Image Storage based on the Photo-induced Ionic Conductivity Jump of Polymer Films containing Azobenzene Liquid Crystal

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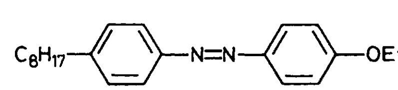
Photochromic phase transition of azobenzene liquid crystal (**1**) leads to drastic ionic-conductivity enhancement (image storage) of (**1**) containing polymer composite film, which easily compensates for surface charges loaded by corona charging, thereby allowing electrostatic image formation based on the surface potential difference between the photo-irradiated and unirradiated regions on the film.

Ion-conducting organic materials that respond to external stimuli, such as light and heat, have potential device applications. We have found already that composite films consisting of poly(vinyl chloride) (PVC), azobenzene liquid crystal (**1**), and the lithium perchlorate–crown ether (12-crown-4) complex, show photo-responsive ionic conductivity.[1] The photo-induced changes in ionic conductivity are attributable to the photochromic phase transition of the azobenzene derivative. U.v. light irradiation of the composite film causes photo-isomerization of the azobenzene derivative from the *trans* to the *cis* form,[2] which leads to a phase transition from the crystal or nematic liquid crystal state of the *trans* form to the isotropic state of the *cis* form. Such a drastic phase transition of (**1**) enhances the ionic conductivity of the composite film by more than two orders of magnitude due to increased ion mobility. The enhanced ionic conductivity of the film was found to be maintained for a while and to revert to the initial state on visible light irradiation. The photo-induced ionic-conductivity changes are reversible. An application of this photo-responsive ion-conducting organic composite film is in photo-induced image storage or optical memory.[3] Here we report a possible application of the ion-conducting polymer composite films of PVC/(**1**)/$LiClO_4$ to image storage, which is applicable to the electrostatic imaging process (Figure 1).

When the polymer composite film containing the azobenzene derivative (**1**) is irradiated with u.v. light through an exposure image (write-in process), the photo-irradiated region is highly ion-conducting due to the photochromic phase transition of the azobenzene derivative. The ionic conductivity in the unirradiated region of the composite film remains unchanged. Thus, the significant ionic conductivity differences between the photo-irradiated and unirradiated regions on the film can lead to image storage, which can be read by corona charging. The corona charging-induced surface charges on the photo-irradiated region are easily compensated for by internal polarization based on the u.v. enhanced ionic conductivity, whereas the unirradiated regions which still have low ionic conductivity are charged in a stable manner by the corona charging. In order to ensure low enough ionic conductivity for effective corona charging on the unirradiated region of the image-storable film, we adopted a very low concentration of Li^+ (the main carrier of ionic conductivity) in the composite film, and fabricated layered films of the ion-conducting main layer and an insulating over-layer (Figure 1). The ion-conducting polymer composite film (thickness ~12 μm) consisted of 62.49 wt% PVC, 35.50 wt%



(**1**)

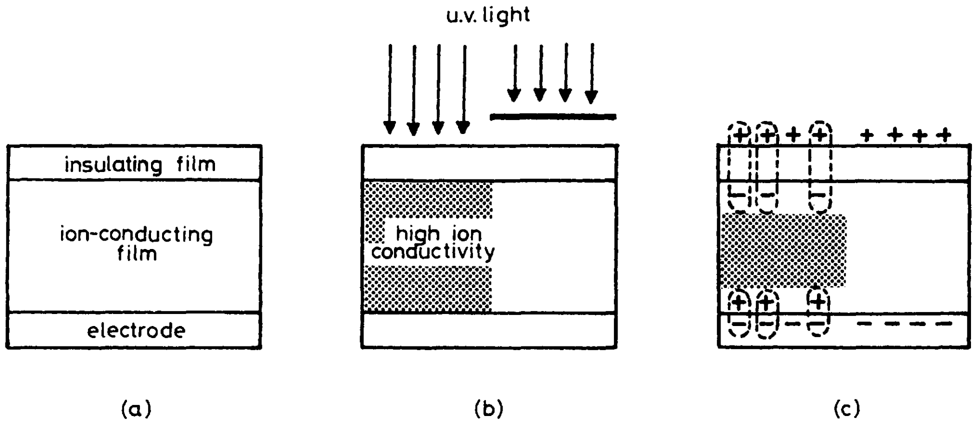


Figure 1. Basic concept of image storage using layered ion-conducting composite film: (a) structure of layered ion-conducting film, (b) formation of a highly ion-conducting region by u.v. light irradiation through exposure image, (c) corona-charging followed by compensation of resulting charges by enhanced ion conductivity.

