

Photo-Induced Change in Wettability and Binding Ability of Azoaromatic Polymers

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Synopsis

Photochromic polymers containing *p*-phenylazoacrylanilide were synthesized and the photo-induced hydrophobicity change on the surface of the polymer film was studied by measuring water wettability. The wettability increased with UV irradiation and returned to the original value with visible light irradiation. This photo-induced reversible change in wettability was considered to be caused by the large change of dipole moment across the azo bonds due to the isomerization of azo dye from *trans* to *cis* form. Furthermore, the photoresponsive polymeric adsorbent prepared from the azo polymer having adsorption behavior of a low molecular weight compound was studied. The binding ability of this polymeric adsorbent was decreased by UV irradiation. These results were attributed to the decreased hydrophobic interaction between the adsorbent and the adsorbate.

INTRODUCTION

Photochromic compounds undergo reversible structural changes by irradiation of light, such as isomerization and ion cleavage, with consequent changes in their physical properties. This photoresponse phenomenon may be utilized for photoregulation of various polymer functions. We have already reported that the photoviscosity effect exhibited in a water-soluble polymer/azo dye complex system is due to the change in the degree of complex formation caused by isomerization of the dye.¹

In another report investigating the adsorption behavior of water-soluble azo dye on polymeric adsorbents, we demonstrated that a reduction in the hydrophobic interaction caused by photoisomerization contributes greatly to the desorption of azo dye from the adsorbent.² This indicates the possibility of photoregulation of adsorption-desorption processes if a suitable polymeric adsorbent is used. In recent years, attention has been paid to a purification method based on hydrophobic chromatography using alkyl or aryl groups as the ligand.³ In this method, compounds to be isolated are adsorbed through the hydrophobic interaction and then eluted with an eluent. If the adsorption and desorption steps can be controlled by light, this would provide an interesting new technique in which eluents are not required.

In order to gain a basic knowledge for the design of useful photoresponsive polymeric adsorbents, we have selected an azobenzene as the typical photochromic compound capable of photo-induced isomerization. The change in hydrophobicity of polymers bearing this azo dye as the side group is discussed

in terms of wettability of the polymer film. Furthermore, the adsorbent was prepared by coating the azo polymer onto insoluble polymeric carrier. The photo-induced change in the binding ability of low-molecular-weight compound is also discussed, with attention to the change in hydrophobicity of the surface.

EXPERIMENTAL

Purification of Materials

2-Hydroxyethyl methacrylate (HEMA) was distilled under reduced pressure of nitrogen, and the fraction with bp 87°C/5 mmHg was used. 2,2'-Azobisisobutyronitrile (AIBN), *N,N*-dimethylformamide (DMF), acetone, and water were purified in the usual way before use. Methyl orange (MO) was used without further purification.

Synthesis of Azoaromatic Polymers

A vinyl monomer of azo dye, *p*-phenylazoacrylanilide (PAA_n), was prepared by condensation of acryloyl chloride with *p*-aminoazobenzene and was recrystallized from water-ethanol (1:1) mixed solvent. Azoaromatic polymers were synthesized by the procedure described below.

Homopolymerization of PAA_n. An acetone solution containing PAA_n and AIBN was taken into a polymerization tube, and the tube was evacuated and sealed under vacuum by conventional methods. Then the tube was shaken at 60°C for 96 h. The contents were cooled to stop the reaction and precipitated by pouring into methanol. The precipitate was collected by filtration and was dried *in vacuo*.

Copolymerization of PAA_n and HEMA. The desired amounts of PAA_n, HEMA, and AIBN were dissolved in DMF and the solutions taken into polymerization tubes. After these tubes were sealed under vacuum, as in the homopolymerization of PAA_n, copolymerization was conducted at 60°C for a given time under shaking. The contents were cooled to stop the reaction, diluted with DMF, and precipitated by pouring into a diethyl ether-ethyl acetate mixed solvent. The precipitate was collected by filtration and was dried *in vacuo*.

Table I shows the composition of the azoaromatic polymers thus obtained. The proportion of PAA_n in the PAA_n-HEMA copolymers was determined from the adsorption coefficient at 345 nm in DMF using poly(PAA_n) as the reference compound.

Measurement of Wettability

The azoaromatic polymers were dissolved in DMF, and film samples were prepared by casting the solution on glass plates, followed by drying under vacuum at 40°C. The contact angle θ of the film with pure water was measured before and after light irradiation using a contact angle goniometer (Erma Kogaku, model G-1). Photoirradiation was carried out with a 500-W ultrahigh-pressure mercury lamp (Ushio Denki, model UI-501C). The Toshiba filter, Type UV-D36C ($\lambda = 350 \pm 50$ nm), was used for UV irradiation; Type Y-47 ($\lambda > 470$ nm) was used for visible light irradiation.

