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Photoviscosity Effect of Polymer Solutions

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Photoviscosity Effect of Polymer Solutions

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ABSTRACT

Poly(methyl methacrylate) and poly(methacrylic acid) having spirobenzopyran in the side groups and polyamide having azobenzene in the main chain were synthesized in attempting to construct photoresponsive polymer systems, the conformation of which can be photoregulated. The solution viscosity in benzene of poly(methyl methacrylate) containing spirobenzopyran groups (9 mole % in base unit) during irradiation was found to be 12% lower than the viscosity in the dark. The viscosity is restored to the initial value in less than 3 min in the dark after cutting off the light. A study of the solvent effect and a spectroscopic study have verified that the photoviscosity effect is due to the self-solvation of the ester side groups to the photoproduced merocyanines. Photoregulation of the polymer conformation was also achieved in methanol for poly(methacrylic acid) having spirobenzopyran and in dimethylacetamide for a polyamide having azobenzene in the main chain.

Photoregulation of the conformation of synthetic polymers has been attempted in several systems [1-4], mainly polyelectrolyte polymers with adsorbed chromophores of derivatives of azobenzene, to obtain

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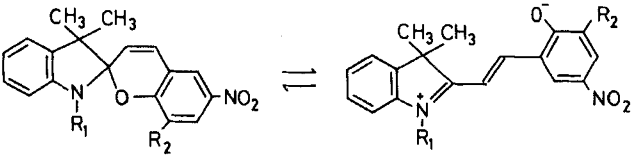
insight into the function of photobiological transducers and also to construct photoreceptor analogs. The basic condition for photoregulating the conformation of polymer chains is to prepare polymer systems containing chromophores capable of transforming the light energy into a change in conformation of the polymer chain. This condition can be achieved by attaching photoisomerizable chromophores to the side or main chains of the polymers by covalent bonds as well as by hydrophobic or electrostatic force.

We wish to report here photoinduced conformational changes observed in poly(methyl methacrylate) and poly(methacrylic acid) containing spirobenzopyran in the side groups and polyamide containing azobenzene in the main chain. Both spirobenzopyran and azobenzene are well known photochromic molecules. Spirobenzopyrans undergo under ultraviolet irradiation ring opening with production of strongly colored merocyanines; the merocyanine can return thermally or photochemically to the colorless spiropyrans, as shown in Eq. (1) [5].



(1)

In polar solvents, such as alcohols, colored mercyanines are formed stably even in the dark in equilibrium with colorless spirobenzopyrans. Photoexcitation of the merocyanines results in the ring closure; the red color disappears on irradiation with visible light.

Polymers containing spirobenzopyrans as side groups were synthesized by copolymerization of 1,3,3-trimethylindolino-6'-nitro-8'-methacryloxymethyl-spirobenzopyrans [R_2 = $CH_2OCOC(CH_3){=}CH_2$, R_1 = CH_3] with methyl methacrylate or methacrylic acid by radical initiation. Photoirradiation was carried out with a high pressure mercury lamp and wavelength was selected by the use of Toshiba cut-off filters. Conformational change of the polymer was follwed by viscosity measurement of the polymer solution with a Ubbelohde-type viscometer.

Figure 1 shows the viscosity of poly(methyl methacrylate) containing spirobenzopyran as side groups (9 mole % base unit) in benzene solution at 30°C in dark as well as during photoirradiation. The intrinsic viscosity during irradiation is 12% lower than the viscosity in dark. The viscosity reduction is reversible, the initial value being attained in less than 3 min in dark after cutting off the light

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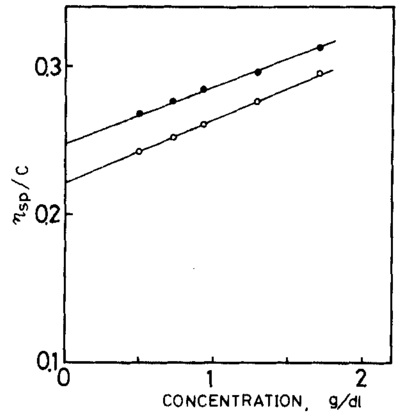

FIG. 1. Viscosity of poly(methyl methacrylate) containing spirobenzopyran in benzene at 30°C: (●) in dark; (○) under irradiation ($\lambda > 310$ nm).