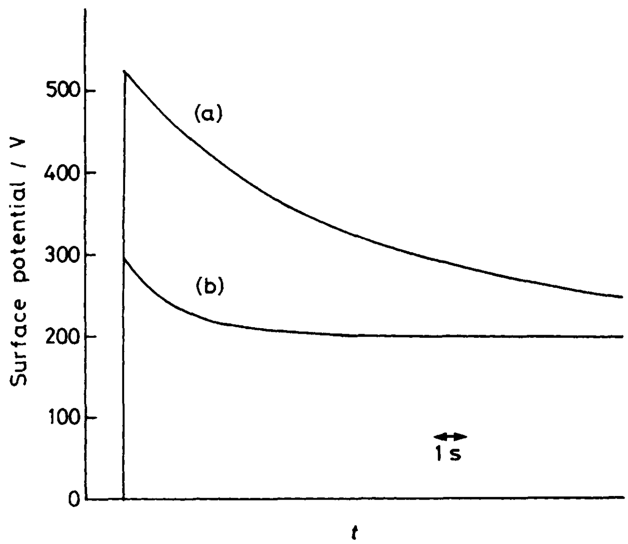


Figure 2. Surface potential induced by corona-charging in a layered ion-conducting film: (a) without u.v. irradiation, (b) after u.v. irradiation.

(**1**), and 0.01 wt% $LiClO_4$. The insulating over-layer was made from a transparent poly(ethyleneterephthalate) film of 2 μm thickness. The resulting layered film was dried under a nitrogen stream at 35 °C overnight. The layered ion-conducting film was positively (+6 kV) corona-charged after irradiation (5 min) with u.v. light (500-W Xe lamp with Toshiba UV-D35 cut-off filter, 320—400 nm) or without photo-irradiation, and the surface potentials induced on the film were measured. Figure 2 depicts a typical difference in the surface potential of the layered film induced by corona charging with and without u.v. irradiation. The u.v. irradiated film has a much lower surface potential than the unirradiated one in the initial stage, the difference in the initial surface potential (V_0) being over 200 V. An attempt was made to duplicate an image by using the image-storable layered ion-conducting film, which had been u.v. irradiated through an exposure image, as an electrostatic printing master in the conventional xerographic method. The u.v. irradiated layered film was successively positively corona-charged, developed by positively charged toner, and transferred to white paper; we obtained an image with sufficient contrast for the toner development, as shown in Figure 3. The time course of the initial surface potentials indicated that the layered ion-conducting film shows long-term memory on image storage. A high-contrast image similar to that shown in Figure 3 could be attained by the xerographic method even after 6 h. This significant memory effect elicits repeated duplication using the image-storable ion-conducting film with a 'one-time write-in' process. Of course, visible light irradiation of the film can restore the u.v. enhanced ionic conductivity to the initial value, the initial surface potential induced by corona charging being similar to that for the film before u.v. irradiation. Thus, the latent image on the layered ion-conducting film, obtained by u.v. irradiation through the exposure image, can be erased readily by visible light irradiation.

Figure 3. Image duplicated using an image-storable layered ion-conducting film as an electrostatic printing master in the xerographic method.

In conclusion, the over-layered ion-conducting composite film of PVC/(**1**)/$LiClO_4$ is a promising material for photo-induced image storage or optical memory. Also, in the application to the electrostatic imaging process, the layered ion-conducting film is the first example of photoreceptors using ionic conduction instead of electronic conduction.

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