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Photophysical characteristics of polyaniline with photochromic azobenzene side groups*

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Photochromic characteristics and optical molecular reorientation in conducting polymer such as polyaniline derivatives containing photochromic azobenzene moieties (PAPNPAPOA) in side chain are studied. Changes in the UV–vis absorption, refractive index, thickness, contact angle and morphology of these films after irradiation of a linearly polarized light with a wavelength of 365nm are measured. The *trans-cis* isomerization of PAPNPAPOA is proved irreversible even after withdrawing the UV light for a long time. That the structure of main-chain attends by the *trans-cis* isomerization of side-chain is confirmed by the absorption and the solution colour during the UV irradiation. These effects are discussed by taking the *trans-cis* isomerization of azobenzene into consideration.

Keywords: polyaniline derivatives, photochromic azobenzene, *trans-cis* isomerization, conducting polymer

PACC: 0765E, 4270J, 8160J

1. Introduction

Conducting polymer (CP) with extended π-conjugation in its main chain has attracted much attention not only from the view-point of fundamental research but also from practical interest in materials used for electrical and optoelectronic devices.[1−4] On the other hand, photochromic molecules[5] and polymers with photochromic azobenzene moieties in their side chains have attracted much attention, because they exhibit photochromism and photo-induced anisotropy due to the *trans-cis* isomerization of azobenzene, which is usually accompanied by a structural change as reflected in the changes of dipole moment and geometry.[6] Azobenzene functionalized polymers are candidates for the materials used for constructing various molecule-based optical devices, nonlinear-optics-based optical devices such as optical switching, optical storage, surface relief gratings, holograms, optical modulates, and command surfaces for aligning liquid crystals.[7]

Most of the studies so far published deal with the synthesis and characteristics of such photochromic azobenzene polymers.[8,9] The chemical molecular structure and the physical characteristics such as refractive index, thickness contact angle and morphology of conducting polymer containing photochromic azobenzene moieties in side chain as well as their changes when the polymer is irradiated by a linearly polarized light with a wavelength of 365nm, however, have been studied only to a limited extent.[10] The investigation on the relation between the molecular isomerization and macroscopical physical characteristics with the polymer irradiated is of considerable interest because of its importance in describing the microstructure of these films.

In this paper, we report on novel photophysical characteristics of conducting polymer with π-conjugated rigid structure of bonds in the main chain and with substituents containing azobenzene moiety as side chains.[11]

2. Experiments

The polyaniline derivatives containing photochromic azobenzene moieties (PAPNPAPOA) were synthesized by use of an existing method.[11] PAPNPAPOA can be dissolved in N-methyl-2-pyrrolidone

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(NMP) solution. The chemical structure of PAPNPAPOA is shown in Fig.1. PAPNPAPOA at appropriate weight ratios was dissolved in NMP and spin-coated on a quartz or silicon plate.

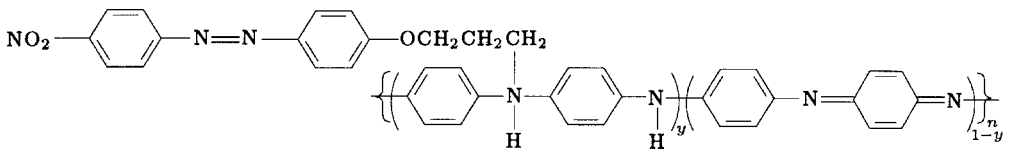


Fig.1. Structure of the PAPNPAPOA.

The UV–vis spectra of the samples were recorded with an HP 8452A UV–vis spectrometer. The irradiating light was from a high-intensity 365 nm UV lamp equipped with 5 inch diameter filter (Cole-Parmer L-97600-05 long wave UV lamp, L-09819-23 filter). The intensity of the lamp is $7000\mu W/cm^2$ at a distance of 15 inches and $21000\mu W/cm^2$ at a distance of 2 inches. The samples were located 10–15cm away from the lamp. The ambient temperature on the sample was adjusted to be ca 30°C using a cold plate. After the irradiation, the dependence of UV–vis spectra of the samples on irradiation or recovery time was measured with HP-8452A or Perkin Elmer Lambda Bio-40 spectrometers. Thickness and refractive index of the film were detected with Sentech SE400 ellipsometers equipped with a He/Ne gas laser with a wavelength of 633nm. Roughness was measured with Digital Instruments Nanoscope IIIa atomic force microscope (AFM). Contact angle was measured with an optical contact angle measuring instrument (Dataphysics OCA20) under ambient conditions: 15–20°C and 50%–60% relative humidity, using yellow light to illuminate the water droplet. Advance angles of ultrapure water on the films were measured. Each point represents an average of at least five measurements.

