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INTRODUCTION

Wettability of a solid surface by a liquid is an interesting phenomenon of interaction between molecular assemblies of liquid and solid and is explained by surface free energy from the viewpoint of interfacial chemistry.¹ The surface free energy of a solid is an important feature of printing, dyeing, and adhesion.² Moreover, attention has been paid to surface free energy in the method of estimating the blood compatibility of polymeric materials for biomedical use.³ If surface free energy, which is the inherent value of material, can be controlled by external physical signals, wide application of new materials is expected.

To regulate polymer properties by light we have already synthesized photoresponsive polymers that contain photochromic azobenzene group in their side chains. In the polymer solution, viscosity, pH, and conductivity can be controlled by photoirradiation.⁴⁻⁶ Further, the contact angle formed by water on the surface of the film prepared from *p*-phenylazoacrylanilide-2-hydroxyethyl methacrylate(HEMA) copolymer is changed by the photoisomerization of the azobenzene moiety.⁷

In this report photo-induced change in the surface free energy of azoaromatic polymer, prepared by the introduction of azobenzene groups into the side chains of hydrophilic poly(HEMA), was investigated. Attention was focused on the contribution of dispersion energy and polar energy components.

EXPERIMENTAL

Materials

HEMA was distilled under reduced pressure of nitrogen and a fraction of bp 63°C/3 mm Hg was used. *p*-Phenylazobenzoyl chloride (PABC) was synthesized by the Coleman method.⁸ The product was recrystallized from ligroine. Other reagents were purified by conventional method before use.

Preparation of Azoaromatic Polymers

HEMA was polymerized in 2-propanol at 60°C in 2 h with 2,2'-azobisisobutyronitrile as initiator. The reaction mixture was cooled and poured into an excess of diethyl ether to precipitate polymer. The molecular weight of poly(HEMA) was 3.8×10^5 by viscosity measurement. Poly(HEMA) was dissolved in a *N,N*-dimethylformamide(DMF)-pyridine mixture and a DMF solution of PABC was added to the polymer solution. The reaction was carried out at room temperature for 40 h. The reaction mixture was poured into an excess of water. The precipitate was dissolved in DMF and the solution was poured into an excess of diethyl ether. The precipitated polymer was filtered off and dried *in vacuo*. The composition of azobenzene moiety in the polymer was determined by the absorption coefficient of poly(methacryl β -hydroxyethyl-4-phenylazobenzoate), which is the homopolymer of the azobenzene moiety, at 325 nm in DMF solution. The results of the preparation of the azoaromatic polymers are shown in Table I.

Contact Angle Measurement

A DMF solution that contained 2.0 wt % of azoaromatic polymer was prepared. A film sample was prepared by casting the solution on a glass plate and drying it *in vacuo* at 40°C. The contact angles formed by liquids on the polymer surface were measured before and after photoirradiation with a contact angle goniometer (Erma, G-1). At least 10 contact angles were averaged for each film

TABLE I
Preparation of Azoaromatic Polymer

PABC/poly(HEMA) unit in feed	Mole fraction of azobenzene moiety	Yield (%)
0.10	0.018	36.4
0.20	0.024	33.2
0.30	0.140	40.8
0.70	0.387	32.8
0.80	0.512	31.8

surface. Photoirradiation was carried out with a 500-W ultrahigh-pressure mercury lamp (Ushio, UI-501C). The wavelength was selected with a Toshiba filter UV-D36C ($\lambda = 350 \pm 50$ nm) for ultraviolet (UV) irradiation or a Y-47 ($\lambda > 470$ nm) for visible light irradiation.

Electronic Spectrum Measurement

The azoaromatic polymer film was cast on a quartz plate from a DMF solution. The electronic spectrum of the film was measured with a spectrophotometer (Shimadzu UV-240) at room temperature.

