

Photoresponse Gas Permeability of Azobenzene-Functionalized Glassy Polymer Films

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Received 15 March 2002; accepted 9 September 2002

ABSTRACT: The gas permeability of membranes composed of a polymer functionalized with azobenzene chromophores (azopolymer) was investigated under different conditions of light irradiation. A series of measurements with He gas showed that the permeability of the membranes increased by 5–10% upon irradiation with blue light, which caused cyclic photoisomerization of the azobenzene chromophores. In contrast, no significant change in gas permeability and no photoisomerization of the azobenzene chromophores were observed upon irradiation with red light. Moreover, using a digital video microscope, we observed

that azopolymer irradiated with blue light spread out from localized particulate domains and thinly covered the surface of the base membrane. Together with the results of the photoresponse permeability measurements, this observation strongly suggested the existence of photoinduced plasticization as discussed in the study of photoinduced surface relief formation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2068–2072, 2003

Key words: gas permeation; azopolymer; films; photoinduced plasticization; photoisomerization

INTRODUCTION

Polymers functionalized with azobenzene chromophores (azopolymers) are among the most investigated photofunctional materials. Azopolymers containing substituted azobenzene chromophores are especially promising candidates for optical data storage, electro-optic modulation, and other applications.¹ Azopolymer thin films exhibit a recently discovered phenomenon known as photoinduced surface relief (PSR) formation, which has drawn much attention because of its unique characteristics. Under light irradiation, azopolymer thin films exhibit surface modulation at the submicron scale. The degree of surface modulation has been shown to be related to the intensity distribution and polarization of the irradiating light.^{2–5} Experimental results have confirmed that PSR formation is reversible and very dependent on the polarization of the irradiating light.^{6,7} Moreover, a model analysis strongly suggested that azopolymers are fluidized and undergo plastic deformation during the relief-forming process.^{4,8–10} Most azopolymers that exhibit PSR formation have a glass transition temperature (T_g) above 100°C and are stable in the solid state at room temperature.^{4,11,12} Moreover, the light intensity required for PSR formation is generally small, and the temperature increase brought about by the light irradiation is

believed to be insufficient to plasticize the polymer.^{2,3,11,12} Therefore, possible photoinduced plasticization is probably not a simple thermal phenomenon. While the plasticization mechanism is being actively discussed,^{10,13–16} it is probable that photoisomerization of the azobenzene chromophore plays some important role.

When a glassy polymer is plasticized and fluidized, the change in state might be reflected to some extent in its gas permeability. Since the gas permeability of rubbery polymers is much larger than that of glassy polymers in general,^{17,18} possible photoinduced plasticization might be detected as an increase in gas permeability. Here, we investigate the influence of light irradiation on the gas permeability of azopolymers and discuss the possibility of photoinduced plasticization.

EXPERIMENTAL

Characteristics of the azobenzene polymer

We used a random copolymer of methyl methacrylate and 2-[ethyl-[4-(4-nitrophenylazo)phenyl]amino]ethyl methacrylate (PMD77) to fabricate our azopolymer thin films.^{12,19} The chemical structure of the polymer is shown in Figure 1. The azobenzene chromophore, introduced in the side chain of the polymer, has a nitro group on one aromatic ring and a dialkylamino group on the other aromatic ring (push–pull type structure). Irradiation with blue light in the wavelength range of 400–440 nm induces a cyclic *trans*–*cis*–*trans* isomeriza-

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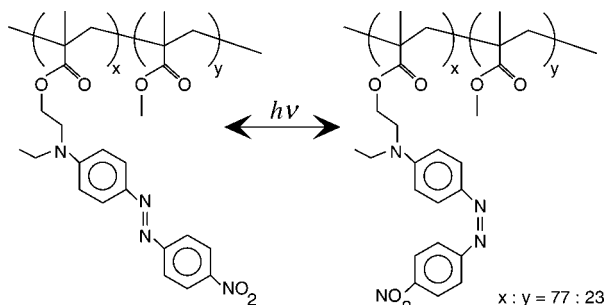


Figure 1 Chemical structure of PMD77.

tion of this chromophore^{8,9} (Fig. 1). The T_g and number-average molecular weight (M_n) of PMD77 are 132°C and 12,000, respectively.

