the power of absorbed radiation. This can readily be measured by monitoring the reactants spectral absorption with time. If the extinction coefficient at the analyzing wavelength is known, then the concentration change can be calculated directly from absorption values.

Results. Both electronic spectral kinetic and photokinetic data were calculated and collected in Tables 2 and 3.

Discussion. As can be seen, incorporated as a pendant group in a polymer film, the dinitrostilbene chromophore was almost 1 order of magnitude more sensitive than the hexatriene or the nitrostilbene moieties. Transmission intensity measured through the film, however, may have been subject to errors caused by increased scatter of the bleached region. In all cases, both extinction and absorption coefficients were extremely high around the measurement wavelengths. Interestingly, the $\lambda_{\max}$ wavelengths show a hypsochromic shift from the thin film to the hexane solution. This is evidence of dipolar interactions in the solid state which acts to lower the excited state energy levels of the chromophores.

Table 2. Absorption and Photochemical Reaction Data for Synthesized Polymers

	abs coeff (a) (10^4 cm^{-1})			quantum yield (Φ)	
polymer ID no.	λ = 488 nm	γ = 514 nm	($\lambda_{\max}$ (nm))	λ = 488 nm ($\times 10^{-5}$)	λ = 514 nm ($\times 10^{-5}$)
I	110	95.4	111 (480)	40.4	38.2
II	73.2	39.9	135 (427)	3.24	3.17
III	190	172	191 (485)	5.92	5.57
IV	99.5	74.7	123 (445)	31.3	33.5

In order to minimize experimental deviations from Beers law and possible chromophore agglomerations, the films were made as thin as possible. Simple experimental checks confirmed also that the chromophore concentration was not too high to preclude the use of Beers law theory.

Examples of the kinetic data obtained on analysis of both transmittance and refractive index change as a function of irradiation dose (time) for a thin film are shown in Figures 3 and 4. The experiments were carried out using the argon ion laser at both 488 and 514 nm wavelengths.

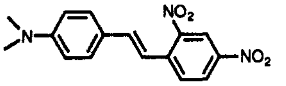
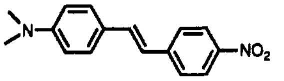
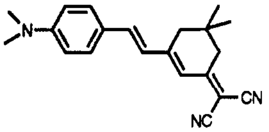
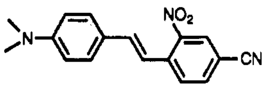
Analysis of the transmission data shown in Figure 3 shows that the graph of $\log[(1-T)/T]$ versus time was not linear. This is consistent with a process whereby the intermediate products have some absorption at the analyzing wavelength. By calculating the tangent to the curve at the initial reaction rate, a measure of the quantum efficiency can be obtained. The refractive index data indicated that even at wavelengths far from resonance (1.3 μm), a substantial index change can be obtained on irradiation. An exact index profile was not calculated, as the WKB analysis method[14] is dependent on first order kinetics and it was not clear from the data if this could be assumed.

In solution, the initial rate method was used in the quantum yield calculations. Analysis was complicated for the *o*-nitrostilbene chromophores, however, as the absorption values after irradiation were unstable due to secondary reactions. The solution sensitivity of both *o*-nitrostilbene chromophores was enhanced to at least 2 orders of magnitude higher than that of the dinitrostilbene thin film. This can be attributed to polymer local free volume restrictions[15] on the molecular rearrangements in the cyclization process. Both *o*-nitrostilbenes had similar quantum efficiencies which were at least 2 orders of magnitude higher than that either of the nitrostilbene or hexatriene moieties. Also, quantum yield values obtained from solution were higher in hexane than in cyclohexanone. This was attributed to possible quenching of the excited state chromophore by the carbonyl group present in cyclohexanone. Although not reported in this paper, solution model chromophore quantum efficiencies were found to be comparable with their corresponding side chain polymers.