RESULTS AND DISCUSSION

Photo-induced Reversible Change in Wettability of Azoaromatic Polymer Surface

Figure 1 shows the absorption spectra of the azoaromatic polymer film in the dark and in a photoequilibrium state. When UV irradiation was carried out, absorbance at 325 nm based on the $\pi-\pi^*$ transition of transazobenzene moiety decreased and that at 420 nm based on the $n-\pi^*$ transition of the cis moiety increased. A photoequilibrium state was reached within 15 min. Isosbestic points were found at 245, 278, and 395 nm. Therefore the change in the absorption spectrum was due to the trans-cis photoisomerization of the azobenzene moieties. Assuming that the absorption of the cis form in the wavelength region of 310–330 nm is negligible compared with that of the trans form, the percentage of cis form was 36.4 at the photoequilibrium state. The absorption spectrum after UV irradiation returned to its original state when the azoaromatic polymer film was allowed to stand in the dark or irradiated with visible light. From these results it was found that the azobenzene moieties of the polymer were isomerized reversibly by photoirradiation, even when the polymer was in a film state.

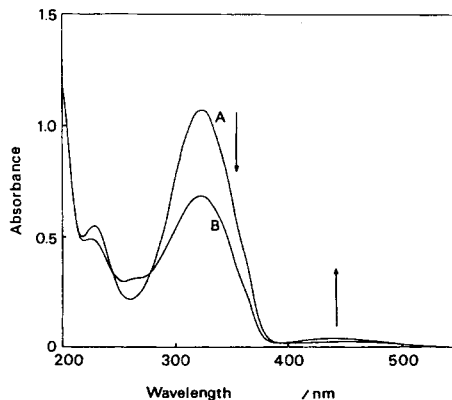


Fig. 1. Absorption spectra of azoaromatic polymer film (A) in the dark and (B) at photoequilibrium state: composition of azobenzene moiety, 0.387; the arrows represent the direction of absorbance change.

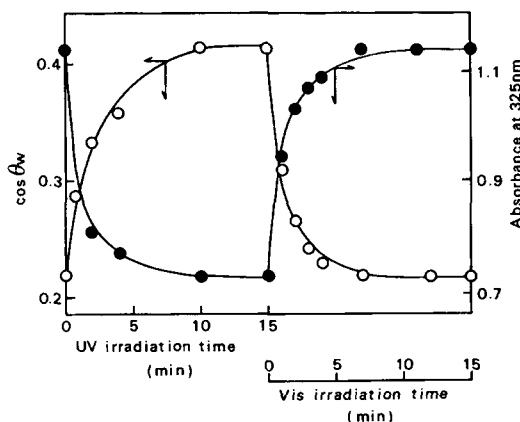


Fig. 2. Photo-induced change in wettability and absorbance of azoaromatic polymer film: θ_w , contact angle by water; UV light, $\lambda = 350 \pm 50$ nm; visible light, $470 \text{ nm} < \lambda$; photointensity, 14.5 mW/cm^2 ; composition of azobenzene moiety, 0.387; (O) wettability; (●) absorbance.

Figure 2 shows the change in wettability of the polymer surface by water ($\cos \theta_w$) and the absorbance at 325 nm, which corresponds to a peak for *trans*-azobenzene moiety, when light was irradiated onto a film of azoaromatic polymer. Figure 2 also shows that when irradiation is carried out, the absorbance of the *trans* form decreased with irradiation time and the photoequilibrium state was obtained within 15 min. The absorbance change was accompanied by an increase in the wettability of the surface of the polymer film. If irradiation by visible light follows, the absorbance of the *trans* form returns to its original level and the wettability decreases once again. The azobenzene derivatives are known to undergo reversible isomerization when irradiated and a consequent change in water solubility.⁹ The large dipole moment across the azo bond is induced by photoisomerization from the *trans* to the *cis* form. Therefore, the photo-induced change in the wettability of the polymer surface observed can be attributed to a structural change in the azobenzene moiety in its side chain. The fact that the wettability is completely recovered by irradiation with visible light shows that the change in the observed wettability is not caused by a temperature change in the polymer surface due to irradiation. These results indicate that the wettability of the polymer surface can be regulated by the photoisomerization of the azobenzene moiety.