TABLE I
 PAA_n-HEMA Copolymerization

PAA _n mole fraction in monomer	PAA _n mole fraction in copolymer ^a	Time, h	Conversion, %
0.155	0.090	1	6.5
0.385	0.180	2.5	26.6
0.555	0.388	12	25.7
0.700	0.534	9	14.6
0.701	0.545	12	21.4
0.884	0.863	24	29.2

^a Determined from absorption coefficient of poly(PAA_n) at 345 nm in DMF ($\epsilon = 1.77 \times 10^4$ L/unit mol-cm); $[M] = 1.0M$, $[AIBN] = 1.0 \times 10^{-2}M$ in DMF.

Preparation of Photoresponsive Polymeric Adsorbents

Photoresponsive polymeric adsorbents were prepared by the following procedure. HEMA microspheres (20 ~ 25 μ) or styrene-divinylbenzene copolymer beads (Amberlite XAD-2, Rohm and Haas Co. Ltd.) were swelled with 1 wt % DMF solution containing azoaromatic polymers for 24 h. After the mixture was filtered through a glass filter, the coded microspheres and beads were dried *in vacuo* to obtain the polymeric adsorbents desired.

Measurement of Adsorption

Batch Method. 0.05-g portion of photoresponsive polymeric adsorbent were transferred to test tubes to which aqueous solutions of MO of a specified concentration were added. The test tubes were shaken for 24 h in a thermostated bath. Preliminary experiments showed that equilibrium becomes complete within this time. The concentration of free MO was determined spectrophotometrically, using a Union Giken SM-401 spectrophotometer. After attainment of equilibrium adsorption in the dark, UV light irradiation was carried out for 1 h.

Column Method. The photoresponsive polymeric adsorbent was packed into a glass column (15 \times 0.8 cm i.d.). A specified concentration of an aqueous solution of MO was passed through the column until the adsorbent was saturated. Then photoirradiation on the column was carried out. In order to obtain high irradiation efficiency, a reflective mirror was used. The concentration of MO in the eluted solution was determined spectrophotometrically.

RESULTS AND DISCUSSION

Photo-Induced Reversible Wettability Change on the Surface of Azoaromatic Polymer

Figure 1 shows the change in wettability ($\cos \theta$) and the absorbance at 336 nm, which corresponds to a peak for *trans*-PAA_n, when light is irradiated onto a film of the homopolymer of PAA_n, poly(PAA_n). It is apparent from the figure that the absorbance of the *trans* form decreases with irradiation time, with attendant increase in wettability. If irradiation by visible light follows, absorbance of the

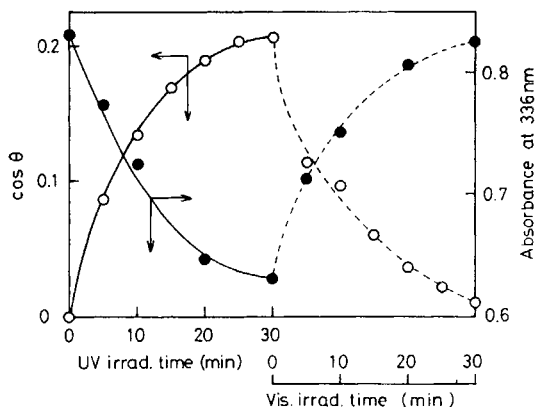


Fig. 1. Photo-induced change in wettability and absorbance of poly(PAA) film: θ , contact angle by water; UV light, $\lambda = 350 \pm 50$ nm; visible light, $470 \text{ nm} < \lambda$; photointensity, 14.5 mW/cm^2 ; (O) wettability; (●) absorbance.

trans form returns to its original level and wettability decreases again. It is well known that the azo dyes generally isomerize by UV light irradiation from the stable trans form to the cis form, while reverse isomerization takes place upon irradiation by visible light. Isomerization from the trans to the cis form decreases the hydrophobicity of an azo dye because of the large dipole moment developed across the azo bond.⁴ The photo-induced change in the hydrophobic nature of poly(PAA) observed can be ascribed to such a structural change of the pendent azo dye groups. The magnitude of this change corresponds to the difference in surface free energy between polystyrene and polymethacrylate resins. This indicates that the polarity of the polymer surface can be regulated by photoisomerization of the azo dye moiety. The fact that wettability is completely recovered by irradiation with visible light shows that the change in the observed wettability is not caused by temperature change of the polymer surface due to irradiation.

