

## Photochemical Generation of Conducting Patterns in Polybutadiene Films

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**ABSTRACT:** Certain polydiene rubbers can be doped by iodine to become electrically conducting. In particular, the conductivity of *trans*-1,4-polybutadiene can be increased by 8 orders of magnitude upon conjugation and self-doping by iodine at room temperature, whereas *cis*-1,4-polybutadiene cannot be made conducting by reaction with iodine under the same conditions. *cis*-1,4-Polybutadiene, however, can be converted into the *trans*-isomer by UV irradiation. On the basis of these previous findings, we have developed a simple and selective method for the photochemical generation of conducting patterns in a nonconducting (iodinated) *cis*-1,4-polybutadiene matrix. This was done by microlithographically patterned photoisomerization of *cis*-1,4-polybutadiene films followed by I<sub>2</sub>-induced conjugation and self-doping of the UV exposed regions. The conducting patterns thus produced have remained stable for 10 months to date. They are colored and show strong fluorescence emission, which enables visualization of the conducting polymer regions. This facile method of conducting pattern generation could make polybutadiene attractive for microelectronic applications.

### Introduction

It is well-known that conjugated sequences with alternating single and double bonds are necessary for a polymer to be electronically conducting.<sup>1</sup> The  $\pi$ -electron conjugated structure has a relatively small energy gap between the valence and conduction bands, with respect to a saturated single or an isolated double bond structure, which facilitates charge transfer upon doping with appropriate electron acceptors (*e.g.*, I<sub>2</sub>) or donors making the polymer conducting. Conducting polymers are of interest for many potential uses in polymer batteries, integrated circuits, field-effect transistors, optical memory storage devices, and electroluminescent and electrochromic displays.<sup>1</sup> The microlithographic formation of conducting patterns is a key prerequisite for most of these applications. With conventional conducting polymers, this is, however, not straightforward, although a few approaches have been recently reported. For instance, Abdou *et al.*,<sup>2</sup> Dao *et al.*,<sup>3</sup> and Cai *et al.*<sup>4</sup> obtained conducting patterns from the soluble form of conjugated polymers, *e.g.*, poly(3-alkylthiophenes), through patterned photo-cross-linking or cross-linking by an electron beam, followed by a solution-based development process. Angelopoulos *et al.*<sup>5</sup> and Venugopal *et al.*<sup>6</sup> demonstrated that conducting patterns can also be made from a mixture of the soluble base form of polyaniline and a photoacid generator, which produced acidic dopants, upon microlithographic irradiation with ultraviolet light, required for generating conducting patterns of the insoluble polyaniline salts. The solubility of the conducting polymers used in these approaches was acquired by covalently bonding conjugated polymers

with soluble side groups or polymeric block chains, which often reduced the conductivity. In addition, the poor solubility of most unfunctionalized conjugated polymers in common organic solvents may limit the general application of the above techniques.<sup>1</sup> On the other hand, Bargon *et al.*<sup>7</sup> and Baumann *et al.*<sup>8</sup> produced conducting patterns through the polymerization of monomers, such as pyrrole, aniline, and thiophene, initiated by HCl which was generated photochemically in a patterned fashion from chlorine-containing polymer matrices, including poly(chloroacrylonitrile), poly(vinyl chloride), poly(chloroprene), and poly(chlorostyrene). The conducting regions formed in these cases are composite materials containing newly formed conducting polymer chains within the nonconducting polymer matrices.

A particularly attractive option is the formation of conducting patterns from a processable (soluble and/or fusible) *insulating* polymeric matrix through, for example, a photochemical transition which can directly convert the microlithographically exposed regions into unsubstituted conjugated sequences. We report here that conducting patterns in an insulating matrix of iodinated *cis*-1,4-polybutadiene can be produced simply by microlithographically photoisomerizing *cis*-1,4-polybutadiene into the *trans*-1,4-isomer followed by I<sub>2</sub>-induced conjugation and self-doping with remaining iodine. The development of our method was based on the previous observations that certain polydienes can react with iodine to become electrically conducting<sup>9,10</sup> and that *trans*-1,4-polybutadiene acquires conductivity upon reacting with iodine at ambient temperature while *cis*-1,4-polybutadiene cannot be made conducting under the same conditions.<sup>9–14</sup> We have previously reported that the reaction between polydienes and iodine could produce conjugated sequences in the polymer backbone through the polar addition of I<sub>2</sub> into the polydiene chains followed by the E-2 elimination of HI, leading to the formation of the conjugated sequences,