Estimation of Surface Free Energy of Azoaromatic Polymer Film

Several methods of estimating the surface free energy of solids from the contact angle by liquids have been used.¹⁰⁻¹¹ For a hydrophilic polymer surface, Kaelble has proposed the following equation by considering the dispersion and polar energy components of surface tension¹²:

$$\gamma_{LV}(1 - \cos \theta) = 2(\gamma_S^d \cdot \gamma_L^d)^{1/2} + 2(\gamma_S^p \cdot \gamma_L^p)^{1/2} \quad (1)$$

where γ_{LV} is the surface tension of liquid, γ_S^d , γ_L^d are the dispersion energy components of solids and liquids, respectively. In eq. (1) are two unknown parameters, namely γ_S^d and γ_S^p . If a pair of liquids is used to measure contact angles γ_S^d and γ_S^p can be calculated.

To estimate the surface free energy of the azoaromatic polymers the contact angles by water (θ_w) and methylene iodide (θ_m) were measured. Figure 3 shows the relation between the wettability of the polymer surface by water and methylene iodide and the composition of azobenzene moiety in the polymers in the dark compared with that in a UV irradiation state. Wettability by water decreased by increasing the composition of azobenzene moiety and became a constant value at 0.4 mol fraction of azobenzene moiety. This result suggests that the composition of the surface of azoaromatic polymer film does not change, even though the composition of azobenzene moiety rises above 0.4. The wettability by water in the dark was changed from 0.56 for poly(HEMA) to 0.24 for the azoaromatic polymer with about 0.4 mol fraction of azobenzene moiety. With methylene iodide the wettability decreased by increasing the composition of azobenzene moiety; however, the change in the wettability was smaller than that by water. The surface tension of methylene iodide is almost

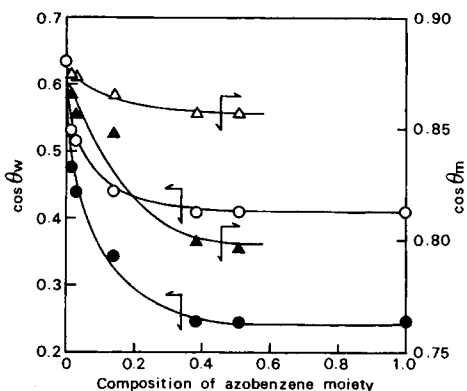


Fig. 3. Relation between composition of azobenzene moiety and wettability in an azoaromatic polymer system: θ_w , contact angle by water; θ_m , contact angle by methylene iodide; (●, ○) wettability by water; (▲, △) wettability by methylene iodide; closed plot in the dark; open plot under UV irradiation.

entirely governed by the dispersion energy component.¹³ Thus it is considered that the contribution of the dispersion energy component to a decrease in wettability was small when the composition of azobenzene moiety increased on the surface of the azoaromatic polymer.

When UV irradiation was carried out the wettability by water increased in all of the azoaromatic polymers. This indicates that the surface became more hydrophilic. The wettability by water under UV irradiation decreased with an increase in the composition of azobenzene moiety in the polymer and became constant like that in the dark. From this result it is considered that the hydrophobicity on the surface of the polymer was changed by the photoisomerization of the azobenzene moiety; however, the distribution state of functional groups was not changed. The wettability by methylene iodide was increased by UV irradiation.

By substitution of the values of wettability obtained in eq. (1) the dispersion energy component (γ_s^d) and the polar energy component (γ_s^p) of the surface tension were calculated. Figure 4 shows the dependence of the composition of azobenzene moiety on γ_s^d and γ_s^p in the dark, compared with that under UV irradiation. The value of γ_s^d decreased with an increase in the composition of azobenzene moiety; on the other hand, γ_s^p slightly increased with an increase in the azobenzene composition. Because polar hydroxy group in the side chain of poly(HEMA) was replaced with nonpolar *trans*-azobenzene group, the polar energy component is considered decreased.