Figure 2 shows the relation of wettability to the composition of PAA_n-HEMA copolymers in the dark and in photostationary states. In the dark state, the contact angle of the homopolymer of PAA_n was $\theta = 90^\circ$ ($\cos \theta = 0$), a level similar

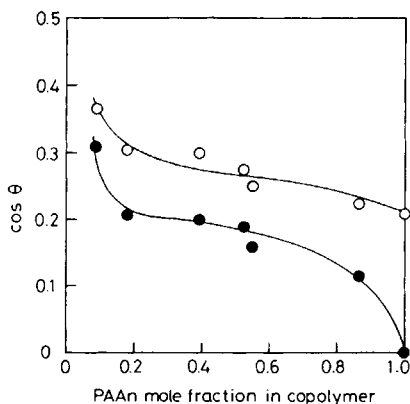


Fig. 2. Relation between PAA composition and wettability in PAA-HEMA copolymer system: θ , contact angle by water; (●) in the dark; (O) in photostationary state.

to that of hydrophobic polystyrene, while the value of $\cos \theta$ for copolymers increased in increasing proportion to HEMA, indicating an enhanced hydrophilic nature of the surface. A sharp rise in the curve at a PAA_n mole fraction of about 0.2 was observed. This behavior is similar to that of HEMA–styrene copolymers⁵ and co-oligomers.⁶ Wettability is higher in the photostationary state than in the dark state for all copolymer compositions, but changes more slowly as HEMA increases in the photostationary state than under dark conditions. Okano et al. have studied the wettability of methyl methacrylate (MMA)–HEMA copolymers of different composition and reported that the wettability changes very slightly with change in composition.⁵

The results obtained with the PAA_n–HEMA copolymers in the photostationary state are similar to this case. This may be explained by assuming that the behavior of PAA_n–HEMA is like that of MAA–HEMA copolymers as a result of the increase in hydrophilicity of the PAA_n components induced by UV light irradiation. Thus, two systems differing in surface free energy—the HEMA–styrene copolymer system and the HEMA–MMA copolymer system—can be developed by irradiating UV light onto a HEMA–PAA_n copolymer. It is also possible to control the range of wettability change by varying the copolymer composition.

Based on the photo-induced polarity change of the photochromic compounds described above, it is possible to design a polymeric adsorbent capable of photocontrolling hydrophobic interaction between molecules. The potential use of such a polymeric adsorbent is in hydrophobic chromatography for compound isolation, particularly when the conventional polystyrene adsorbent requiring organic solvents cannot be applied. This may become feasible by using water as the only solvent.

Photoregulated Adsorption of a Low-Molecular-Weight Model Compound Onto Photoresponsive Polymeric Adsorbent

A model experiment was conducted by the batch and column methods using MO, which shows no photochromism in water.⁷ Figure 3 shows the change in

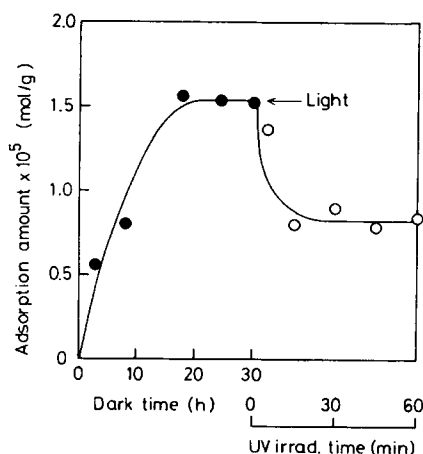


Fig. 3. Photoresponse in amount of adsorption of MO for poly(HEMA) beads coated with poly(PAA_n) at 25°C: (●) in the dark; (○) in light.

the amount of MO adsorbed onto a polymeric adsorbent both in darkness and under light irradiation. It is clear that the amount of adsorption gradually increases in darkness and ultimately becomes saturated, and that it begins to decrease with the irradiation of light and reaches equilibrium after about 30 min. This time period is similar to that required for completion of the photo-induced polarity change in the adsorbent surface. It is apparent that the MO molecules adsorbed onto the polymer film through hydrophobic interaction are desorbed as a result of decreased hydrophobicity of the adsorbent surface.

When the reciprocal of the amount of adsorption was plotted against the reciprocal of the equilibrium concentration, a straight-line isotherm was obtained. The slope and the intercept of this straight line gave the binding constant of MO onto the polymeric adsorbent.⁸ Thus, the free energy change for the binding can be calculated from the binding constant. The value for the free energy change was -5360 cal/mol prior to irradiation with light and -5160 cal/mol after irradiation. This means that the adsorption of MO onto the adsorbent by photoirradiation occurs with difficulty.

