

Conducting polymer image formation with photoinduced electron transfer reaction

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Conducting polymers are promising materials which show attractive electric and optical properties with potential importance in advanced technologies. Electrochromism is one of the noteworthy characteristics of conducting polymers and is effective in forming conducting polymer images and patterns on an electrode. Space selective image formation is also possible without an electrode by means of the combination of photoinduced electron transfer reaction with electrochromism. This has potential as a novel method of surface modification for any geometry in any place and for micropatterning. In this article, some recent aspects of (1) the electrochromism of conducting polymers and (2) the polymerization and electrochromism of conducting polymers induced by photoillumination leading to image formation are considered from the materials viewpoint. Further, possible future applications for these materials and systems are commented upon.

Traditional photography plays an important role in our life for storing momentary dynamic and transient information, and printing enables us to make large numbers of copies. These technologies have now been extended to digital imaging, 3D holography, lithography for memory devices and related information recording systems. Common to all, is that photoenergy is utilized as a power source. Image formation materials thus play an important role, and high sensitivity and high resolution are required to convert photoenergy effectively and to produce high contrast images. In the conventional photographic process, the image is composed of silver converted from silver halide by photoreduction and the developing process. The quality of images depends on the characteristics of the image forming material. Silver in photography, ink in printing and photopolymers in lithography provide excellent images, but the resulting image lacks additional functionality. It is a passive image. If an image could be composed of a functional material such as a conducting polymer with optical and electrical properties and be formed by photoillumination, it would open up a wide range of applications leading to organic molecular systems with an active image whose activity might be controlled by external stimuli after image formation (Fig. 1).

It was discovered two decades ago that shiny poly(acetylene) could be prepared with dramatically different conductivity depending on doping with oxidizing or reducing agents.¹ Numerous other conducting polymers were subsequently developed.² Some were commercially produced and were applied to electronic devices. Particularly, batteries containing conducting polymers as the cathodic material were marketed. Conducting polymers also have great interest because of their optical properties. Changes in the electronic structure resulting from electrochemical doping and dedoping results in different absorption spectra, which could be applied for passive display materials.³ Recently, conducting polymers having certain electronic characteristics have become strong candidates for active displays such as organic electroluminescent devices.⁴ Attention has been focused increasingly on exploiting this new class of conducting polymers for commercial flat panel displays.

Changes in conductivity of eight orders of magnitude (from semiconductor to conductor or *vice versa*) and dramatic color changes with electrochemical stimuli can be achieved

depending on doping and dedoping. Doping a conducting polymer makes the oscillator strength, associated with the valence band–conduction band transition, shift into the free carrier of the visible and infrared region. Therefore, if the energy gap between the valence and the conduction band is large enough, doping will be accompanied by a dramatic spectral change. This phenomenon is particularly induced by electrochemical stimuli and is called electrochromism. However, electrochromism (even for inorganic materials) has not penetrated the display market yet despite having better color variation, wider spectral range, and larger viewing angle and memory effects than liquid crystals. The slower response times in electrochromism due to mass (ion) transport effects limit its application.

Recently, a potential target for the application of electrochromism has been directed toward curtainless smart windows for heat and daylight control, anti-dazzling rear-view mirrors for vehicles, solar panel technology *etc.* Such kinds of electrochromism are also assumed to be applicable to materials for image formation because fast response is not a prerequisite.

In this feature article, some recent aspects of electrochromism in conducting polymers will be considered first. Then, polymerization and electrochromism of conducting polymers induced by photoillumination leading to image formation will be considered from a materials viewpoint. The formation of images with tunable functions (including electrochromism) by illumination will also be discussed from the viewpoint of active images.

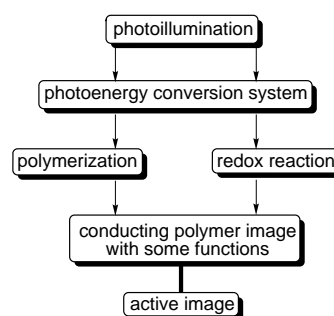


Fig. 1 Pathways to form conducting polymer image with some functions

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Electrochromism in conducting polymers

Electrochromism is one method of image formation and has been investigated mainly among inorganic materials. Inorganic materials show better electrochromic characteristics and reliability and durability although the organic electrochromic materials are gradually improving. Tungsten trioxide (WO₃) based electrochromic devices have already been applied to sunglasses and camera viewfinders (Nikon F5). However, why have such materials not become more familiar in everyday life? It might be due to the slower response times, higher cost, and so on. Color variation is also a problem in inorganic electrochromic materials.

In contrast, organic materials have the advantage in that color variation due to easier molecular design can be produced over a wider range. Chemical substitution of π -conjugated groups or other functional groups in a substance is one approach to realizing this kind of modification and to adjusting properties. This approach is particularly effective in organic conducting polymers because the electronic state of their large π -conjugated polymer backbone system is very sensitive to chemical or physical modifications. Further, by utilizing conducting polymers, conventional and simple film manufacturing process can be applied in device fabrication because polymers are more flexible and processible than low molecular mass materials. On this basis, many kinds of electrochromic conducting polymers have been reported. These are broadly divided into three categories; (1) electrochromic conducting polymers, (2) electrochromic conducting polymers with electrochromic dopants, (3) electrochromic conducting polymers with inorganic electrochromic materials.

Electrochromic conducting polymers

The electrochromic characteristics of conducting polymers were reported for poly(*N*-methylpyrrole) by Diaz *et al.* in 1981⁵ and extensive work has been carried out since then. Initially, target conducting polymers were focused on poly(pyrrole), poly(aniline), poly(thiophene) and their derivatives. For poly(pyrrole), it was found that oxidation of pyrrole led to a black powder with high conductivity in 1968 by Dall'Olio *et al.*⁶ However, the electrochemical characteristics of poly(pyrrole) have been more intensively studied since the preparation of a conducting film by electropolymerization.⁷ Generally, poly(pyrrole) was prepared by electropolymerization with a constant current or constant potential method, *e.g.* for the constant potential method, pyrrole was electropolymerized by applying 0.8–1.3 V (*vs.* standard calomel electrode SCE) to obtain a film with reasonable mechanical stability.⁸ The film obtained exhibited a single reversible redox couple at around -0.2 V (*vs.* SCE) in its cyclic voltammogram. The film is brown-black in the oxidized state, and turns pale-yellow on going to cathodic potential. Several kinds of pyrrole derivatives such as *N*-substituted pyrroles were polymerized and their electrochromic characteristics were studied.⁹ Further, several anions were investigated as dopants to extend the color variation. However, almost all of these films showed limited color changes from brown-black or -red in the oxidized state to pale yellow in the neutral state, despite the fact that the conductivity of poly(pyrrole derivatives) is sensitive to substituted groups and dopants.¹⁰