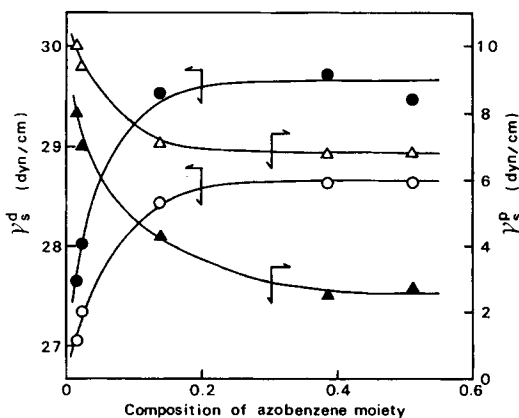


Fig. 4. Relation between composition of azobenzene moiety and surface tension in azoaromatic polymer system: γ_s^d , dispersion energy component of surface tension; γ_s^p , polar energy component of surface tension; (●, ○) γ_s^d ; (▲, △) γ_s^p ; closed plot in the dark; open plot under UV irradiation.

When UV was irradiated to the azoaromatic polymer film an increase in γ_S^d and a decrease in γ_S^p were observed. The increase in γ_S^d was 4 dyn/cm and the decrease in γ_S^p was 0.75 dyn/cm by UV irradiation; the mole fraction of azobenzene moiety was 0.4. Therefore the increase in the hydrophilicity on the surface of the azoaromatic polymers by UV irradiation was explained not by the result of the decrease in γ_S^d but by the increase of γ_S^p .

This surface free-energy change of the azoaromatic polymer by light should apply to the lithographic printing process as a positive working presensitized plate, because hydrophobic images can be formed on unexposed sections, and/or to photocontrolled hydrophobic adsorption chromatography, because the hydrophobic interaction between adsorbent and adsorbate can be regulated.

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References

1. F. M. Fowkes, *Contact Angle, Wettability, and Adhesion*, ACS Adv. Chem. Series, No. 43, American Chemical Society, Washington, DC (1964).
2. M. Sumida, *Yukagaku*, **18**, 839 (1969).
3. B. Sedlacek, C. C. Overberger, and H. F. Mark, Ed., *Medical Polymers, Chemical Problems*, *J. Polym. Sci. Polym. Symp.* No. 66, Wiley, New York (1979).
4. N. Negishi, K. Ishihara, and I. Shinohara, *J. Polym. Sci. Polym. Chem. Ed.*, **20**, 1907 (1982).
5. N. Negishi, T. Matsuo, K. Tsunemitsu, and I. Shinohara, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.*, **20**, 1017 (1979).
6. K. Ishihara, N. Negishi, and I. Shinohara, *J. Polym. Sci. Polym. Chem. Ed.*, **19**, 3039 (1981).
7. K. Ishihara, A. Okazaki, N. Negishi, I. Shinohara, T. Okano, K. Kataoka, and Y. Sakurai, *J. Appl. Polym. Sci.*, **27**, 239 (1982).
8. G. H. Coleman, G. Nichols, C. M. Mcloskey, and H. D. Ansporn, *Org. Synth. III*, 713 (1965).
9. G. S. Hartley, *Nature (London)*, **140**, 281 (1937); *J. Chem. Soc.*, **1938**, 633 (1938).
10. L. A. Girifalco and R. J. Good, *J. Phys. Chem.*, **61**, 904 (1957).
11. F. M. Fowkes, *Ind. Eng. Chem.*, **56**, 40 (1964).
12. D. H. Kaelble, and K. C. Uy, *J. Adhes.*, **2**, 50 (1970).
13. S. Wu, *J. Polym. Sci. Part C*, **34**, 19 (1971).

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