

SHORT COMMUNICATION

Photoresponse of Polystyrene Having Malachite Green Leucohydroxide Side Groups

Naoki NEGISHI, Katsuaki TSUNEMITSU, and Isao SHINOHARA

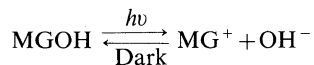
*Department of Polymer Chemistry, Waseda University,
Ohkubo, Shinjuku-ku, Tokyo 160, Japan.*

(Received June 30, 1980)

KEY WORDS Photoregulation / Photochromism / Malachite Green
Leucohydroxide / Ion Cleavage / Conductivity / Wettability /
Photoresponsive Polymer /

Photochromic compounds undergo reversible structural changes by irradiation with light, such as isomerization and ion cleavage, with a consequent change in physical properties. This photoresponse phenomenon may be utilized for the photoregulation of various polymer functions.¹ We have already reported the photoviscosity effect² and the photoregulation of pH³ with azo dyes, and the photo-induced reversible change in wettability of polymers having azobenzene and spiropyran side groups.⁴

This paper discusses the photoresponse of a polymer (PMG) having Malachite Green leucohydroxide (MGOH) side groups. On irradiation with light in a polar solvent such as ethanol, MGOH undergoes photo-induced ion cleavage to form a dye having absorption peaks in the visible region, causing the solution to turn green. When the solution is allowed to stand in darkness, this green color gradually disappears, and the solution ultimately returns to its original colorless state. The photochromism involved in this system can be expressed as follows,⁵



In order to obtain a basic understanding of the functional control of PMG based on photo-induced ion cleavage, several photo-induced property changes, other than photochromism, are examined in this study.

PMG was synthesized by the reaction of poly-

styrene ($M_w = 1.71 \times 10^5$) with Michler's Ketone according to the method of Braun.⁶ The polymer obtained was purified by precipitation from a benzene solution with methanol. Elemental analysis showed a degree of Malachite Green substitution of 13%.

A 500W ultra-high-pressure mercury lamp (Ushio Electric, Model UI-501 C) was used as the light source. The wavelength was selected with a Toshiba filter UV-31 ($\lambda > 310 \pm 8$ nm). The light intensity measured with a UV-meter (ORC, Model UV-3) was about 25 mW cm⁻².

Conductivity was measured for PMG solutions held at $20 \pm 0.1^\circ\text{C}$ at an electrode distance of 2 mm, using a Shimadzu Conductivity Meter, Model CM-30.

The wettability measurement was conducted in the same way as in our previous paper.⁴ PMG film was prepared on a glass plate by casting a tetrahydrofuran (THF) solution of the polymer; its contact angle with pure water, θ , was measured with a contact angle goniometer (Erma, Model G-1).

Figure 1 illustrates the photo-induced change in resistance of PMG in a tetrahydrofuran(THF)-H₂O mixed solvent (10:1). It can be seen from the figure that the solution resistance drops as the irradiation time is increased, leveling off at a certain value. This can be ascribed to the formation of hydroxide ions through photo-induced ionization of PMG, that is, a photo-induced conversion of the neutral polymer into a polycation form, PMG⁺.

Irradiation with UV light on a THF solution of

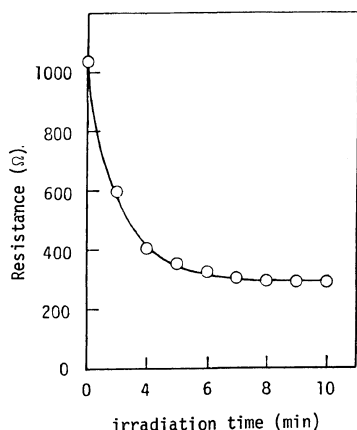


Figure 1. Photo-induced resistance change of PMG in THF-H₂O (10:1) at 20°C: [PMG], 0.1 g dl⁻¹, light intensity, 25 mW cm⁻².