For poly(thiophene derivatives), their electrochromic characteristics have been intensively studied since 1982–1983.^{11–13} Poly(thiophene) showed a change from blue in the oxidized state to red in the neutral state. Despite this limited color variation and the lack of a colorless state, poly(thiophene derivatives) are expected to be promising electrochromic conducting polymers. It has been reported that the response time between each state is several tens of milliseconds and that color changes can be cycled more than 10⁵ times

without serious damage to the polymer.¹⁴ This electrochromic characteristic seems to be better than that of poly(pyrrole). Poly(thiophene) has other advantages relating to chromic properties. Substitution of alkyl groups on the thiophene ring gave a polymer soluble in organic solvents on reduction. Solutions containing poly(3-alkylthiophene) showed solvatochromism as well as electrochromism.¹⁵

Further, poly(3-alkylthiophene) enables Langmuir–Blodgett films to be prepared when mixed with stearic acid.¹⁶ This possibility is useful in preparing thin films for chromic devices. In order to prepare pin-hole free flexible thin films and to narrow the absorption band, oligothiophene of well-defined structure was substituted on a non-conjugated vinyl polymer as side chain pendant, and its electrochromic characteristics were studied.¹⁷ This polymer underwent a reversible clear color change from green to yellow and *vice versa* in contrast to common poly(thiophene) with its electrochromic color change from red to blue. This kind of π -conjugated system pendant polymer is expected to lead to a new family of organic π -electron systems.

The electrochromic characteristics of poly(aniline) were pointed out at an early stage,¹⁸ but work was only intensively begun since 1984.¹⁹ One of the most attractive advantages for poly(aniline) as compared with the above mentioned conducting polymers is color variation. Poly(aniline) showed multiple color changes from pale yellow to green, to blue, to deep purple at -0.2 to 1.0 V (*vs.* SCE).¹⁹ This electrochromic behavior was unstable on repetition over this potential range, but was very stable with repetition of more than 10⁶ times if the potential range was limited to that causing a color change from pale yellow to green or *vice versa*. This performance is better than other conducting polymers.

Poly(aniline) was commonly prepared *via* chemical or electrochemical oxidation in acidic solution. Electrochromic characteristics were also evaluated in acidic solution. Problems using acidic aqueous solution have been reported, for example degradation of poly(aniline) during polarization with wide potential ranges in acidic aqueous solution.²⁰ The preparation and characterization of poly(aniline) and its derivatives in non-aqueous solution without a proton donor have already been reported,^{21–24} and similar color changes as that seen in acidic aqueous solution obtained. By preparing poly(aniline) at a lower temperature, its electrochemical characteristics were improved. The degradation was also restricted by employing a specific counter anion (dopant). The electrochemical characteristics and film properties of poly(aniline) depend on the counter anion, similarly to other conducting polymers. By employing camphorsulfonic acid, the post-cycling stability in acidic solution was improved.²⁵ Extended color variation was attempted by employing chemical substitution of the poly(aniline) backbone. Poly(*N*-naphthylaniline) has been reported to show reversible and durable multicolor changes from pale yellow to red to purple to dark blue at 0.5 – 0.8 V *vs.* Ag/AgCl (Fig. 2).²⁶ The possibility of multicolor electrochromism with colors of blue, green and red (BGR) was also observed by operating three poly(aniline derivatives) of poly(*o*-phenylenediamine) (pale yellow $U \leftrightarrow$ blue), poly(aniline) (pale yellow $U \leftrightarrow$ green) and poly(metanilic acid) (pale yellow \leftrightarrow red) independently (Fig. 3).²⁷ The response time of the color change is also an important factor when materials are applied to electrochromic devices. Very short response times were obtained for poly(2-methoxy- or 2-ethoxy-aniline) films of about 50 nm thickness. The film was mentioned to have adequate contrast and uniformity. This electrochromism required less than 2.5 ms switching time for about 90% conversion in relative transmission at 633 nm for both oxidizing and reducing potential changes.²⁸ The film thickness may be one factor for this very fast response.

Other conducting polymers have also been investigated as novel electrochromic materials. Poly(isothianaphthene)²⁹ and

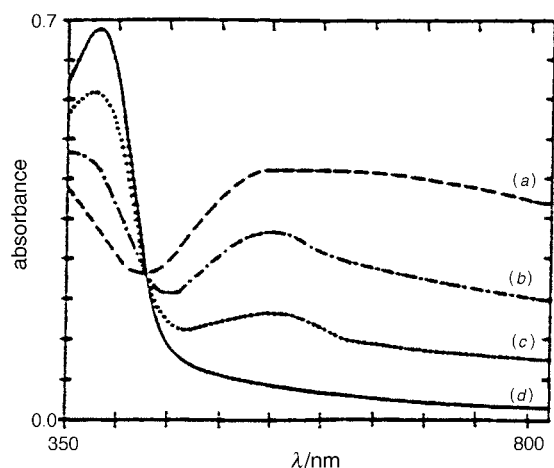


Fig. 2 Absorption spectra of a poly(*N*-naphthylaniline) film dipped in 1 M LiClO₄-CH₃CN at various applied voltages: (a) blue (0.8 V), (b) purple (0.7 V), (c) red (0.6 V) and (d) yellow (0.0 V). (Reproduced by permission from ref. 26.)

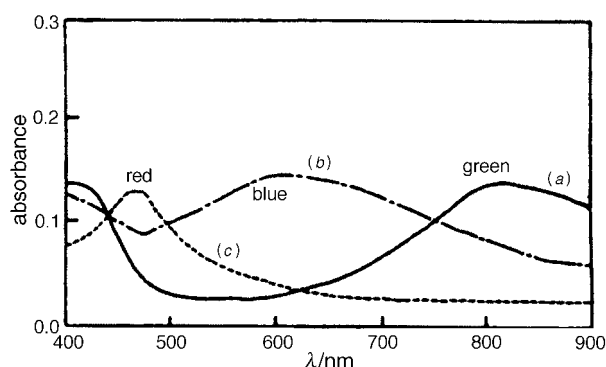


Fig. 3 Absorption spectra of (a) PA, (b) PMA and (c) PPD, films oxidized at 0.6 V (Ag/AgCl) in 0.2 M LiCl containing 0.01 M HCl. (Reproduced by permission from ref. 27.)

poly(*N*-methylisindole)³⁰ showed unique electrochromic character. Each monomer unit has an extra benzene ring with the thiophene or pyrrole unit, and the presence of this extra benzene ring allows resonance structures with quinoid and benzenoid groups, which are expected to affect its electronic properties considerably. Each polymer showed a color change from a colored state to near colorless on oxidation due to absorption in the near infrared but low absorption in the visible region in the doped polymer. This color change is the opposite to that for common p-type conducting polymers. A similar color change from highly opaque to colorless has been reported for poly(dithieno[3,4-*b*:3',4'-*d*]thiophene).³¹ This is expected to have application in optical shutter-like liquid-crystal devices. On the other hand, for multicolor purposes, a series of poly(diarylamines),³² a series of poly(pyrrolopyrroles),³³ metal-complexed poly(thiophenes),³⁴ dinuclear Co^{II} polymer complex with pyrrole substituents³⁵ and a ruthenium complex conducting polymer³⁶ have been reported.