Selection of base membrane and preparation of the azopolymer thin layer

Since irradiation with blue light can effectively fluidize the azopolymer, a base membrane must be used to support the polymer layer. We selected the aromatic amide ultrafiltration membrane P0200 (Toyo Roshi Kaisha, Ltd., Tokyo, Japan; molecular weight cutoff: 20,000) because of its good gas permeability and good solvent resistance.

We found that the gas permeability of the base membrane decreased significantly when the membrane filter was exposed to dichloromethane. Thus we coated the surface of the base membrane with a protective layer of sodium polyacrylate (NaPAA) by dipping the base membrane in 0.1% NaPAA aqueous solution, washing it with water to remove excess polymer, and then drying it at room temperature under vacuum.

The azopolymer thin layer was formed on the base membrane by spin-coating 0.5 mL of a dichloromethane solution of PMD77 at a spinning rate of 2000 rpm. Three different concentrations of azopolymer solution (2.5, 1.0, and 0.5%) were used to prepare the azopolymer thin-film samples (samples 1, 2, and 3, respectively).

Permeability measurements and microphotographic observation of samples

We investigated the effect of photoirradiation on the gas permeability of azopolymer membranes by using a gas permeation cell equipped with a quartz window. The configuration of the experimental system is shown in Figure 2. The azopolymer membrane (25 mm in diameter) was placed in the gas permeation cell, and the permeability for He gas was measured as a gas flow rate for a certain differential pressure ΔP . Before the measurements, the samples were pretreated with a certain period of blue light irradiation to stabilize their permeation property.

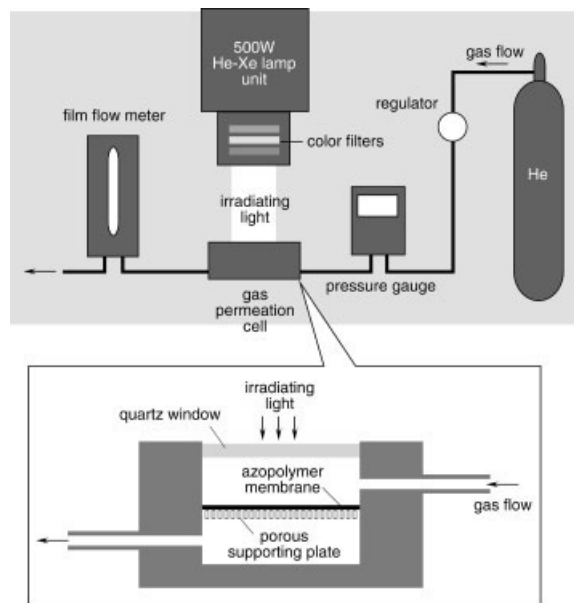


Figure 2 Experimental setup for measurement of gas permeability.

A 500-W Hg-Xe lamp (SX-UID500M, Ushio, Inc., Tokyo, Japan) was used as a light source. Blue light (400–450 nm, 100 mW/cm²), which brings about isomerization of the azobenzene chromophore, and red light (550–750 nm, 180 mW/cm²), which causes no isomerization, were isolated from the light source by using various combinations of color filters. A film flow meter (STEC, Inc., Kyoto, Japan) was employed for the permeability measurements, and the gas flow rate was continuously measured under various conditions of light irradiation.

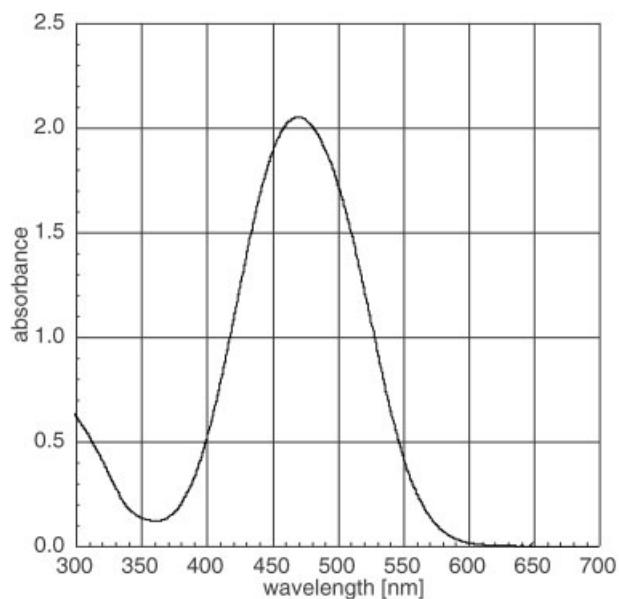


Figure 3 Absorption spectrum of a chloroform solution of PMD77.