Photochemistry

Effect of Irradiation on the Electronic Absorption Spectrum. The solution behavior of the model dinitrostilbene chromophore was shown to be indicative of a

Table 3. Absorption and Photochemical Data for Model Chromophores in Solution

	extinction coeff (hexane) ($\times 10^4$ cm^{-1} dm^3 mol^{-1})			quantum yield (Φ) (hexane)		extinction coeff (cyclohexanone) ($\times 10^4$ cm^{-1} dm^3 mol^{-1})			quantum yield (Φ) (cyclohexanone)	
	λ = 488 nm	λ = 514 nm	(λ_{max} (nm))	λ = 488 nm	λ = 514 nm	λ = 488 nm	γ = 514 nm	(λ_{max} (nm))	λ = 488 nm	λ = 514 nm
	26.2	10.0	29.3 (458)	0.11	0.065	23.2	19.2	23.3 (483)	0.033	0.029
	12.5	4.32	27.4 (408)	3.7×10^{-4}	3.3×10^{-4}	14.3	5.36	28.1 (441)	6.6×10^{-5}	3.5×10^{-5}
	26.9	10.3	30.1 (474)	8.6×10^{-4}	8.0×10^{-4}	30.4	30.7	31.7 (502)	8.5×10^{-5}	5.2×10^{-5}
	19.5	7.8	26.8 (426)	0.073	0.071	16.8	7.8	26.3 (438)	0.025	0.021

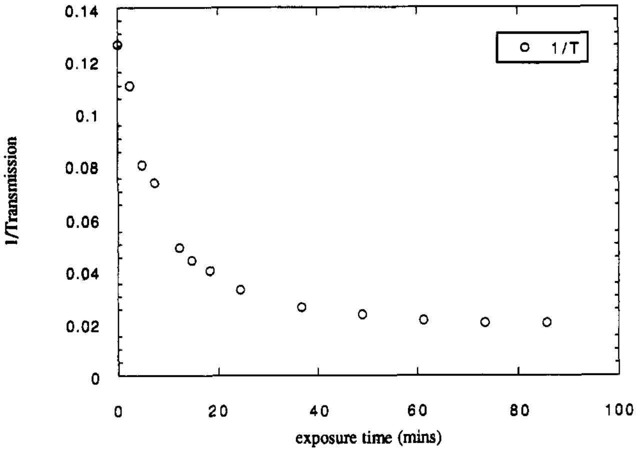


Figure 3. Thin film of polymer I irradiated by an argon ion laser at 488 nm.

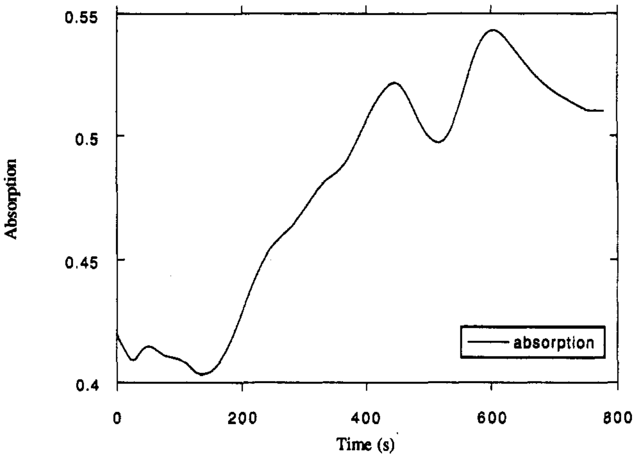


Figure 5. Optical density of a solution of (dimethylamino)-dinitrostilbene in hexane after irradiation. Measured at 480 nm.