The ruthenium complex conducting polymer is of particular interest. The polymer underwent vivid color changes corresponding to seven stable oxidation states of the ruthenium complex (Table 1). The color observed in each oxidation state is distinct. This film also showed very rapid electrochromic response times for 90% conversion of several tenths of a millisecond. Further, the stability of the film was retained on repeatedly stepping the potential for a total of 5×10^5 cycles. Although the color change is due to the redox reaction of the ruthenium complex, incorporation of a metal complex into a conducting polymer moiety is one way to realize stable multicolor electrochromism.

Table 1 Electrochromic properties of ruthenium complex conducting polymer³⁶

oxidation state	solution color
2	orange
1	purple
0	blue
-1	green-blue
-2	brown
-3	rust
-4	cherry red

Electrochromic conducting polymers with electrochromic dopants

Conducting polymers were commonly prepared *via* chemical or electrochemical polymerization as described above. As-prepared conducting polymers were obtained in the oxidized (doped) state unless subjected to further treatment. Therefore, during polymerization, anions coexisting in the polymerization solution were incorporated into a conducting polymer matrix through electrostatic interaction. If one employed a functional anion showing electrochromic properties as the conducting polymer dopant, its electrochromism can be combined or mixed with that of the conducting polymer. This combination potentially produces the problem of interference of each material resulting in spectroelectrochemical behavior more complex than the simple superimposition of these constitutive building blocks. However, this strategy is useful and an easy method of extending color variation and realizing multicolor electrochromism in a device.

Anionic phthalocyanine was successfully incorporated into a poly(pyrrole) matrix as dopant, and its electrochromic characteristics were studied.³⁷ By scanning a potential ranging from -1.6 to 1.2 V *vs.* SCE, each electrochromism was found independently and four distinct colors could be obtained (Fig. 4). The film was more stable as an electrode material than poly(pyrrole) alone, and had a higher degree of crystallinity. The same research group also examined ferrocene or porphyrin incorporated poly(pyrrole) to obtain stable and durable multicolor electrochromism.³⁸

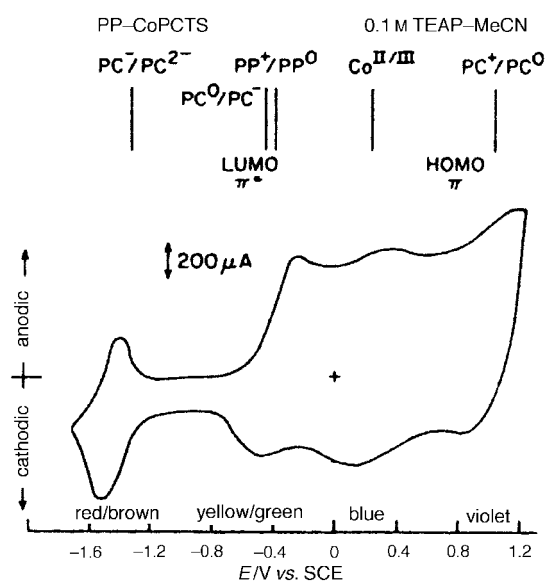


Fig. 4 Cyclic voltammogram of a PP-TSCoPC film on an indium-tin-oxide electrode in 0.1 M TEAP-acetonitrile. (Reproduced by permission from ref. 37.)

Other anionic metal complex was also examined as a dopant for cationic poly(pyrrole).³⁹ Positively charged poly(pyrrole) incorporating quaternized pyridine moieties was prepared and combined with an anionic iron phenanthroline complex. The resulting composite showed electrochromism with color change from bright red to transparent brown within 100 ms (ΔOD : 10–90%). This color change was due to the redox reaction of the incorporated iron complex, with the cationic poly(pyrrole) moiety working as an electron wire. An interesting property of this system is that other electro-optical functions can be introduced by varying the metal complex. When an anionic ruthenium complex was employed as dopant, electrogenerated chemiluminescence was observed in the resulting composite.

Electrochromism is just like a game of ball (electron) between wall (electrode) and player (organic material). Undoubtedly, fatigue (durability) becomes a problem in a player (organic material) sooner or later. Since metal complexes may be classified as inorganic materials rather than organic, their stability and durability imparts sufficient stability and durability on the organic material.

The dopant mentioned above is purely anionic because it is used for p-type conducting polymers which have superior stability compared with n-type. Examples of incorporating cationic dopants into p-type conducting polymers have been also reported. Methylene Blue is a cationic molecule and is known to show a color change from colorless to blue on oxidation. Methylene Blue has been incorporated into poly(pyrrole)⁴⁰ or poly(aniline).⁴¹ The resulting film showed better electrochromism than the conducting polymer alone. In particular, in the case of poly(aniline) doped with Methylene Blue bound to anionic Nafion film, the film had improved mechanical strength. Poly(aniline) not only worked as an electrochromic material, but also provided a conducting network in a Nafion matrix.

Electrochromic conducting polymers with inorganic electrochromic materials

Inorganic materials have also been employed as electrochromic dopants or particles. It is well known that inorganic electrochromic materials have narrow color variation, but excellent durability, reliability and stability. If a suitable combination between conducting polymer and inorganic electrochromic material is achieved, the resulting system would possess both characteristics.

When pyrrole was electropolymerized in suspended solution containing WO_3 particles, WO_3 incorporated poly(pyrrole) was obtained.⁴² Since WO_3 shows electrochromism (colorless to blue in the reduced state) the resulting film showed color change from blue to pale yellow to black with appropriate composition (Table 2).

WO_3 incorporated poly(aniline) was also examined to obtain multicolor changes.⁴³ By changing the potential from negative to positive, the color of the composite film changed from blue, which is due to WO_3 in the reduced state, to pale yellow to green, due to the poly(aniline) in its oxidized state. The combination of conducting polymer and WO_3 has been widely studied and their composite based electrochromic cells have been reported.^{44–46}

Table 2 Dual electrochromisms which will appear under an ideal condition at polypyrrole films containing WO_3 ⁴²

conductivity type	insulating		conducting
composition	reduced PPy and H_xWO_3	reduced PPy and WO_3	oxidized PPy and WO_3
color	pale blue (H_xWO_3)	pale yellow (reduced PPy)	black (oxidized PPy)
	← negative	$E_{WO_3}^0$	E_{PPy}^0 positive →

Prussian Blue is another electrochromic inorganic material. It becomes blue in its oxidized state in contrast to WO_3 . Therefore, it has frequently been used as a counter electrode for WO_3 .⁴⁷ Electrochromic Prussian Blue has also been incorporated into poly(aniline).⁴⁸ Since this color characteristic is similar to poly(aniline), enhanced electrochromism has been obtained in comparison with poly(aniline) alone. In addition, stability over 4×10^4 cycles was observed in its composite films.