3. Results and discussion

For photochromic pigments, it is known that the photo-induced *trans-cis* isomerization of azobenzene can change the absorption spectrum and affect the movements of molecules. Therefore, a linearly polarized light with a wavelength of 365nm was used in an attempt to change the isomerization of the PAPNPAPOA solution and film. Figures 2(a) and (b) show the UV–vis absorption spectra of the PAPNPAPOA solution and film with different irradiation times, respectively.

As can be seen from Fig.2(a), the absorption at 338nm strongly decreases upon UV irradiation, which should be interpreted as the π-π^* transition of the *trans*-azobenzene units. On the other hand, the absorption intensity at 440nm increases, which can be attributed to the n-π^* transition of the *cis*-azobenzene units. Meanwhile, the absorption peak at 625nm, due to the exciton absorption of the quinoid rings of PANI, is blue-shifted so much as vanished upon irradiation with UV light due to the effect of photoisomerization of azobenzene units. These suggest that the PAPNPAPOA film has changed its structure from *trans*-isomer to *cis*-isomer upon light irradiation. Many hydrogen-bonds have come into being in the *cis*-structure which is stable and leads to the irreversibility of the photochromic of PAPNPAPOA after withdrawing the UV light. The blue-shift (from 640 to 605nm) in the UV absorption spectrum can be explained as follows.

The repeating units of polyaniline contain two different entities at different relative weights: a reduced state, with y=1 (leucoemeraldine) and an oxidized state with y=0 (pernigraniline). Here the y is the proportion of the reduced state in the repeating units of polyaniline. The semioxidized state, in which the numbers of oxidized and reduced units of PAN are equal to each other (y=0.5), is known as the polyaniline emeraldine base (PAN-EB). Owing to the UV irradiation for a long time, the polyaniline has changed its entity from emeraldine base to a reduced state. Therefore the colour of PAPNPAPOA solution is gradually varied from blue to yellow during the UV irradiation. Meanwhile, owing to the increase of the torsional angle twisted by the *trans-cis*-azobenzene photoisomerization between adjacent rings through the alkaneoxynitroazobenzene groups attached on the N sites in the backbone, the degree of orbital overlap between the phenyl π electrons and the nitrogen lone pair decreases. These effects decrease the extent of π conjugation and result in the increase of the energy level of LUMO πq.

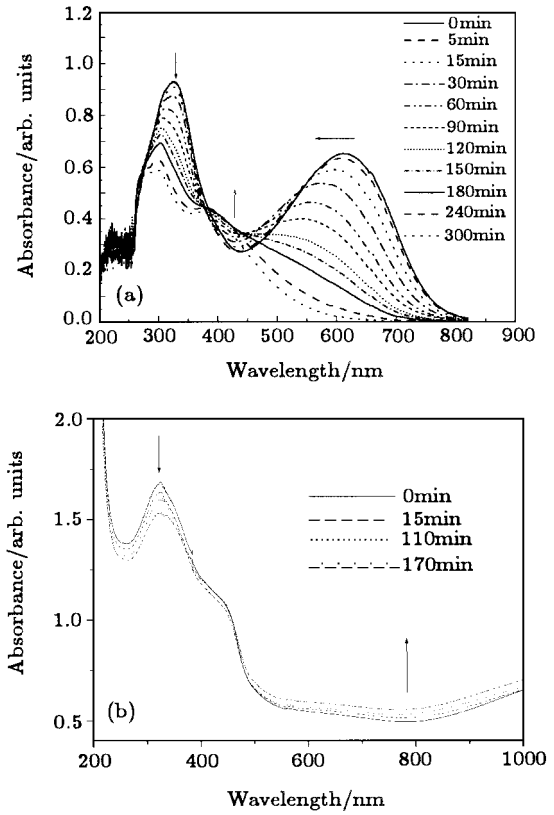


Fig.2. Changes of absorption spectra of the PAPNPAPOA NMP solution (a) and the PAPNPAPOA film (b) upon light irradiation.