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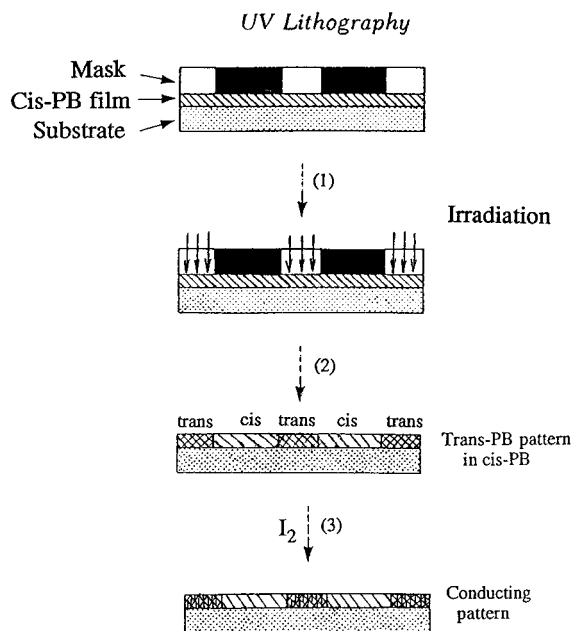
which can be self-doped by iodine to become electrically conducting.<sup>14–17</sup> It has also been shown that the absence of an insulator–semiconductor transition for *cis*-1,4-polybutadiene upon reacting with iodine is due to an unfavorable combination of electronic and steric interactions within the iodinated polymer backbone, which inhibits the E-2 elimination of HI and thus halts the formation of the conjugated sequences required for conductance.<sup>14</sup> However, *cis*-1,4-polybutadiene can be photoisomerized into the *trans*-isomer, and the isomerized material is then amenable to I<sub>2</sub>-induced conjugation and subsequent self-doping with iodine, leading to a semiconductor material.<sup>14</sup>

We have exploited these properties of 1,4-polybutadienes for the microlithographic formation of conducting patterns on a micrometer scale in *cis*-1,4-polybutadiene films. We have found that with use of a microlithographic mask the *cis*-isomer can be photoisomerized in a *patterned* fashion without significant lateral diffusion and that only the photoisomerized regions are capable of generation of conjugated double bonds upon exposure of the entire polybutadiene film to iodine at room temperature. The selective conjugation of microlithographically exposed regions by iodine thus produces conducting patterns consisting of conjugated *trans*-1,4-polybutadiene within a nonconducting matrix of iodinated *cis*-1,4-polybutadiene. In this paper we present the detailed imaging process and the spectroscopic/microscopic evaluation of the resultant conducting patterns.<sup>18</sup> In view of the ease with which *cis*-1,4-polybutadiene can be spin coated, solvent cast, or melt extruded into thin films, this simple and selective method for the generation of patterned conductance in stable polybutadiene thin films is of promise for various practical applications, including fabrication of polymeric microelectronic devices.

## Experimental Section

**Materials.** *cis*-1,4-Polybutadiene (Aldrich, 98% *cis*,  $M_w = 2\,500\,000$  g/mol) and *trans*-1,4-polybutadiene were of commercial origin. The nominal *trans*-1,4-polybutadiene material (Aldrich,  $M_w = 420\,000$  g/mol) consisted, however, of 55% *trans*-1,4-isomer, 36% *cis*-1,4-isomer, and 9% 1,2-addition isomer.<sup>14</sup> No samples with a higher *trans*-1,4-addition content could be sourced commercially. Analytical grade toluene (Aldrich), methanol (Aldrich), reagent grade diphenyl disulfide (Aldrich), and iodine (General Chemical Co.) were used as received.

**Microlithographic Process and Conducting Pattern Formation.** The *cis*-1,4-polybutadiene films (typically, thicknesses ranging from 1 to 10  $\mu\text{m}$ ) were prepared by spin-coating from a 5% (w/w) *cis*-1,4-polybutadiene solution in toluene. The solution also contained 0.3% (w/w) diphenyl disulfide as sensitizer. Spin-coating was performed onto various substrates, including a microscope cover slip, chromium-coated glass, and quartz, and was followed by vacuum-drying. Patterned photoisomerization was carried out by placing a microlithographic photomask on the spin-coated *cis*-1,4-polybutadiene film and exposing the assembly to UV radiation of wavelength 351 nm, generated by an XeF excimer laser (LPX100, Lambda Physik Instrument), with an exposure energy of ca. 1.3 J/cm<sup>2</sup>. The photoisomerized film was then immersed into a solution of iodine in methanol at room temperature. Figure 1 schematically shows the steps of the imaging process. The extent of reaction between iodine and the polybutadiene film was controlled by the time of immersion and the concentration of iodine in the I<sub>2</sub>/MeOH solution. Typically, immersion in an I<sub>2</sub>-saturated MeOH solution for a few minutes was sufficient for the development of the *trans*-1,4-polybutadiene pattern in the initially colorless film. This was evidenced by the appearance of a brassy color in the