The combination of a conducting polymer and another material has many advantages, as described above. Since conducting polymers alone cannot provide sufficient characteristics such as stability and mechanical strength at present, such a combination should help remove the basic problems seen when an electrochromic cell is assembled. This methodology is simple because hundreds of electrochromic materials are potential candidates, but at the same time, mechanistic complexities may be a problem. Such combinations may yet realize outstanding systems.

Photopolymerization leading to conducting polymer images

Electrochromism is one of the most successful ways to obtain conducting polymer images on an electrode. However, on closer inspection of the process and mechanism of electrochromism, one notices that electron transfer between electrode and the material is required to form the image, and color change is difficult without an electrode. If color change including conducting polymer image formation could be realized at any place by external stimuli, this would open up a wide range of applications for image recording systems, micro-patterning, memory devices and microelectronics, as well as image formation.

It is certain that light plays an important role in the microelectronics and computer industries from the viewpoint of high speed information transmission and as an energy source. Therefore, light is a promising candidate as the external stimulus for forming conducting polymer images. On this basis, conducting polymer image formation by illumination has received much interest and many studies have been reported. One way to form conducting polymer images is photopolymerization. As-prepared colored conducting polymers can be obtained in an oxidized (doped) state unless subjected to further treatment. Accordingly, illumination through a suitable mask would produce a clear conducting polymer image on a substrate *via* photopolymerization. Such photopolymerizations leading to conducting polymer images are broadly divided into two categories according to their mechanism (Fig. 5); (1) photopolymerization leading to conducting polymers with photocatalytic systems; (2) photoexcitation of the monomer itself leading to conducting polymers.

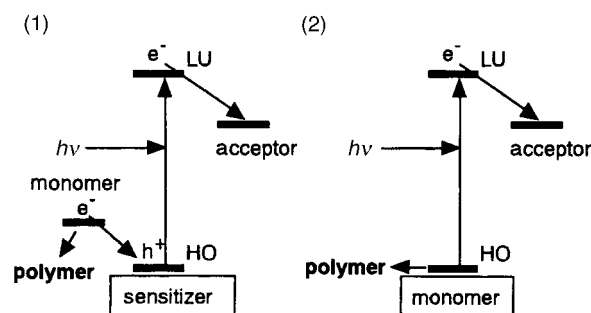


Fig. 5 Schematic representation of each photopolymerization leading to conducting polymer image: (1) photocatalytic system and (2) monomer photoexcitation system.

Photopolymerization leading to conducting polymers with photocatalytic systems

The first attempt involved photoelectrochemical deposition of poly(pyrrole) on n-type GaAs⁴⁹ or n-type Si wafers⁵⁰ under an applied external bias to prevent photodegradation of the GaAs surface in its application in solar cells. The investigation of photopolymerization of conducting polymers for the purpose of image formation was begun about five years later. In the early stages, inorganic semiconductors such as n-type TiO₂⁵¹ deposit and n-type Si wafer⁵² were employed to induce a photoelectrochemical polymerization of pyrrole. In these efforts, an external bias was applied to the semiconductor electrode to perform the polymerization.

However, after pointing out some disadvantages of an electrode system, light-localized deposition of poly(thiophene) and poly(pyrrole) on n-type Si wafer was achieved.⁵³ In this system, photogenerated holes in the n-type Si wafer could oxidize pyrrole or thiophene derivatives initiate polymerization. The remaining electron in n-type Si wafer could reduce Ag ions, which exist in the reaction solution, leads to Ag deposition at the back surface of the Si wafer. Contrast is not sufficient due to the dark and shiny Si wafer surface, but a good light-localized pattern has been reported. The particle size of TiO₂ was also employed to initiate photopolymerization of pyrrole.⁵⁴ Illumination at less than 300 nm in a solution containing Ag⁺, anionic porphyrin, pyrrole and TiO₂ gave poly(pyrrole) on particulate TiO₂. This procedure is effective in modifying the TiO₂ particle surface. The reduction in the size of sensitizing materials may open up a new direction in molecular modification leading to molecular opto-electronics.

In photosensitizing systems, including photopolymerization, photoinduced electron transfer plays an important role. It is certain that photoinduced electron transfer in inorganic semiconductors proceeds with higher efficiency. However, the diminution of the size of features on inorganic materials is limited by processing techniques and quantum effects. Photoinduced electron transfer has also been found in functional molecules. Since these functional units are smaller than inorganic particles and are easily modified by chemical substitution, a system employing photoinduced electron transfer between functional molecules would be useful for easier fabrication of molecular functional systems. On this basis, photopolymerization leading to conducting polymers with photoinduced electron transfer between functional molecules has been performed.

Ruthenium and cobalt complexes were used as photosensitizers and electron acceptors to achieve photopolymerization of pyrrole (Fig. 6).⁵⁵ The conductivity of the photopolymerized poly(pyrrole) was $3 \times 10^{-4} \text{ S cm}^{-1}$ which is lower than that of the chemically polymerized one. However, when each complex was incorporated into a Nafion matrix and was illuminated through a mask, a pattern of poly(pyrrole) with 10 μm width was successfully obtained. A copper complex⁵⁶ was also used as photosensitizer to obtain photopolymerized poly(pyrrole).

A characteristic of the above mentioned molecular systems is that visible light is employed for illumination. In contrast to the above, UV (254 nm) light induced photopolymerization of pyrrole was carried out in halogenated solvent with pyrrole and ferrocene or iron-arene salts.⁵⁷ Photogenerated halogen attacked the growing chain, resulting in the loss of π -conjugation of the poly(pyrrole) obtained. Therefore, a lower conductivity ($10^{-5} \text{ S cm}^{-1}$) and lower electrochemical activity were obtained.

Poly(aniline) was also photocatalytically obtained in the bilayer system composed of ruthenium complex-incorporated Nafion and viologen-pendant-poly(siloxane) in acidic aqueous solutions.⁵⁸ It is interesting that photopolymerization does not occur in acidic solution containing only aniline. *N*-phenyl-*p*-phenylenediamine (PPD, head-to-tail coupling dimer of aniline) was necessary to induce photopolymerization. The

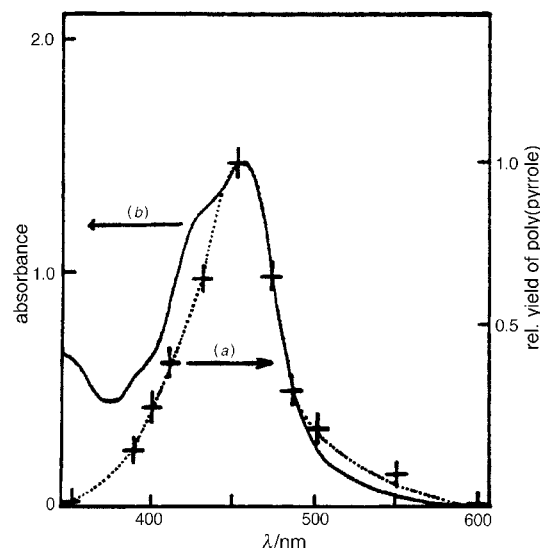
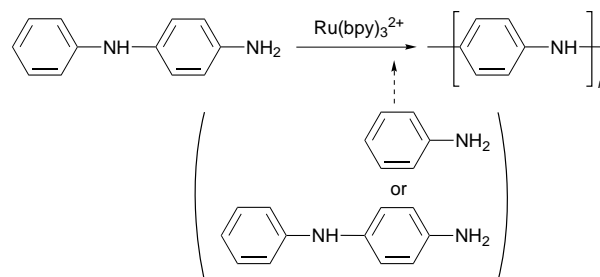