Figure 4 shows the change in the adsorption amount of MO on PAA_n-HEMA copolymers plotted against the copolymer composition. It is clear that the amount of adsorption in darkness increases as the fraction of the hydrophobic PAA_n component increases and the copolymer becomes more hydrophobic. It is suggested that the hydrophobicity of the polymer surface has influence on the adsorption of MO onto the adsorbent. On irradiation with light, though the adsorption amount decreases for all copolymer compositions, their dependence on PAA_n composition is small. This fact correlates with the fact that the wettability of PAA_n-HEMA copolymer changes slightly in the light with change in composition. The difference in the adsorption amount of MO between the darkness and after irradiation represents the desorption amount of MO from the polymeric adsorbent by photoirradiation. Apparently the value of the desorption amount increases with increase in PAA_n composition.

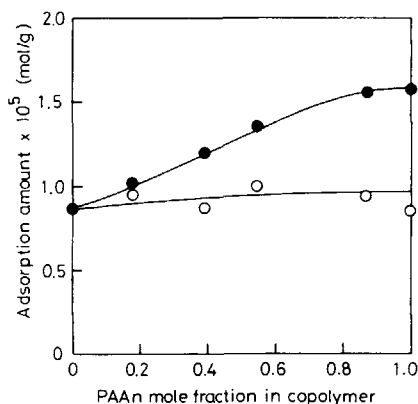


Fig. 4. Relation between PAA_n composition and amount of adsorption of MO for poly(HEMA) beads coated with PAA_n-HEMA copolymer at 25°C: (●) in the dark; (○) in photostationary state.

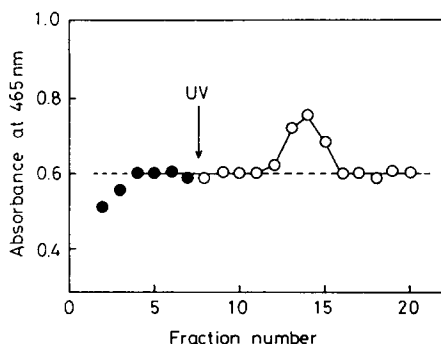


Fig. 5. Chromatography of MO on column packed with polystyrene coated with poly(PAA) at 25°C: flow rate, 1 ml/min; fraction volume, 3 ml; $[MO]_{in\ feed} = 2.4 \times 10^{-5}$ mol/L; (●) in the dark; (○) in light.

Chromatography of MO on Column Packed with Photoresponsive Polymeric Adsorbent

Figure 5 represents the result of an experiment in which MO was adsorbed on the photoresponsive polymeric adsorbent packed in a column and then desorbed by irradiation of light. As can be seen from the figure, when an aqueous solution of MO was allowed to pass through the column in darkness, the absorbance of the effluent became equal to that of the feed solution (broken line). This shows saturated adsorption of MO on the adsorbent. When light is irradiated in this state, the absorbance of the effluent increases, indicating the desorption of MO as a result of photo-induced hydrophobicity change on the surface of the adsorbent. Thus, it would be possible to isolate and purify a substance which cannot be desorbed from adsorbents by the gradient elution methods because its solubility in organic solvent is too low, such as cephalosporin antibiotics,⁹ by utilizing this type of photoresponsive polymeric adsorbents in a system using water as the single solvent.

References

1. N. Negishi, M. Takahashi, A. Iwasawa, K. Matsuyama, and I. Shinohara, *Nippon Kagaku Kaishi*, 1035 (1977).
2. N. Negishi, K. Ishihara, and I. Shinohara, *J. Polym. Sci. Polym. Lett. Ed.*, to appear.
3. R. Epton, Ed., *Hydrophobic, Ion Exchange, and Affinity Methods*, Halsted, New York, 1979.
4. G. S. Hartley, *J. Chem. Soc.*, 633 (1938).
5. T. Okano, J. Aoyagi, and I. Shinohara, *Nippon Kagaku Kaishi*, 161 (1976).
6. T. Okano, M. Katayama, and I. Shinohara, *J. Appl. Polym. Sci.*, **22**, 369 (1978).
7. R. Lovrien, P. Pesheck, and W. Tisel, *J. Am. Chem. Soc.*, **96**, 244 (1974).
8. I. M. Klotz and J. M. Urquhart, *J. Am. Chem. Soc.*, **71**, 841 (1947).
9. N. Negishi, K. Ishihara, I. Shinohara, T. Okano, F. Kataoka, and Y. Sakurai, *Makromol. Chem., Rapid Commun.*, **2**, 95 (1981).

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