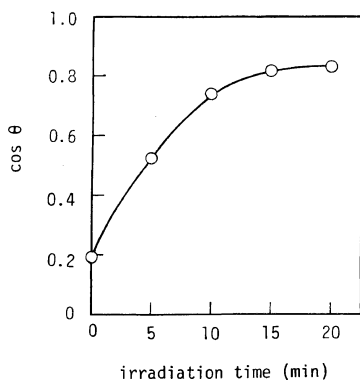


Figure 2. Photo-induced wettability change on the surface of a PMG film: θ , contact angle with water; light intensity, 25 mW cm⁻².

PMG turned the colorless solution to dark green. When this colored solution was allowed to stand in darkness, the intensity of the absorption peaks developed in the visible region gradually decreased with the passage of time, and this is consistent with the results on PMG reported by Fruit.⁷ However, the absorption spectra did not recover their original state and the photochromism of PMG was incomplete. The reversibility of photo-induced property changes in conductivity and wettability described below was invariably poor and these properties did not resume their initial state in darkness.

It was demonstrated that the limit to which a mixed solvent ratio (THF/H₂O) could dissolve the

leuco PMG was 10:1, and additional water caused precipitation of the polymer. However, if a PMG solution in THF-H₂O (10:1) is irradiated with light, no precipitation occurs on adding water. This indicates the larger hydrophilicity of colored PMG (PMG⁺). This change in PMG from hydrophobic to hydrophilic was also confirmed by wettability measurements on the polymer film. As is apparent from Figure 2, $\cos\theta$ increased with irradiation time, indicating increased wettability of the film toward water. The observed change in wettability was very great, from a level of hydrophobic poly(methyl methacrylate) to a level of hydrophilic poly(vinyl alcohol), reflecting a marked increase in the polarity of PMG after irradiation. The change in wettability induced by irradiation is due to the enhanced hydrophilic nature of the film surface brought on by the ionization of the MGOH sites in the molecule. This property makes PMG applicable to the lithographic printing process as a positive working presensitized plate, since oleophilic (hydrophobic) images can be formed at unexposed sections.

Acknowledgement. We should like to thank Professor Y. Sakurai, Dr. T. Okano, Dr. K. Kataoka, and Assistant Professor T. Akaike for their helpful comments.

REFERENCES

1. R. Lovrien, *Proc. Natl. Acad. Sci. U.S.A.*, **57**, 236 (1967); G. Van der Veen and W. Prins, *Photochem. Photobiol.*, **19**, 191, 197 (1974); G. Smets, J. Braeken, and M. Irie, *Pure Appl. Chem.*, **50**, 845 (1978); A. Aviram, *Macromolecules*, **11**, 1275 (1978); M. Irie, A. Menju, and K. Hayashi, *Macromolecules*, **12**, 1176 (1979); A. Ueno, J. Anzai, T. Osa, and Y. Kadoma, *Bull. Chem. Soc. Jpn.*, **52**, 549 (1979).
2. N. Negishi, M. Takahashi, A. Iwasawa, K. Matsuyama, and I. Shinohara, *Nippon Kagaku Kaishi*, 1035 (1977).
3. N. Negishi, K. Tsunemitsu, T. Suzuki, I. Shinohara, *Kobunshi Ronbunshu*, **37**, 293 (1980).
4. N. Negishi, K. Tsunemitsu, K. Ishihara, I. Shinohara, T. Okano, K. Kataoka, T. Akaike, and Y. Sakurai, *Kobunshi Ronbunshu*, **37**, 287 (1980).
5. E. O. Holmers, Jr., *J. Phys. Chem.*, **61**, 434 (1957); G. H. Brown, Ed., "Photochromism," Wiley-Interscience, New York, N.Y., 1971, pp 294-366.
6. D. Braun, *Makromol. Chem.*, **30**, 181 (1959).
7. M. P. Fruit, French Patent, 1365308 (1963); *Chem. Abstr.*, **61**, 16260 (1964).