Fig. 6 (a) Wavelength dependence of photo-sensitized polymerization of pyrrole by Ru(bpy)₃²⁺ and (b) absorption spectrum of Ru(bpy)₃²⁺. Relative yield of poly(pyrrole) was obtained from the absorbance change at 800 nm due to poly(pyrrole) formation. (Reproduced by permission from ref. 55.)

photopolymerization mechanism was assumed, and PPD worked as an initiator for the photopolymerization (Scheme 1). When both ruthenium complex and methyl viologen were incorporated in a Flemion matrix, polymerization efficiency was considerably enhanced. A clearly defined image with *ca.* 2 μm could be easily obtained by visible light illumination with a conventional xenon lamp through a suitable photomask (Fig. 7).⁵⁹

Photoexcitation of monomer itself leading to conducting polymer

Another way to induce photopolymerization is by the direct photoexcitation of monomer leading to conducting polymer without photosensitizer. The advantage of this method is to simplify the process of conducting polymer image formation because photosensitizer as a system component to initiate the polymerization is not necessary. 1,2-Poly(azepine) was obtained by photolysis (photopolymerization) of phenyl azides. This photopolymerization was reported to proceed *via* intermediates which in turn were formed from the excited singlet state of phenyl azide, and was performed in either inert gas or solvent. The slightly oxidized polymer obtained was easily oxidized on exposure to I₂ or AsF₅, resulting in a color change and an increase in conductivity to $10^{-2} \text{ S cm}^{-1}$. High-resolution patterns with less than 10 μm width were obtained when the irradiation was performed through a photomask (Fig. 8).⁶⁰ The well-known conducting polymer, poly(pyrrole), was also obtained by photopolymerization without photosensitizer. The procedure is very simple, only involving the exposure of an acidic aqueous solution of pyrrole to sunlight, but it has the



Scheme 1 Schematic representation of the photopolymerization of aniline derivatives with ruthenium complex

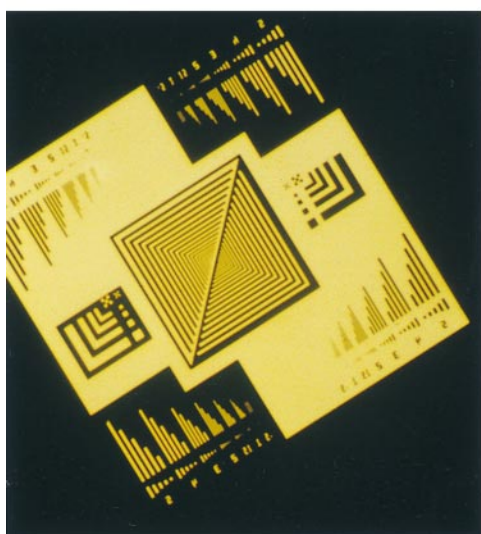
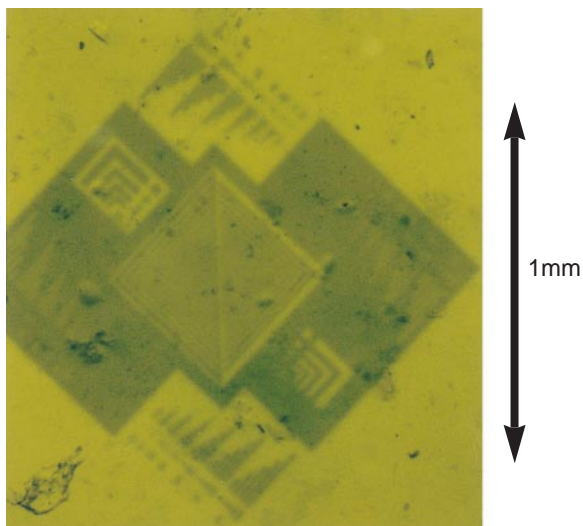


Fig.7 Micrographs of photopolymerized poly(aniline) pattern (top) and photomask (bottom).

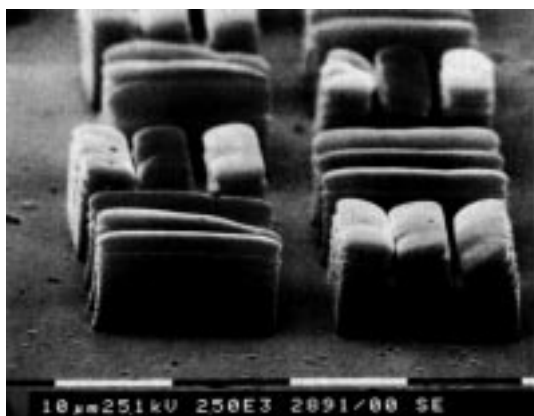


Fig.8 SEM photograph of 1,2-poly(azepine) as grown pattern-wise on fused silica with so-called contact illumination. The bars represent 10 microns. The mask used exhibits equal lines and spacers. (Reproduced by permission from ref. 60)

disadvantage in that it takes a long time to obtain the poly(pyrrole) pattern (100 nm after 15 h).

1,3-Dihydroisothianaphthene (DHITN)⁶¹ or oligothiophene⁶² was photopolymerized in acetonitrile solution in the presence of CCl_4 or *p*-dinitrobenzene as an electron acceptor. In the former case, photopolymerization was initiated by the intermediate which in turn was produced by electron transfer

from DHITN to CCl_4 or oxygen. This photopolymerization seems to include the contribution of photoinduced cationic polymerization. In the latter case, the photopolymerization was initiated by electron transfer from the photoexcited oligothiophene to the electron acceptor. The molecular mass of the polymer obtained was not so high (weight-averaged molecular mass *ca.* 400–700), but it was affected by the concentration of the electron acceptor. Poly(aniline) was also obtained by irradiating an Au electrode with a Nd:YAG laser in a solution containing aniline under an applied external bias.⁶³ Visible Ar laser irradiation also produced polymer on the electrode. A detailed polymerization mechanism is not known, but is of interest from the viewpoint of microprocessing.

From the viewpoint of technological applications of the resulting conducting polymer, photodeposition of amorphous poly(diacetylene derivative) from monomer solution is interesting.⁶⁴ Despite the considerable volume of literature available on solid state polymerization of diacetylene derivatives, solution state photodeposition has never been reported, as far as we know. It was pointed out that the resulting films with thicknesses of 1 μm had optical qualities superior to that grown by standard techniques. The resulting films exhibit good third order non-linear susceptibilities.