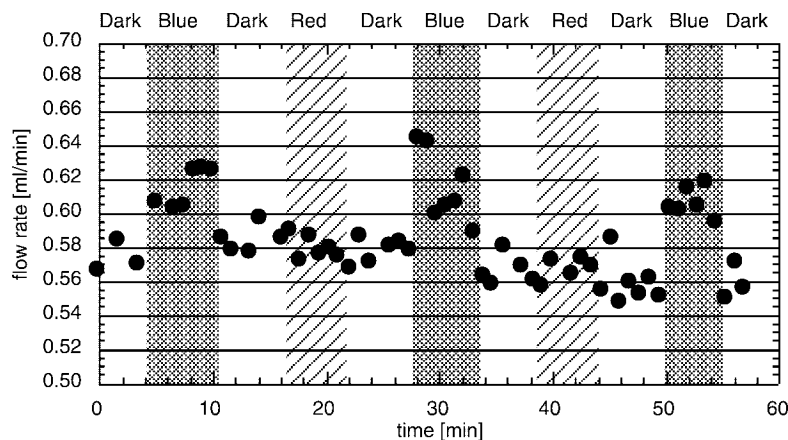


Figure 4 He gas permeability of sample 1 in response to light irradiation.

The microscopic surface morphology of the samples before pretreatment of blue light irradiation (immediately after preparation) and after repeating light irradiation was observed with a VH-8000 digital video microscope (Keyence Corp., Woodcliff Lake, NJ).

RESULTS AND DISCUSSION

Figure 3 shows the absorption spectrum of a chloroform solution of PMD77 prior to irradiation. Under this condition, all of the azobenzene chromophores in PMD77 are in the *trans* form, and the absorption spectrum exhibits an absorption maximum at 470 nm.

We measured the permeability of sample 1 for He gas under several irradiation conditions. Prior to measurement, we placed the sample in the gas permeation cell and irradiated it with blue light for 1 h to stabilize the permeation property of the membrane. ΔP was set to be 0.20 MPa during the permeability measurement. The flow rate of permeating He gas increased by about 5% during irradiation with blue light and returned to its original value after cessation of irradiation (Fig. 4). In contrast, irradiation with red light produced no detectable change of flow rate, even though the red light was more intense than the blue light. These observations suggest that photoisomerization of the azobenzene chromophores had some effect on increasing the permeability of the sample. The microscopic surface morphologies of sample 1 before pretreatment of blue light irradiation (immediately after preparation) and after repeating irradiation are shown in Figure 5. Before pretreatment of light irradiation, many localized particulate domains of azopolymer (as large as $\sim 1 \mu\text{m}$) were found at the surface. In contrast, after repeating irradiation, we observed that the azopolymer spread out from localized particulate domains and thinly covered the surface of the base membrane.

Next, we studied the He gas permeability of sample 2. In this case, we set ΔP to be 0.10 MPa. The flow rate of permeating He gas increased by about 10% during

irradiation with blue light and returned to its original value after cessation of irradiation (Fig. 6). Among the samples, sample 2 exhibited the greatest increase in permeability, and confirmed that the change in gas flow rate could be brought about repeatedly by controlling the irradiation conditions. The microscopic surface morphologies of sample 2 before pretreatment