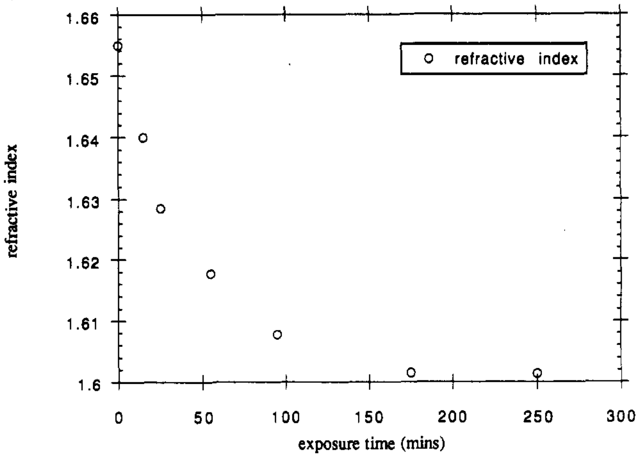


Figure 4. Effect of exposure dose of an argon ion laser at 488 nm on refractive index of polymer I. Measured on SiO_2 substrate at 1.3 μm by prism coupling.

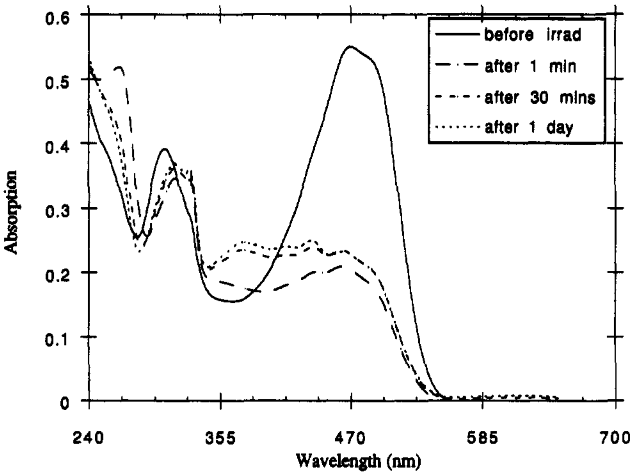


Figure 6. Absorption spectrum of a thin film of polymer I before irradiation using the argon ion laser at 488 nm and then at intervals after irradiation.

multistep chemical scheme. On examination of the UV absorption spectra of the photoproducts after irradiation, a reproducible time dependence was observed. The absorption maximum value was shown to oscillate with time, indicating that secondary processes are occurring independent of photon energy input. This behavior is shown in Figures 5 and 6.

Figure 5 illustrates the time dependent absorption behavior after irradiation of the dinitrostilbene solution in hexane at 480 nm. There is a considerable concentration change of the absorbing species which is believed to be due to thermally activated secondary reactions. Figure 6 shows the full electronic absorption spectra at time intervals after irradiation. Initially, the main absorption peak is at 470 nm, corresponding to the transition between ground and excited states of the complete chromophore. The higher energy peak at around 310 nm has been attributed[10] to the aminostyryl fragment. It can be seen that, immediately after irradiation, new peaks have been formed at 265 and 315 nm, and the main absorption maximums at 470 and 307 nm have been substantially

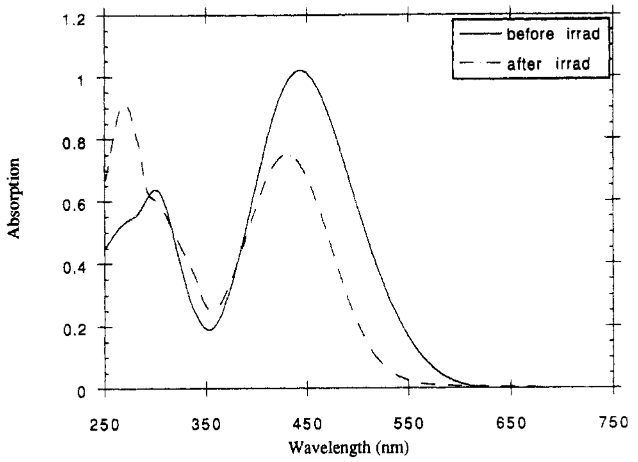


Figure 7. Selective photobleaching of polymer IV. Rapid initial photobleaching occurs until the dinitrostilbene chromophore has completely reacted, leaving the nitrostilbene.

reduced. After a further period of time, the peak maximum at 315 nm increased and a broader maximum at 437 nm was observed, which also intensified with time, while the intermediate peak intensity at 265 nm reduced. The peak at 437 nm is believed to be the transition for the fully conjugated isatogen as it forms after irradiation. The higher energy peaks are associated with aromatic fragments of the molecule. In this case, irradiation was not complete, as seen from the shoulder at 470 nm from the original chromophore.