Photoinduced electrochromism leading to conducting polymer images

Photoinduced electron transfer is an attractive reaction to convert photoenergy to electrical energy. In the preceding section, it was mentioned that photoinduced electron transfer plays an important role in oxidizing monomers leading to conducting polymers by photoexcited sensitizer. If such a reaction is also applied to oxidize or reduce the reduced or oxidized state of a conducting polymer respectively, combination of photoinduced electron transfer and electrochromism must enable us to induce electrochromism by photoillumination. Photoinduced electrochromism, called photoelectrochromism, has been investigated and reported.

Photoelectrochromism (photooxidation) of poly(*N*-methylpyrrole) on an *n*-Si surface has been performed.⁶⁵ The polymer was photoelectrochemically prepared on an Si surface under an applied external bias. Even though the oxidation of the polymer was performed in this way with a light pulse (photoelectrochromism was not therefore performed only by light) the possibility of optical memory was demonstrated. In this work, the polymer was electrochemically or photoelectrochemically prepared on an Si surface. A simple casting method from polymer solution seems viable. Since this work, the photoredox reaction of conducting polymer with photosensitizer has developed in detail and scope. This research is broadly divided into three categories (two are shown in Fig. 9): *i.e.* (1) photoreduction systems; (2) photooxidation systems and (3) others.

Photoreduction for conducting polymer image formation

WO_3 incorporated poly(aniline) was prepared as a photoelectrochromic film by electropolymerization of aniline in solution containing suspended WO_3 . By illuminating this film, photoexcited electrons generated in WO_3 reduced the oxidized state of poly(aniline) to induce the color change, photoelectrochromism. The reduced pattern could be oxidized by electrochemical reaction *via* electrode, and the repetition of photoreduction and electrooxidation could be cycled (Fig. 10).⁶⁶ TiO_2 was also incorporated in poly(aniline) by the same method as WO_3 incorporation.^{67–69} It is of interest that the photoreduction of deprotonated poly(aniline) can be performed even in aqueous neutral solution. Generally, the deprotonated poly(aniline) (quinone diimine form) is electroinactive despite it being converted to a protonated form. In this system, since methanol added in the reaction solution

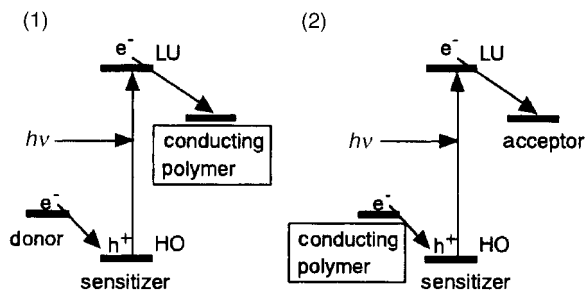


Fig. 9 Schematic representation of each photoredox reaction leading conducting polymer image (1) photoreduction system and (2) photo-oxidation system

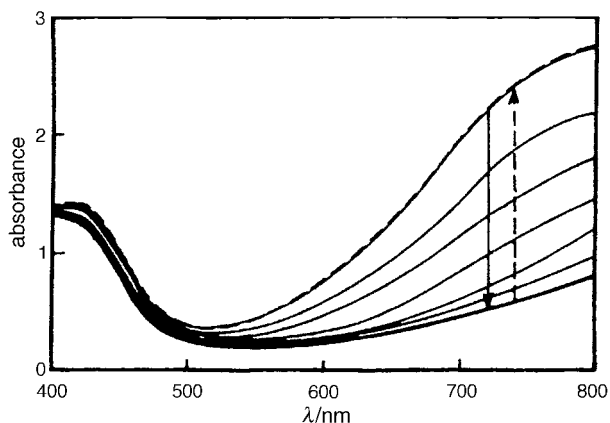


Fig. 10 Change in absorption spectra of poly(aniline)- WO_3 film caused by illumination with a 500 W xenon lamp under open circuit (solid line) taken at 10 s intervals in PC + DME (1 : 1) containing 20v/o methanol and 1 M LiClO_4 , and absorption spectrum obtained by succeeding polarizing at 0.7 V vs. SCE for 5 s (broken line). (Reproduced by permission from ref. 66.)

works as a scavenger for holes photogenerated in TiO_2 , methanol was oxidized by UV irradiation to generate protons. The attachment of these released protons to the deprotonated poly(aniline) occurs to induce the photoreduction even in neutral aqueous solution (Fig. 11). This explanation was confirmed by monitoring the change in mass with a quartz crystal microbalance. CdS was also incorporated in poly(aniline) to compare it with the TiO_2 system.⁷⁰ However, spreading of the photoreduced image was found for the CdS system. This is due to the escape of the protons released beyond the illuminated area by diffusion. Such a spreading was also found when the photoreduction in the TiO_2 system was carried out in

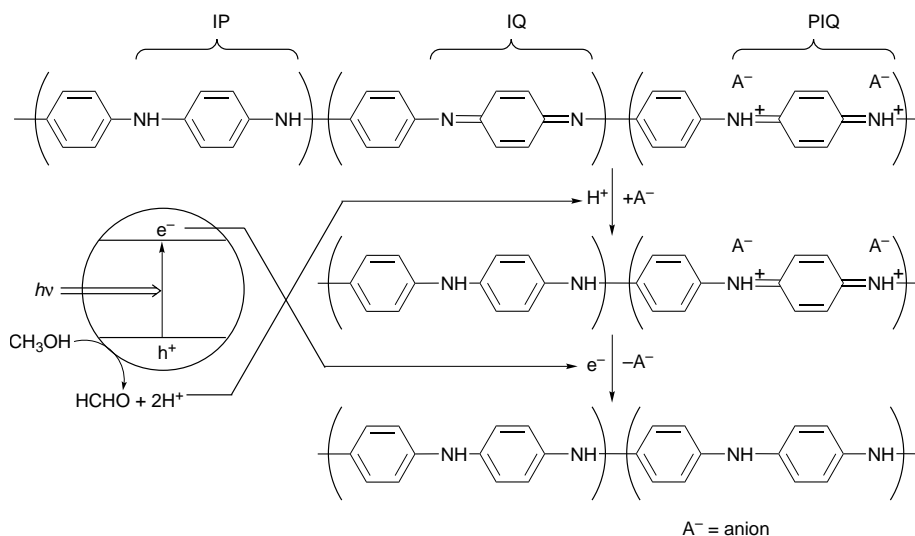


Fig. 11 Schematic illustration of the photoreduction of the deprotonated form in methanol solution (ref. 69)



Fig. 12 Light image formation on poly(aniline)- TiO_2 film immersed in 0.5 mol dm^{-3} phosphate buffer (pH 7) containing 20 wt% methanol by projecting the positive image on the poly(aniline)- TiO_2 film with illumination by 500 W xenon lamp for 1 min. (Reproduced by permission from ref. 68.)