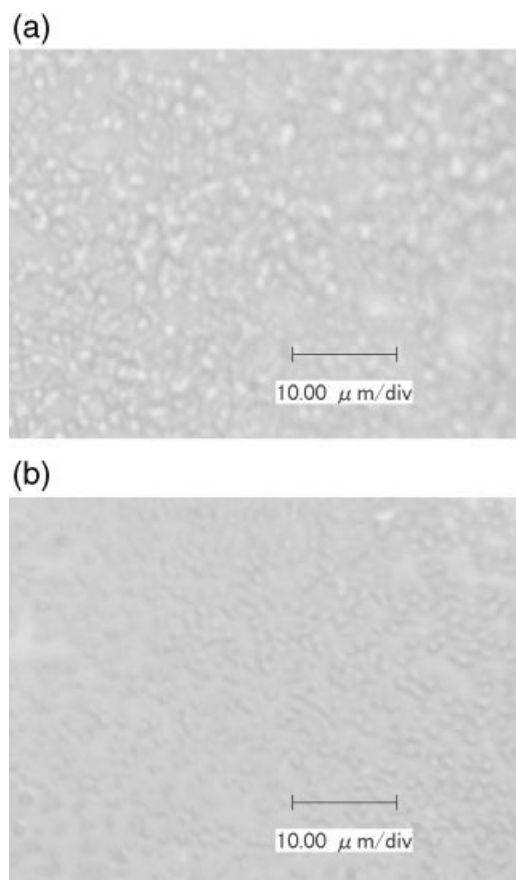


Figure 5 Microscopic surface morphology of sample 1 (a) before pretreatment of blue light irradiation and (b) after repeating light irradiation.

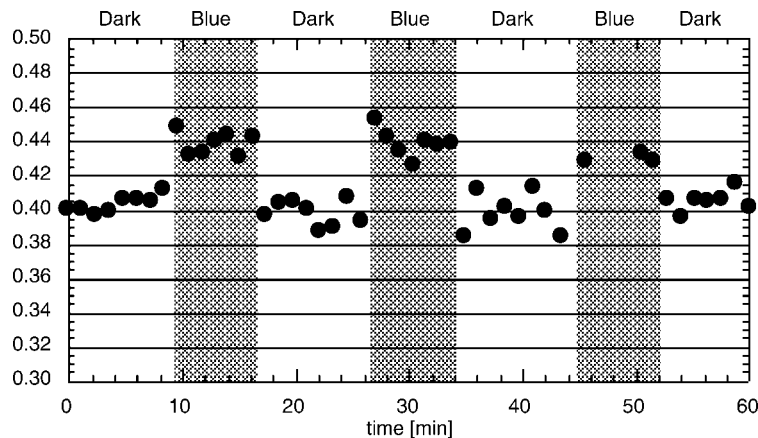


Figure 6 He gas permeability of sample 2 in response to light irradiation.

of blue light irradiation and after repeating irradiation (Fig. 7) were similar to those of sample 1, and as with sample 1, the azopolymer spread out under irradiation with blue light.

As described above, we experimentally confirmed that a certain period of pretreatment with blue light was necessary to stabilize the permeation property of the membrane. We believe that there is a connection

between this pretreatment and the change of the membrane surface described above. After pretreatment, the permeation property of the membrane stabilized and the wavelength-dependent behavior shown in Figures 4 and 6 was observed. Therefore, we suggest that the photoresponsive permeability of the membrane was derived from the thin-layer region formed by the spreading azopolymer. The color of the thin-layer region was relatively light (Figs. 5 and 7), indicating that the blue light irradiating the thin layer reached the surface of the base membrane with sufficient intensity to cause effective photoisomerization of the azobenzene chromophores throughout the thickness of the layer. This scheme is supported by the fact that the greater increase in permeability was observed for sample 2, in which the area of the thin-layer region was larger and thickness of the layer was thinner. These experimental results suggested that the photoinduced change in the bulk characteristic of the azopolymer, such as the increase of free volume brought by the cyclic photoisomerization of azobenzene chromophores, was reflected in the change of the permeation property.

In the case of sample 3, which was prepared with 0.5% azopolymer solution, no significant change of permeability was brought about by irradiation with blue light. Microphotographic observation of sample 3 before pretreatment of blue light irradiation [Fig. 8(a)] showed that the azopolymer did not form localized particulate domains on the membrane surface and that the azopolymer was distributed heterogeneously. These results confirm that both defect-free coverage of azopolymer over the base membrane and formation of localized particulate domains were necessary for the emergence of photoresponsive permeability.