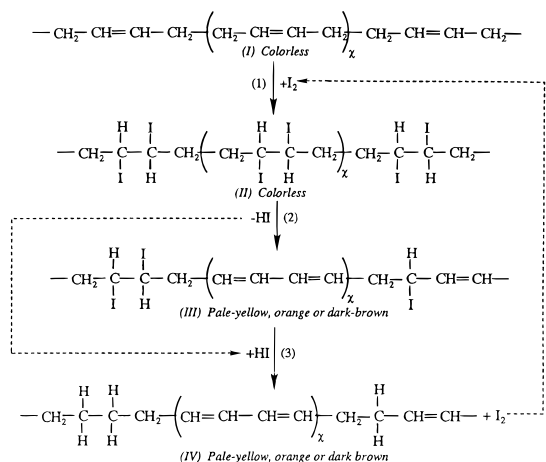
**Figure 1.** Schematic representation of the formation of conducting patterns in *cis*-1,4-polybutadiene films. Patterned exposure to 351 nm excimer laser irradiation results in *cis*–*trans* isomerization of the exposed regions. The photo-patterned structure is then developed by immersion in an iodine/methanol solution.

photoexposed regions upon reacting with iodine. Control of the immersion time was important since prolonged contact with iodine led to deterioration of the contrast ratio, as iodine can also induce *cis*–*trans* isomerization,<sup>14</sup> which, however, was sufficiently slow at room temperature to be negligible over the time required to develop the photoisomerized *trans*-1,4-polybutadiene pattern. The I<sub>2</sub>-reacted polybutadiene film was thoroughly rinsed with pure methanol and vacuum-dried to remove residual unreacted iodine. The resultant brassy (conducting) patterns in the colorless matrix of iodinated *cis*-1,4-polybutadiene were then evaluated by various spectroscopic and microscopic techniques.

In comparison with the conventional I<sub>2</sub>(vapor)-doping method,<sup>19</sup> we noted that the solution method led to a higher selectivity, and hence a better contrast ratio for the resultant conducting patterns, presumably due to kinetic effects. However, apart from this, similar spectroscopic results and conductivity were recorded for the doped samples in both cases. The conventional I<sub>2</sub>(vapor)-doping method was used to fabricate nonpatterned reference films, for spectroscopic investigations, by simply exposing the polymer samples to iodine vapor at room temperature. The extent of reaction with iodine vapor was controlled primarily by the exposure time. The excess, unreacted iodine was pumped off under a dynamic vacuum (ca. 10<sup>–5</sup>  $\tau$ ) prior to spectroscopic analyses.

**Characterization of Polybutadiene Films.** Ultraviolet/visible (UV/vis) absorption spectra were measured on polymer samples cast onto quartz, using a Hewlett-Packard HP-8451A spectrophotometer, while fluorescence spectra of the same samples were recorded on a Perkin-Elmer MPF-4 fluorescence spectrophotometer. Fourier transform infrared (FTIR) spectra of free-standing polybutadiene films were recorded using a Mattson Alpha Centauri FTIR spectrometer. X-ray photoelectron spectroscopy (XPS) analyses were performed on a VG Escalab V spectrometer using nonmonochromatic Mg K $\alpha$  radiation at a power of 200 W.<sup>20</sup> Fluorescence micrographs of conducting patterns formed in the *cis*-1,4-polybutadiene films cast on quartz were recorded using an Olympus IMT2 fluorescence microscope, while corresponding optical microscopic images were made on a Nikon Labophot-2 reflection light microscope. In some cases, the polymer films were cast onto a glass slip precoated with a thin chromium layer in order to obtain a highly reflective surface underneath the polybutadiene film for a high imaging contrast of conducting patterns in