Compared with the absorption spectra of PAPNPAPOA solution (as shown in Fig.2 (a)), the absorption spectra of the PAPNPAPOA film upon light irradiation reveal evident differences (as shown in Fig.2(b)). Firstly, a peak of 325nm, attributed to the π-π^* transition of the *trans*-azobenzene units, strongly decreases upon UV irradiation and the shoulder at 447nm attributed to the n-π^* transition of the *cis*-azobenzene units slightly increases. Secondly, a new absorption peak at 860nm is observed, which is identical to the absorption feature of the emeraldine salt form (ES) of PANI.[12] Thirdly, the extents of increase (447nm) and decrease (325nm) of the peaks in Fig.2(b) are smaller than those in Fig.2(a). These differences in the absorption spectra of the PAPNPAPOA film upon light irradiation can be explained in what follows.

The photophysical properties of the chromophores are more complex when the azoaromatic groups are studied in polymeric film. It is well known that the isomerization reactions of the azo chromophores are much lower in polymer films than in solution, as a direct consequence of their reactivity sensitive to the local mobility of reactants and heterogeneity of reaction sites in solid state.[13] Owing to the fact that the resistance of photoisomerization is larger in a form of film than in a form of solution, the intensity of the absorption spectra in Fig.2(b) is weak and the transforming time needs longer, which suggests that the process of photoisomerization is a function of time and site resistance.

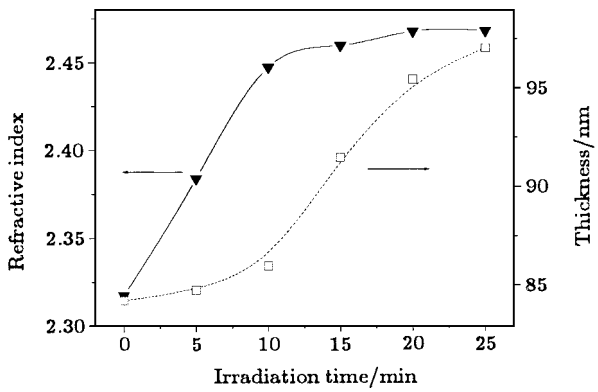


Fig.3. Changes of refractive index and thickness of the PAPNPAPOA film with irradiation time.

The increase of the refractive index and the thickness of the PAPNPAPOA film with the irradiation time can be found in the Fig.3. Upon the irradiation of UV light, the photochromic process consisting of a *trans-cis* isomerization of the N=N bond forms in PAPNPAPOA (see Fig.4). The stable *trans*-isomer is converted to the *cis* form under the UV illumination, whereas the reverse *cis-trans* reaction neither occurs under irradiation with a visible light.[14] The concept of "free volume" has previously been accepted and used to explain the photoisomerization processes. There exists a fact that the free volume of *cis*-azobenzene is larger than that of *trans*-azobenzene. This means that *trans*-to-*cis* isomerization gives rise to an increase in the free volume of azobenzene, namely from contraction to expansion, and that the extent of changes increases with the irradiation time. Therefore, the thickness of the film increases under UV light irradiation, but the density of the film decreases. The assembly of molecule turns from close to loose in structure and the spacing between the adjacent molecules increases. This means that the velocity of light C_v in the film slows down. As we know, the refractive index is defined as

$$n = C_v/C_m, \tag{1}$$

where C_v is the velocity of light in vacuum and C_m is the velocity of light in medium. In Eq.(1), C_v is constant and n is inversely proportional to C_m. Consequently, the refractive index n naturally increases with the irradiation time.

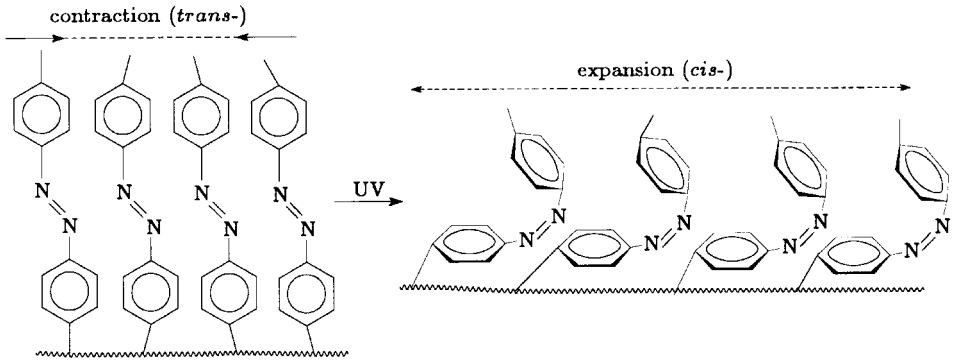


Fig.4. Schematic representation of the reversible photoinduced volume changes of PAPNPAPOA film irradiated by UV light.