acidic aqueous solution. The reason spreading was not found for the TiO_2 system in neutral aqueous solution is explained by the character of the TiO_2 surface. Since TiO_2 has many surface hydroxy groups which are involved in proton dissociation and association in aqueous solution, photogenerated protons are likely to be rapidly trapped by these surface hydroxy groups and give high acidity only in the illuminated area. This prevented the spreading of the image for the TiO_2 system. Further, a quantum efficiency of ca. 10% was obtained for this light image formation determined at 355 nm under low illumination intensity. By employing a TiO_2 system, an excellent picture image was demonstrated (Fig. 12).⁶⁸

Photooxidation for conducting polymer image formation

The above mechanism is believed to be due to photoreduction of the oxidative state of poly(aniline) by photoexcited inorganic semiconductor particles. Therefore, the illuminated part was bleached, and this provided a positive-type images. Image formation by utilizing photooxidation was also examined. The photooxidation system provided a negative-type image because the illuminated part was colored; this might be applicable to photographic and optical disk systems. Photooxidation of poly(aniline) with photoinduced electron transfer between a ruthenium complex and viologen was reported.⁷¹ Since photoinduced electron transfer between molecules was employed, it would be useful for easier fabrication of molecular functional

systems. Ruthenium complex incorporated Nafion was coated on the poly(aniline) deposited on an ITO electrode. This electrode in acidic aqueous solution containing methyl viologen was illuminated and a colored image of poly(aniline) was obtained. In this system, poly(aniline) was oxidized by the oxidation state of the ruthenium complex generated *via* photo-induced electron transfer between the photoexcited ruthenium complex to methyl viologen. This photooxidation of poly(aniline) was also performed in an all solid state cell by employing a polymer electrolyte composed of Flemion. Its application to optical memory and compact disk systems was indicated.⁷²

Instead of using casting methods to prepare the poly(aniline) film, a negative poly(aniline) image was also formed *via* photopolymerization in a Nafion film electrostatically incorporating a ruthenium complex and methyl viologen. This image could be erased by immersing the film in a hydrazine solution, and the erased image was reproduced by illumination. Repetition between photooxidation and reduction with hydrazine was therefore obtained as shown in Fig. 13.⁵⁹

Further, the study to induce not only photooxidation of poly(aniline) but also its reduction photocatalytically in a system was examined. One easy method is the combination of a ruthenium complex incorporated into a Nafion with TiO₂ system.⁷³ The repetition between photooxidative image formation and photoreductive image erasing was successful for films composed of photopolymerized poly(aniline) and Flemion containing a ruthenium complex and TiO₂ as shown in Fig. 14. Photooxidation and photoreduction were induced by visible illumination and UV illumination, respectively. Therefore, this poly(aniline) system enabled photolytically tunable conductivity and electrochromism leading to image formation. This system showed good memory effects, an advantage characteristic of electrochromism. The work must be regarded as preliminary, however. There are some problems such as slow response and durability to overcome. Further analysis must be carried out to fabricate more attractive systems.

Photochemical doping, photocrosslinking, photodecomposition and others

Photochemical doping, photocrosslinking and photodecomposition were employed to form conducting polymer images. An advantage of these systems is easier fabrication of solid state systems, but tunability and repetition are problems. For photochemical doping systems, tetraphenylidonium tetrafluoroborate and diphenyliodonium hexafluoroarsenate were used as photoinduced dopants because these are known to release BF₄⁻ and AsF₆⁻ upon illumination. By illuminating a

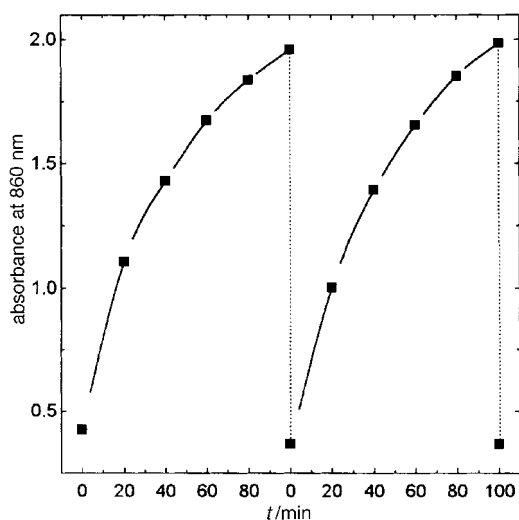


Fig. 13 Time course of absorbance changes at 860 nm induced by photooxidation (—) and chemical reduction (···) for the single layer film

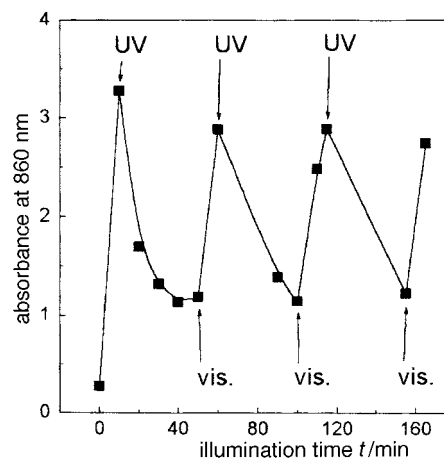


Fig. 14 Time course of absorbance changes at 800 nm induced by photooxidation and photoreduction for the single layer film in 1.0 M HCl solution with 10 vol% MeOH.

film of poly(3-hexylthiophene) containing one of these chemicals, a colored and insoluble conducting polymer pattern was obtained.^{74,75} Since the solubility of the pattern decreased upon illumination because the dopant worked as crosslinker between polymer chains (Fig. 15), only the illuminated image was obtained on the substrate by washing the illuminated film with appropriate solvent. This is expected to be an alternative and unique technique of lithography.

It was also reported that the repetition of photochemical doping and electroreduction could be obtained when poly(3-hexylthiophene)-gel electrolyte (containing photoinduced dopant) bilayer was sandwiched between indium-tin-oxide (ITO) electrodes. The electrolyte layer contained low molecular mass solvent to facilitate mass transport, but this could indicate a possibility for a solid state rewritable optical recording system. This photochemical doping can be called a kind of negative type photoresist. Similar work was reported for poly(3-hexylthiophene) with no other dopant.⁷⁶ A crosslinked insoluble polymer pattern was obtained by illumination at 422 nm. The mechanism of the crosslinking reaction was explained by the photooxidation of the alkyl side chain leading to crosslinking or Diels-Alder addition of photoexcited singlet state of oxygen to the main chain thienyl residue. The resulting polymer pattern could be oxidized by nitrosonium tetrafluoroborate to give a bulk conductivity of *ca.* 6 S cm⁻¹. *cis*-1,4-Poly(butadiene) was studied to prepare fluorescent conducting patterns with good stability.⁷⁷ The conductivity of *trans*-1,4-poly(butadiene) could be increased by eight orders of magnitude upon conjugation and self-doping induced by I₂ at room temperature, whereas *cis*-1,4-poly(butadiene) could not be made conducting by reaction with I₂ under the same conditions. Since this photoisomerization from *cis* to *trans* can

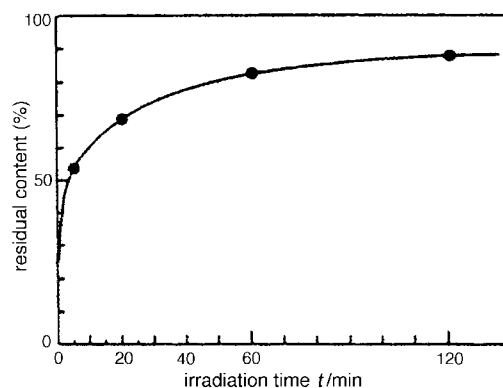


Fig. 15 Residual content of poly(3-hexylthiophene) film remaining after light irradiation and then washing with chloroform relative to the original. (Reproduced by permission from ref. 75.)

be achieved by UV irradiation, I₂ treatment of the irradiated film produces a conducting polymer image. The image shows strong fluorescence emission and has remained stable for 10 months in air.