### Scheme 1. Reaction of 1,4-Polybutadiene with Iodine

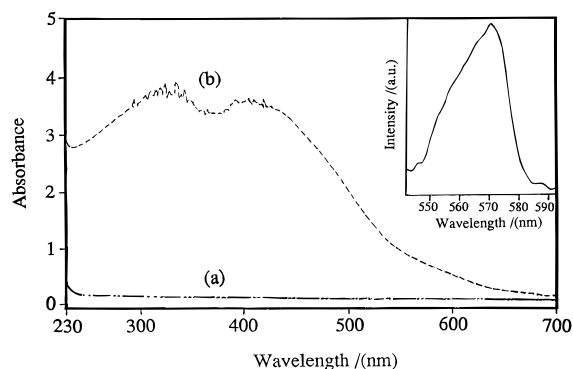


reflection microscopy. The conductivity was measured by using the standard four-probe method.<sup>15,19</sup>

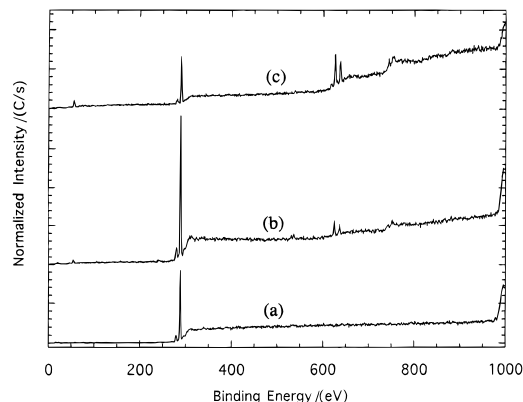
## Results and Discussion

**I<sub>2</sub>-Induced Conjugation of *trans*-1,4-Polybutadiene).** We have previously studied the I<sub>2</sub>-induced conjugation of 1,4-polybutadienes in *solution*.<sup>14</sup> The reaction sequence leading to the formation of conducting polymer from 1,4-polybutadiene upon reacting with iodine is summarized in Scheme 1.<sup>14</sup> The products of reaction between *cis*-1,4-polybutadiene and iodine were quite different from those of its trans-counterpart: for *cis*-1,4-polybutadiene the reaction sequence terminated, at room temperature, at product II, whereas for the *trans*-isomer the reaction sequence proceeded toward product III and/or product IV, thus leading to the formation of conjugated sequences with alternating single and double bonds which can be self-doped by remaining iodine, thus becoming electrically conducting.<sup>1,19</sup> Previous results demonstrated that it was the unfavorable electronic and steric interactions within the iodinated *cis*-1,4-polybutadiene backbone (product II) that inhibited the elimination of hydrogen iodide through the E-2 elimination mechanism (reaction 2 of Scheme 1) at room temperature and hence halted the formation of conjugated sequences in the case of *cis*-1,4-polybutadiene.<sup>14</sup>

Analogous reaction sequences also apply to the reaction between iodine and *trans*-1,4-polybutadiene in the *solid* state, as attested by UV/vis, fluorescence, XPS, and FTIR spectroscopic analyses of the polybutadiene films before and after reacting with iodine vapor. As shown in Figure 2a, the pristine film of *trans*-1,4-polybutadiene is colorless over the range of wavelengths from 230 to 700 nm, as would be expected for an isolated double bond structure. As the reaction with iodine proceeds, the colorless polybutadiene films turn pale yellow and then dark brown. The optical density increased strongly throughout the wavelength region, accompanied by the appearance of two broad peaks at about 300 and 400 nm, respectively, for the heavily doped polymer film (Figure 2b). These changes are closely analogous to those reported for 1,4-polyisoprene upon reacting with iodine vapor in the solid state. The observed absorption peaks have been attributed to charge transfer complexes formed between the newly produced conjugated sequences and iodine.<sup>15</sup> The above results suggest a similar mechanism for the iodine-induced conjugation reactions in polyisoprene and *trans*-1,4-polybutadiene



**Figure 2.** UV/vis spectra of *trans*-1,4-polybutadiene film before and after reacting with I<sub>2</sub>(vapor): (a) unreacted; (b) I<sub>2</sub>-reacted for 27 h. The inset shows the fluorescence emission ( $\lambda_{\text{ex}} = 415$  nm) of an I<sub>2</sub>-reacted *trans*-1,4-polybutadiene film (a.u. represents arbitrary units).