The contact-angle measurement is a powerful and convenient method for studying the surface wettability which is closely related to the molecular packing density of PAPNPAPOA film. Since azobenzene moiety of PAPNPAPOA is terminated by nitryl groups, the change of contact angle in water droplet on the PAPNPAPOA film will alter the microscopic structure of the film. Owing to the irradiation of UV light, the *trans-cis* isomerization of azobenzene occurs. The N atoms in the bond of —N=N— have a chance to be exposed on the surface of PAPNPAPOA film. Both nitryl groups and —N=N— are hydrophobic groups. Their synergic effects cause the contact angle to enlarge with irradiation. Contact-angle measurements are principally based on such a consideration and displayed in Fig.5.

Obviously, the film tends to have a larger contact angle as irradiation time increases, suggesting that the quality of the film increases with irradiation time. The contact angle increases quickly at the beginning and then slow. At the present stage, the mechanism for this time-dependence is not yet clear. We deem that it is due to molecular reorganization in the film, which may require a relatively short time for rearrangement derived from a short chain.

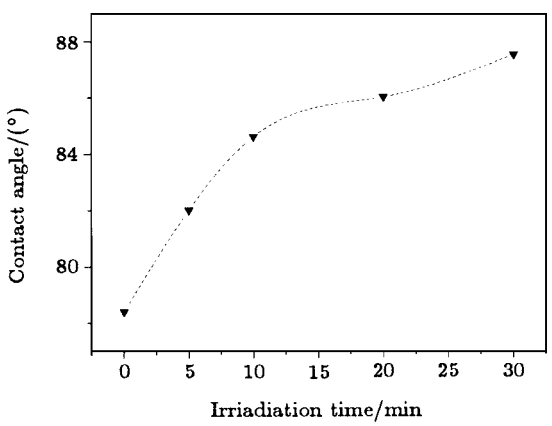
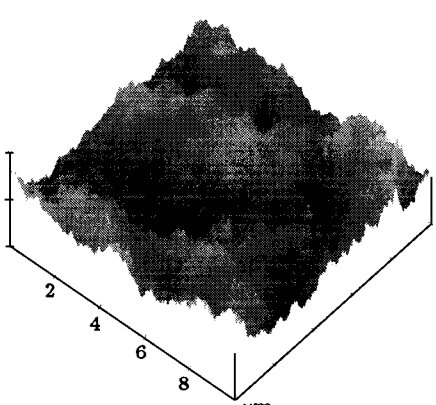
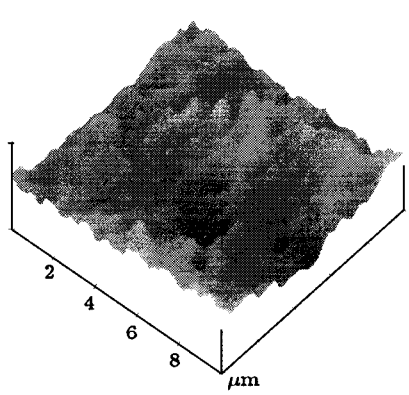


Fig.5. Change of contact angle of the PAPNPAPOA film with irradiation time.

The AFM images of PAPNPAPOA film before and after irradiating the film by UV light prove the above analyse and are shown in Figs.6(a) and (b).



(a) before irradiation
height 80.00nm
scan size 10.00μm
roughness 13.208nm



(b) after irradiation
height 80.00nm
scan size 10.00μm
roughness 9.358nm

Fig.6. AFM images of the PAPNPAPOA films before (a) and after irradiation (b).

From the images one can find the roughness of PAPNPAPOA film after irradiation decreases but its thickness increases, which is coincident with the features in Fig.4. Furthermore, the undulatory forms of PAPNPAPOA film before and after irradiation also transform from a sharp aiguille form to an up-and-down desert form, which causes the wettability of PAPNPAPOA film to change from large to small. This suggests that the high quality of PAPNPAPOA film can be obtained after it has been irradiated by UV light.

4. Conclusion

In polyaniline derivatives PAPNPAPOA, photochromism due to the *cis-trans* isomerization of azobenzene moieties in the side chain has been observed. Owing to irradiation of UV light, the underlying change appears in different physical properties of PAPNPAPOA, such as its UV–vis absorption, morphology, refractive index, thickness, contact angle and morphology. The *trans-cis* isomerization of PAPNPAPOA is proved irreversible even after withdrawing the UV light for a long time. That the structure of main-chain attends by the *trans-cis* isomerization of side-chain has been confirmed by the absorption and the solution colour during the UV irradiation. Photoisomerization of azobenzene in PAPNPAPOA is discussed in terms of reorientation of azobenzene moieties in the side chains.

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