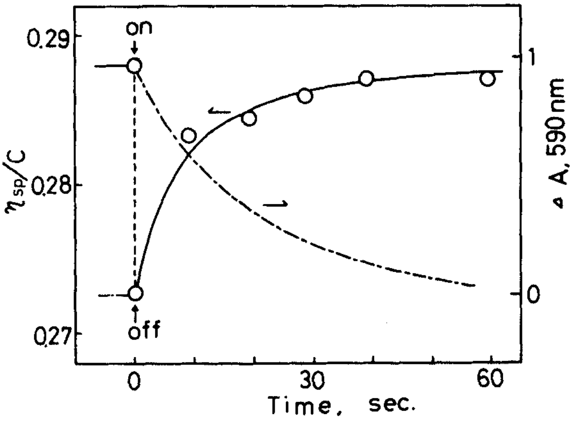

FIG. 2. Recovery of viscosity of poly(methyl methacrylate) containing spirobenzopyran and fading of the absorption at 590 nm in benzene at 30°C in dark.

as shown in Fig. 2. The recovery behavior of viscosity correlates well with the fading of the absorption at 590 nm.

The decrease/recovery cycles of the viscosity can be repeated many times; they are nicely reproducible and show no noticeable

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TABLE 1. Effect of Solvent on Viscosity Change of Poly(methyl Methacrylate) Containing Spirobenzopyran Induced by Photoirradiation ($\lambda > 310$ nm)

Solvent	ϵ	$[\eta]_p/[\eta]_d$
Benzene	2.3	0.83
Ethyl acetate	6.0	0.93
THF	7.4	0.95
Dichloroethane	10.4	0.99

fatigue. The possibility of the decrease due to thermal effect can be rejected, since the viscosity measurement and photoirradiation were carried out in a well controlled thermostat bath (less than ± 0.05°C).

The decrease depends on the polarity of the solvent, as shown in Table 1. The viscosity change in polar dichloroethane is only 1%, while in nonpolar solvent, such as benzene or toluene, it is higher than 10%. In tetrahydrofuran the decrease is intermediate between benzene and dichloroethane. The polarity effect predicts that the shrinkage of the polymer chain is caused by the intramolecular solvation of the ester side groups of methyl methacrylate chain to the polar merocyanine, produced by irradiation of the spirobenzopyran. In order to confirm this assumption we measured the photoviscosity of benzene solution of polystyrene, which has no polar group in the chain containing spirobenzopyran. We could not observe any appreciable decrease of the viscosity by photoirradiation of this polymer (less than 2%).

Spectroscopic study also supported the self-solvation of the ester groups to the merocyanines. The absorption maximum of the merocyanine bound to poly(methyl methacrylate) in benzene is 583 nm as shown in Fig. 3. The maximum shifted to shorter wavelength by 17 nm in comparison with the maximum of the absorption of low molecular weight analog of 1,3,3-trimethylindolino-6'-nitro-8'-dimethylcarboxymethylspirobenzopyran [$R_1 = CH_3$, $R_2 = CH_2OCOC(CH_3)_2$]. The blue shift indicates that the local polarity of merocyanine bound to poly(methyl methacrylate) is higher than the polarity around the low molecular analog in benzene. The higher polarity is considered due to the intramolecular solvation of the ester side groups to the merocyanine, which results in the decrease of the viscosity.

The self-solvation process can be directly followed by the measurement of the time-resolved absorption spectrum of the merocyanine in very short time region by the use of laser photolysis method. The merocyanine has an absorption maximum at 595 nm immediately

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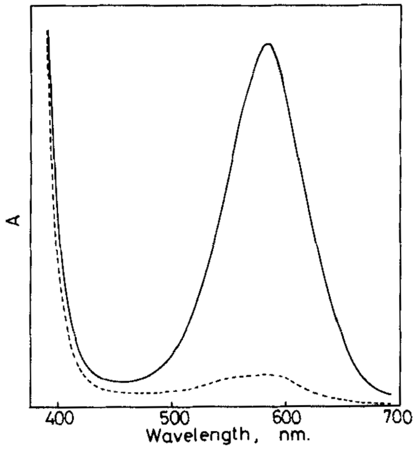

FIG. 3. Absorption spectra of poly(methyl methacrylate) containing spirobenzopyran in benzene: (--) in dark and (—) after irradiation by ultraviolet light.