CONCLUSIONS

We confirmed experimentally that the gas permeation property of a polymer film with an azobenzene chro-

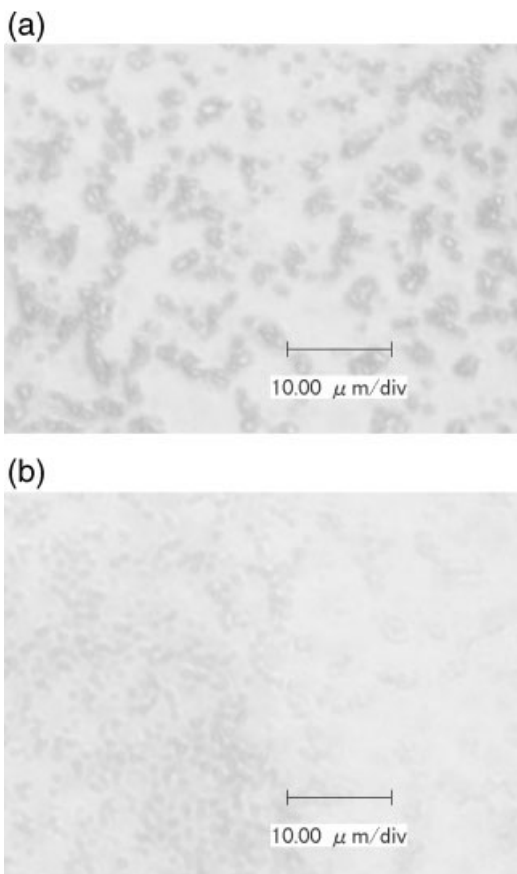


Figure 7 Microscopic surface morphology of sample 2 (a) before pretreatment of blue light irradiation and (b) after repeating light irradiation.

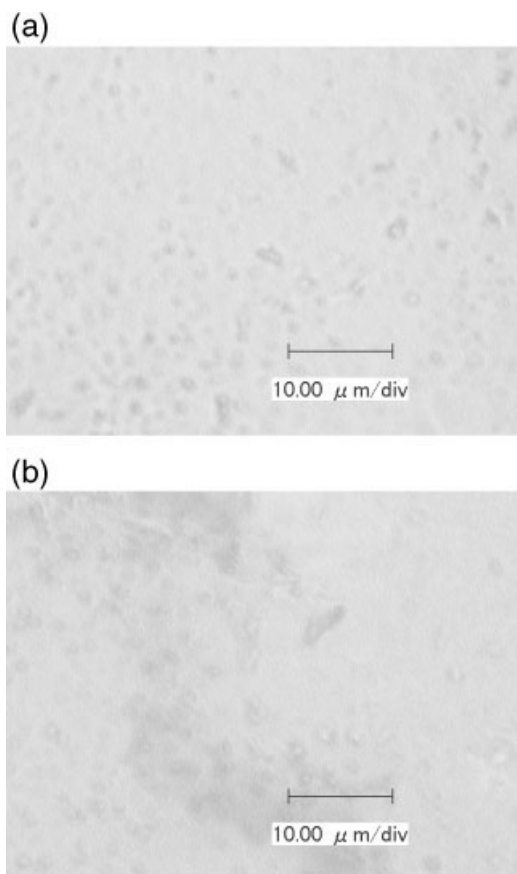


Figure 8 Microscopic surface morphology of sample 3 (a) before pretreatment of blue light irradiation and (b) after repeating light irradiation.

mophore having a push-pull structure in the side chain is reversibly changed by photoirradiation. The experimental results obtained under several photoirradiation conditions suggested that the cyclic *trans-cis-trans* isomerization of azobenzene chromophores in this polymer is closely related to this change of permeation property. Since the observed permeability change was at most 10%, it is difficult to regard these experimental results as direct evidence of the photoinduced plasticization discussed in the study of PSR formation. However, we observed that azopolymer irradiated with blue light spread out from localized particulate domains and thinly covered the entire surface of the base membrane. This experimental result supports the possible existence of photoinduced plasticization and fluidization of the azopolymer.

On the other hand, the photoirradiation can be localized and switched on and off immediately in contrast to the temperature change or chemical stimulations. Therefore, by combining with the appropriate optical system, gas permeation control by photoirradiation will likely become an important technique in applied fields such as the development of microchip reactors. Also from this applied point of view, we consider the results obtained in this study to give important information.

We acknowledge Dr. T. Fukuda of the National Institute of Advanced Science and Technology for kindly providing the azopolymer and for helpful discussions about the characteristics of the azopolymer thin film.

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