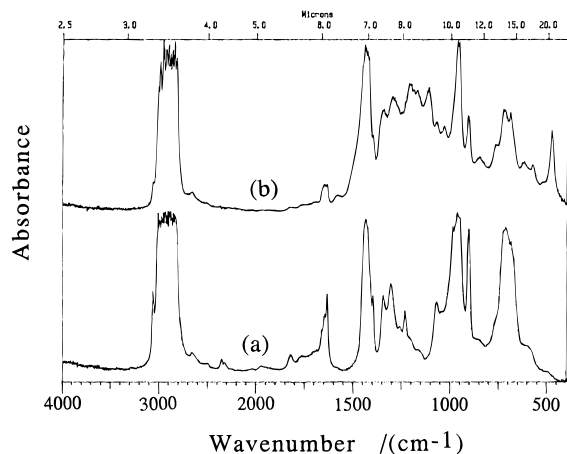


**Figure 3.** XPS survey spectra of the nominal *trans*-1,4-polybutadiene before and after reacting with I<sub>2</sub>(vapor): (a) unreacted; (b) I<sub>2</sub>(vapor)-reacted for 2 h; (c) I<sub>2</sub>(vapor)-reacted for 14 h (C/s represents counts per second).

films. Also included in Figure 2 (inset) is the corresponding fluorescence emission peak recorded with an excitation wavelength of 415 nm. The possibility that structures irrelevant to the newly formed conjugated sequences are responsible for the observed fluorescence emission can be ruled out not only because no emission is observed for the polybutadiene film before or after reacting with iodine vapor for an appropriate period of time shorter than the induction time required for formation of the conjugated sequences (*vide infra*)<sup>15</sup> but also because there is good agreement between the excitation and absorption spectra for the conjugated polybutadiene film.

The addition of iodine to double bonds was detected by XPS analysis (Figure 3). The XPS survey spectrum of the *trans*-1,4-polybutadiene film (fabricated from the sample consisting of 55% *trans*-isomer) contained only a C 1s peak, which was centered at 284.8 eV (Figure 3a). The peak may comprise two components, located at 284.7 and 285.0 eV corresponding to  $\text{—C=}$  and  $\text{—C—}$  structures,<sup>21</sup> respectively, but the presumed components were not resolved (the line width (fwhm) of the C 1s peak of polyethylene on the XPS instrument used was 1.8 eV). A satellite transition associated with the nonmonochromatic X-ray source is also visible at a slightly lower binding energy.

Figure 3b shows the XPS survey spectrum recorded on the *trans*-1,4-polybutadiene film after reacting with iodine vapor for 2 h. The peaks observed at 50 eV (I 4d<sub>3/2</sub> binding energy), 619 eV (I 3d<sub>5/2</sub>) and 630 eV (I 3d<sub>3/2</sub>) are diagnostic of iodine.<sup>22</sup> The broad band located at

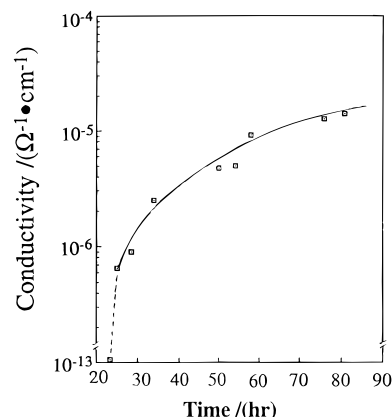


**Figure 4.** FTIR spectra of the nominal *trans*-1,4-polybutadiene (a) before and (b) after being reacted with I<sub>2</sub>(vapor) for 11 days.

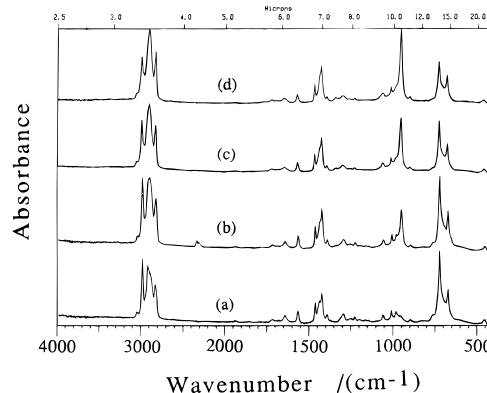
*ca.* 740 eV is assigned to an Auger signal from iodine.<sup>22</sup> The relative intensity of the peaks corresponding to iodine increased on reacting with iodine for longer durations (Figure 3c). The position of the C 1s peak shifted slightly toward a higher binding energy, consistent with a mild electron-withdrawing effect from C–I bonds. Thus, the XPS spectra indicate covalent addition of iodine into the polymer backbone.