Poly(aniline) also has good stability in air and could be a promising candidate for an image formation material. Poly(aniline) containing triphenylsulfonium hexafluoronate (onium salt) was studied as a negative type photoresist.⁷⁸ Since the onium salt dissociated into the acid and protons by irradiation with UV light or electron beam, only the irradiated part of poly(aniline) was oxidized *via* doping of the photo-generated acid and proton. The resulting oxidized state of poly(aniline) became insoluble in *N*-methylpyrrolidin-2-one. By employing an electron beam, conducting polymer lines with a high resolution of 0.25 μm were patterned in thick films. Since electron beams can be focused as small as 10 nm, this system has considerable interest as an alternative method to the current lithographic processes.

As another unique negative-type photoresist, polymeric films containing poly(bipyridine) complexes of ruthenium have been studied.⁷⁹ Two sequential photochemical ligand substitutions occurred in a stepwise manner in the film upon illumination to vary the absorption spectrum and redox potential of the film in three stages. Line patterns composed of different stage components with image resolution below 10 μm could be obtained. Interestingly the potential control of the underlying ITO electrode allows for selective oxidation of one or both stage components and spatially controlled color change in image films. The polymer shows redox conducting behavior, which is strictly speaking different from the above mentioned conducting polymers. However, this gives an interesting direction for the preparation of active images with multi-photo and electric functions.

It is well known that positive type (photodecomposition type) photoresists also play an important role in the field of photolithography. Conducting polymer image formation with positive type photoresists was also examined. Copolymers of thiophene and thiophene derivatives and other poly(thiophene) derivatives were illuminated with a high pressure mercury lamp to shorten the π-conjugation system.⁸⁰ This could be confirmed by absorption spectra. The former copolymer in particular showed no redox activity after illumination.

Poly(3-alkylthiophene) containing FeCl₄⁻ was also prepared as a positive type photoresist.⁸¹ Upon illumination at 366 nm, a drastic change in the conductivity from 6 to 10⁻⁵ S cm⁻¹ was found. This conductivity change was explained by the direct photodegradation of FeCl₄⁻ as a dopant or photoreduction of FeCl₄⁻ *via* photoinduced electron transfer from a bipolaronic residue. The above two systems enable the formation of conducting polymer images by distinguishing the illuminated less-conductive pattern from the unilluminated conductive pattern. Irrespective of whether they are of positive or negative type, the conductive image can be fabricated more easily in the above mentioned systems than in commercial photoresists possibly because these enable a decrease in the number of processing steps to be made. Further improvement on response and resolution will, however, be required to give the application of these systems a firmer foundation.

Future application

This article has given an overview of conducting polymer image formation with electrochemical reaction or photo-induced electron transfer reactions. The former is called electrochromism, and its application is directed mainly toward large-scale technologies such as smart windows and solar energy related technology. The latter seems to be advantageous for smaller scale technologies. The characteristics of images composed of conducting polymers depend on the features of the conducting polymer employed. Such materials would give

some tunable functionality such as tunable conductivity unlike conventional metal images.

Light is an attractive tool to write conducting polymer images on an appropriate canvas. The image can be prepared space-selectively, meaning that one can attach functions depending on the conducting polymer for any geometry in any place. Such a technique may explore new technologies beyond the mere application to photolithography, photographic systems, optical recording systems or optical memory devices. A promising example is the use of photodeposited images composed of amorphous poly(diacetylene derivatives)⁶⁴ which exhibit good third order non linear susceptibilities. It may be useful to fabricate photofunctional elements on a microchip for advanced technology. The other example is easier fabrication of photoenergy conversion systems. The conducting polymer photochemically prepared on a photosensitizer works as a donor for photosensitizers. Therefore, efficient photoenergy conversion systems composed of conducting polymers as donor-photosensitizer-acceptor can be simultaneously fabricated during photopolymerization, because the conducting polymer would be prepared so that the photoenergy for photopolymerization is converted most efficiently in the system. Such a system can also be fabricated on inorganic semiconductors instead of photosensitizing molecules. This indicates a possibility to modify the surface of semiconductor chips with photofunctional conducting polymers. Further, since many photosensitizers act as phosphors, microelectroluminescent devices may also be prepared in a chip if the system configuration, relative energy level of each material, electrode contact and other problems are solved.

Reviewing the character of conducting polymer produced by photochemical reaction from the viewpoint of these applications, photochemical reactions mentioned in this paper seem to produce sufficient quantities of conducting polymer on a substrate although there is a problem with response time. Thus prepared conducting polymers show similar physicochemical characteristics such as conductivity and electrochemistry to that obtained by other methods.

For fabricating a device with such a conducting polymer, connecting an electrode to the photochemically prepared conducting polymer pattern may be a problem on a sub-micron or nanometre scale. However, STM and AFM techniques would be useful in achieving this. Further, if complete optical control were to become feasible in a system, it is not necessary to consider electrodes. Some of the resulting images are fairly robust for device fabrication. For example, the pattern composed of I₂ treated *trans*-1,4-poly(butadiene) remains stable for about 10 months in air,⁷⁷ and poly(aniline) also has good stability in air. However, it is necessary to analyze stability (chemical stability, physical aging and so on) under more severe conditions in order to employ materials in practical applications.

It is also certain that we have to overcome many barriers related to the total system to realize these exciting technologies and their applications. Detailed analysis is needed to clarify relative molecular arrangements, each mechanism concerning photoexcitation at a photosensitizer, photoinduced electron transfer reaction in the system, the following polymerization or redox reaction and the total electron transfer throughout the system.

Extensive research on conducting polymers concerning design, preparation method, conduction mechanism and application has been carried out world-wide. Further, photoinduced electron transfer systems have also been studied extensively. Both of these have independently gathered scientific and technological interests, and their combination is of great interest. Simple ways to combine these two independent fields are mixing, layering and chemical modification. Since each method has both benefits and disadvantages, each does not provide enough results to satisfy the many demands on the system. However, the combination of these two independent

fields is believed to have the potential to generate entirely unexpected attractive technologies in the near future. We hope this article will be of some help in awakening interest for further investigations and applications of conducting polymer image formation with photoinduced electron transfer.

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