Figure 7 illustrates the effect on the electronic spectrum of the same dose of irradiation on terpolymer IV. As can be seen, initially, the absorption spectrum is a combination of both individual chromophores. On irradiation, however, the dinitrostilbene chromophore undergoes an intramolecular photochemical reaction whereas the nitrostilbene chromophore remains unreacted. The intensity of the resultant absorption peak at 430 nm is therefore a function of the aminonitrostilbene terpolymer ratio. This illustrates the possibility of selective photobleaching of the dinitrostilbene chromophore and tailoring of the final refractive index through polymer composition.

Infrared Spectral Analysis. Infrared spectra were collected before and after irradiation of polymer I in order to obtain a more detailed understanding of the nature of the photochemistry. It can be seen that peaks assigned to the stilbene C–H out of plane deformation[16] at 960 cm^{-1} are no longer present after irradiation. A reduction in intensity of the NO_2 symmetrical stretching vibration band at around 1337 cm^{-1} was also observed, as was the C=C stilbene stretch at 1600 cm^{-1}. This substantiates the hypothesis that the *o*-nitro group is participating in some sequence of reaction steps which may culminate in formation of the isatogen. A positive isatogen identification was not possible; however the new shoulder at 1680 cm^{-1} suggests the presence of a carbonyl group. The IR spectra before and after irradiation have been collected and shown in Figure 8.

Summary

A range of photosensitive polymers based on the dinitrostilbene chromophore as a pendant group were synthesized, and a full spectral and kinetic characterization was carried out. This revealed that the absorption spectra underwent both a hypsochromic shift and oscillator strength reduction on irradiation. As predicted by the Sellmeier equation, this resulted in a lower refractive index material, thus making it prospectively interesting for photochemical waveguide cladding, either incorporated in the active layer as lateral cladding or imposing a dielectric loading as the upper cladding layer.

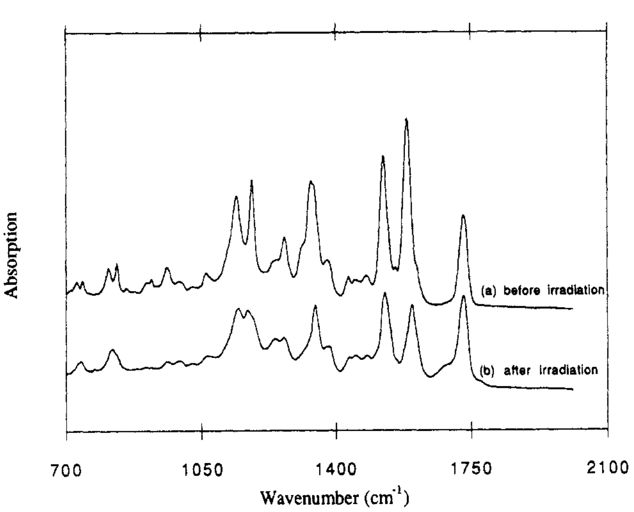


Figure 8. Infrared spectra of a thin film sample of polymer I before and after irradiation.

Quantitatively, it was shown that *o*-nitrostilbene chromophores were more sensitive than both the nitrostilbene and hexatriene chromophores currently utilized in devices and that a refractive index change at 1.3 μm of more than 0.05 could be obtained. The reaction kinetics were more complicated, however, as illustrated by both the absorption behavior after irradiation as well as the nonlinearity of the plot of $\ln[(1 - T)/T]$ versus irradiation dose. In solution, a quantum efficiency as high as 0.11 was obtained for the dinitrostilbene chromophore but could not be reproduced in the solid state.

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