The FTIR spectra of the nominal *trans*-1,4-polybutadiene film recorded before and after reacting with iodine vapor provided additional evidence for the reaction of iodine with the polymer backbone. As shown in Figure 4, the spectrum recorded before reacting with iodine (Figure 4a) shows bands at about 715 and 960 cm<sup>-1</sup> attributable to the =CH out-of-plane (bending) deformation of the *cis*- and *trans*-components, respectively.<sup>14,23,24</sup> After reacting with iodine vapor, a new band was observed at 495 cm<sup>-1</sup> while a significant loss of intensity occurred for the bands at about 715 and 960 cm<sup>-1</sup> as well as the band at 1650 cm<sup>-1</sup> associated with a stretching vibration of isolated C=C bonds (Figure 4b). These changes are indicative of the polar addition of I<sub>2</sub> into the –C=C– double bonds of polybutadiene chains (*i.e.*, reaction 1 of Scheme 1). The band at 495 cm<sup>-1</sup> has been previously assigned to a C–I stretching vibration.<sup>14,24</sup> In addition, a broad band appeared at about 1590 cm<sup>-1</sup>, a frequency consistent with the stretching mode of conjugated C=C bonds,<sup>15</sup> and the bands in the region 800–1350 cm<sup>-1</sup> increased considerably in intensity and broadened, leading to a spectrum very similar to that of highly conjugated 1,4-polyisoprene.<sup>15</sup> The above changes in the FTIR spectra are consistent with the iodine-induced conjugation of *trans*-1,4-polybutadiene chains in the polymer film through the addition of I<sub>2</sub> to the isolated double bonds followed by elimination of HI, as shown in Scheme 1. The presence of the strong C–I peak at 495 cm<sup>-1</sup> even after a prolonged reaction with iodine, at least partially, supports the notion that the iodine atoms covalently bonded onto the *cis*-1,4-polybutadiene chains in the nominal *trans*-1,4-polybutadiene sample (see Experimental Section) cannot be eliminated through the E-2 elimination of HI at room temperature.<sup>14</sup>

Figure 5 shows the time dependence of four-probe electrical conductivity for the *trans*-1,4-polybutadiene film during reaction with iodine vapor at ambient temperature. The observed kinetic curve resembles that for the reaction between iodine vapor and 1,4-polyisoprene, suggesting, once again, a similar reaction



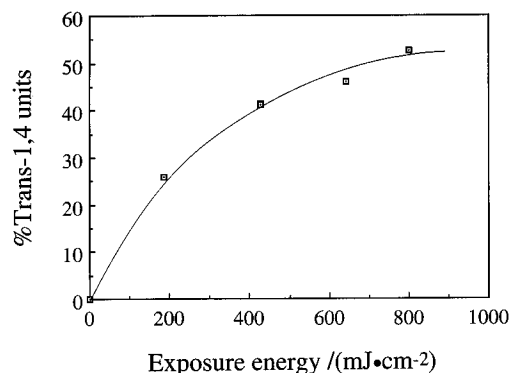
**Figure 5.** Electrical conductivity of the nominal *trans*-1,4-polybutadiene film as a function of the exposure time to iodine vapor at room temperature. The first point in this figure (*i.e.*, the conductivity of the pristine polybutadiene) is from ref 9.



**Figure 6.** FTIR spectra of a *cis*-1,4-polybutadiene film: (a) after fresh spin casting; (b) after UV irradiation for 186 mJ/cm<sup>2</sup>; (c) after UV irradiation for 429 mJ/cm<sup>2</sup>; (d) after UV irradiation for 800 mJ/cm<sup>2</sup>.

mechanism in both cases.<sup>15</sup> As can be seen in Figure 5, the conductivity of the *trans*-1,4-polybutadiene film increased by 8 orders of magnitude, with a long induction time (*ca.* 23 h). This is in good agreement with previous results<sup>11,15</sup> and suggests that the formation of conjugated sequences through Scheme 1 in the solid state is characterized by slow kinetics.<sup>15</sup> Although only modest conductivities of up to 10<sup>-5</sup> Ω<sup>-1</sup>·cm<sup>-1</sup> have been attained in the present study, the conductivity could be, in principle, improved by further optimizing conditions for the I<sub>2</sub>-induced conjugation reaction, probably together with those for the photoisomerization reaction in the case of conducting pattern formation. This is because previous studies<sup>9,14–16</sup> have demonstrated that conduction in the conjugated polydiene system is closely related to the nature of the resultant polymer backbone, indicating possibilities for improving the conductivity through control of macromolecular structures.

**Photoisomerization of *cis*-1,4-Polybutadiene films.** The photosensitized *cis*–*trans* isomerization of 1,4-polybutadiene in solution using diphenyl disulfide as sensitizer has been studied previously.<sup>14,25</sup> The analogous conversion of *cis*-1,4-polybutadiene to the *trans*-isomer can also be achieved in the solid state. Figure 6 shows FTIR spectra recorded on a *cis*-1,4-polybutadiene film containing diphenyl disulfide before and after UV irradiation (351 nm) without using a photomask. The spectrum of the pristine (nonirradiated) *cis*-1,4-polybutadiene film (Figure 6a) shows bands at 715 and 1650 cm<sup>-1</sup> attributable to the =CH out-of-plane

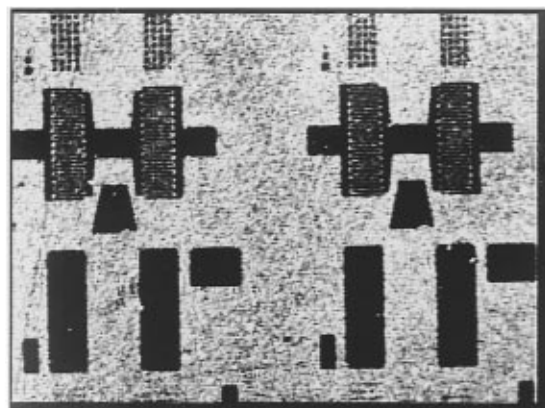


**Figure 7.** Dependence of percentage trans content on exposure energy during the photosensitized *cis*–*trans* isomerization of *cis*-1,4-polybutadiene in the solid state.

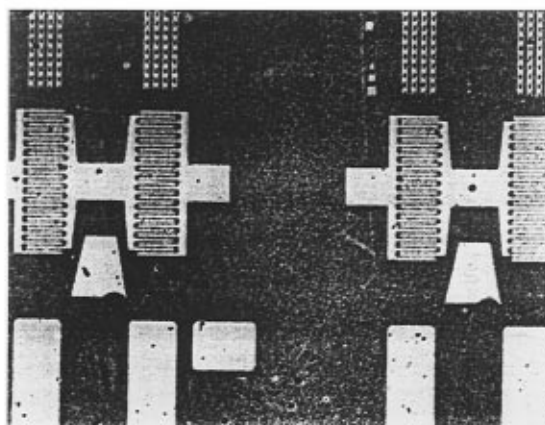
bending of the *cis*-isomer and  $\text{C}=\text{C}$  stretching modes, respectively. The bands at 1450 and  $2700\text{--}3000\text{ cm}^{-1}$  were assigned to  $\text{CH}_2$ - and  $\text{CH}$ - stretching modes of the polymer backbone.<sup>14,23,24</sup> The presence of diphenyl disulfide was mainly manifested by the bands at 450, 660, and  $1560\text{ cm}^{-1}$ .

Upon UV irradiation, the FTIR spectrum changed considerably, most notably by the growth of a band at  $960\text{ cm}^{-1}$  attributable to *trans*-1,4-polybutadiene.<sup>14,23</sup> The intensity of this band increased with the UV exposure energy (Figure 6b–d), while the intensity of the peak at  $715\text{ cm}^{-1}$  arising from the *cis*-isomer decreased considerably. The wavelength region of  $2700\text{--}3000\text{ cm}^{-1}$ , which contained multiple  $\text{CH}_2$ -/ $\text{CH}$ - stretching absorption bands also showed marked changes, from a spectroscopic pattern characteristic of *cis*-1,4-polybutadiene to one more indicative of *trans*-1,4-polybutadiene.<sup>14</sup> These changes in the FTIR spectra clearly indicate the occurrence of photoisomerization of *cis*-1,4-polybutadiene to a mixed polymer film containing a substantial fraction of the *trans*-isomer. The percentage trans content is shown in Figure 7 as a function of exposure energy.<sup>26</sup> The quantum yield of  $\text{C}_6\text{H}_6\text{S}^{\bullet}$  radical formation in the present study was estimated to be 0.033 from a corresponding value of 0.046 reported for photolysis of diphenyl disulfide using  $\lambda = 253.7\text{ nm}$ .<sup>27</sup> For the given amount of the polymer sample under the UV exposure, therefore, we can estimate that on average each  $\text{C}_6\text{H}_6\text{S}^{\bullet}$  radical can isomerize about 300 double bonds before termination, indicating a rather high efficiency with respect to unsensitized isomerization.<sup>28</sup> Up to 79% conversion of the *cis*- to the *trans*-isomer in solution has been recorded by nuclear magnetic resonance (NMR) measurements.<sup>14</sup> When performing the photoisomerization in a patterned fashion, the extent of isomerization was controlled by the irradiation time and monitored by FTIR measurements on a reference film subjected to UV irradiation under the same conditions.

**Formation of Conducting Patterns.** Prior to the fabrication of conducting patterns in *cis*-1,4-polybutadiene films, the reaction between iodine vapor and the photoisomerized *trans*-1,4-polybutadiene film was investigated. Spectroscopic changes similar to those for the reaction between iodine vapor and the commercially available *trans*-1,4-polybutadiene were observed, indicating that the polymer obtained by photoisomerization of the *cis*-isomer behaves in the same way as the commercially sourced *trans*-isomer. Subsequently, patterned photoisomerization was carried out by placing a photomask on the *cis*-1,4-polybutadiene film (Figure 1). The partially exposed film was then reacted with iodine



(b)



(a)

**Figure 8.** (a) Optical microscopy image of a pattern obtained by reacting the patternwise photoisomerized *cis*-1,4-polybutadiene film on chromium-coated glass with an  $\text{I}_2$ -saturated MeOH solution. The dark areas are regions of the conjugated polybutadiene. (b) Fluorescence micrograph of the conducting pattern ( $\lambda_{\text{ex}} \approx 410\text{ nm}$ ).

by immersing the entire film into a saturated solution of iodine in methanol at ambient temperature. The pattern was unobservable after UV exposure but became visible upon development for a few minutes. The  $\text{I}_2$ -reacted sample was thoroughly rinsed with pure methanol and vacuum-dried. The developed areas had a yellow color. An example of the conducting patterns thus generated is shown in Figure 8a, it is a close replication of the photomask structure. Conducting “wires” on a micrometer scale are clearly evident; the spatial resolution is limited by the resolution of the photomask used.

As shown in the inset of Figure 2, the  $\text{I}_2$ -reacted *trans*-1,4-polybutadiene shows strong fluorescence emission. This prompted us to examine the resultant conducting pattern under a fluorescence microscope. A fluorescence microscopic image of the conducting pattern is shown in Figure 8b. It shows the same features as the optical micrograph given in Figure 8a, but with inverse intensities in the image. The dark regions characteristic of the  $\text{I}_2$ -reacted *trans*-1,4-polybutadiene in Figure 8a gave rise to bright fluorescence emission in Figure 8b, consistent with the fluorescence emission originating from the conjugated structures (*vide supra*).<sup>29–32</sup> The dark regions in Figure 8b represent nonfluorescent components associated with the

cis-isomer. As seen under the fluorescence microscope, the intensity of the fluorescence emission increased as the sample was aged, suggesting continuing, slow progress of the I<sub>2</sub>-induced conjugation reaction in the solid state, in agreement with observations made on the reaction between iodine and 1,4-polyisoprene films.<sup>15</sup> Preliminary experimental results indicate that the conducting pattern has remained stable for 10 months in air. The good stability may result from the restricted mobility of the conjugated sequences by the strands of the neighboring polydiene segments, since it has been demonstrated that improved stability of certain conducting polymers, *e.g.*, poly(3-alkylthiophenes), can be achieved by restricting their chain mobility.<sup>33</sup> The longer-term stability of the patterned conducting structures is currently under investigation.

## Conclusions

In summary, spectroscopic and microscopic analyses have demonstrated that patterned photoisomerization can be performed in a thin film of *cis*-1,4-polybutadiene. The photoisomerized *trans*-1,4-polybutadiene pattern thus prepared can be selectively reacted with iodine to give a conducting pattern. The conducting regions comprise conjugated sequences of alternating single and double bonds self-doped with iodine. While the photoisomerized *trans*-1,4-polybutadiene pattern is unobservable after UV exposure, the conducting pattern formed after I<sub>2</sub>-induced conjugation and self-doping has a yellow color and strong fluorescence emission, which enable visualization of the conducting regions. Furthermore, the conducting patterns thus produced have remained stable in an ambient atmosphere for 10 months. The combination of this simple method for the generation of conducting patterns and the fact that *cis*-1,4-polybutadiene can easily be spin coated, solvent cast onto various substrates, or melt extruded into thin free-standing films offer possibilities for novel applications of polybutadiene rubber in, for example, microelectronic devices.

**Acknowledgment.** We thank Drs. D. Winkler and R. Urquhart for discussions and O. Johansen and G. Heath for assistance with some of the spectroscopic measurements.

## References and Notes

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