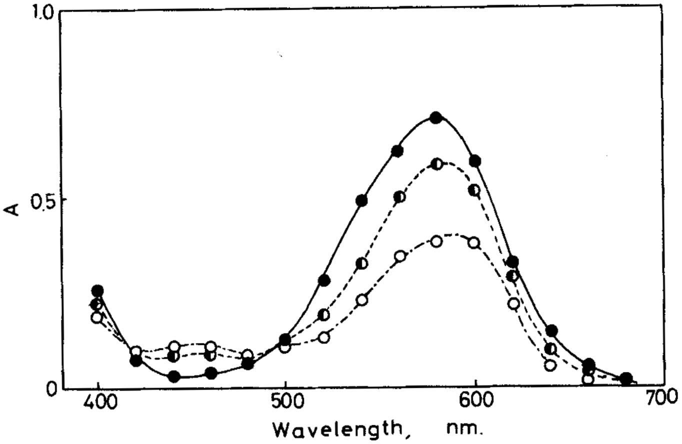

FIG. 4. Transient absorption spectra of poly(methyl methacrylate) containing spirobenzopyran in benzene (○) immediately; (◐) 100 nsec after the pulse; (●) 1 μsec after the pulse.

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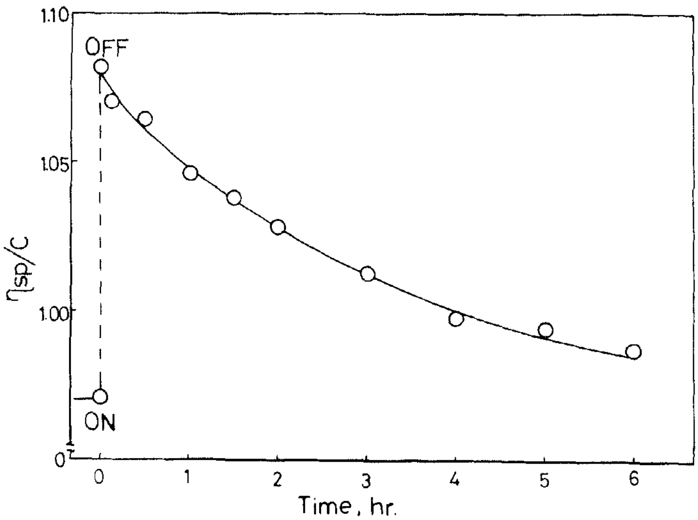

FIG. 5. Recovery of viscosity of poly(methacrylic acid) containing spirobenzopyran in methanol at 20°C in dark.

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after the pulse, while the maximum shifts to shorter wavelength of 580 nm in 1 μsec as shown in Fig. 4. The shifts directly reflect the dynamic change of microenvironments around the merocyanines produced by pulse excitation. This is caused by the self-solvation of the ester side groups of the polymer chains to the merocyanines.

Poly(methacrylic acid) containing spirobenzopyran as side groups shows reverse photochromism in methanol, as noted before. Colored merocyanines undergo under visible light irradiation ring closure with production of colorless spirobenzopyrans; the spirobenzopyran can return thermally to the merocyanines. The viscosity of the above poly(methacrylic acid) in methanol increased concomitant with the bleaching of the color of the merocyanines by visible light irradiation. The increased viscosity also is restored to the initial value in 8 hr in dark as shown in Fig. 5.

The recovery of viscosity was accelerated by ultraviolet irradiation to less than 10 min as shown in Fig. 6, and the increase/recovery cycles can be repeated many times by alternate irradiation of visible and ultraviolet light.

Another mechanism for the photoregulation of polymer conformation can be demonstrated by employing photoisomerizable group in the backbone. Isomerization from trans to cis form of azobenzene in the backbone is expected to kink the chain conformation. Azobenzene

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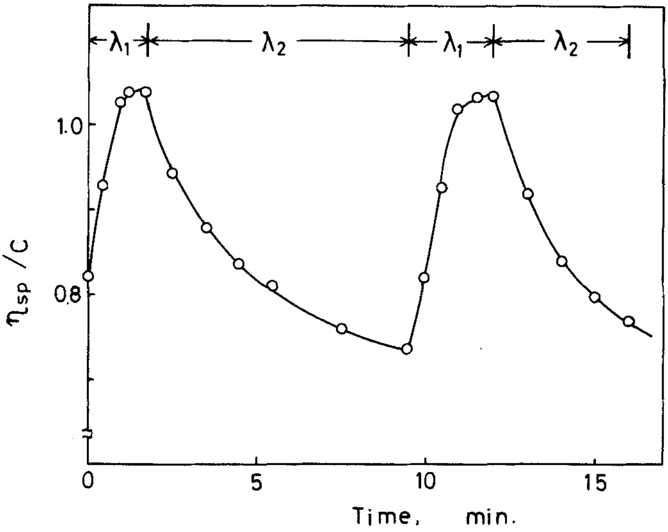

FIG. 6. Viscosity change of poly(methacrylic acid) containing spirobenzopyran in methanol on alternate irradiation by ultraviolet light (400 nm $> \lambda_1 >$ 310 nm) and visible ($\lambda_2 >$ 470 nm) light.

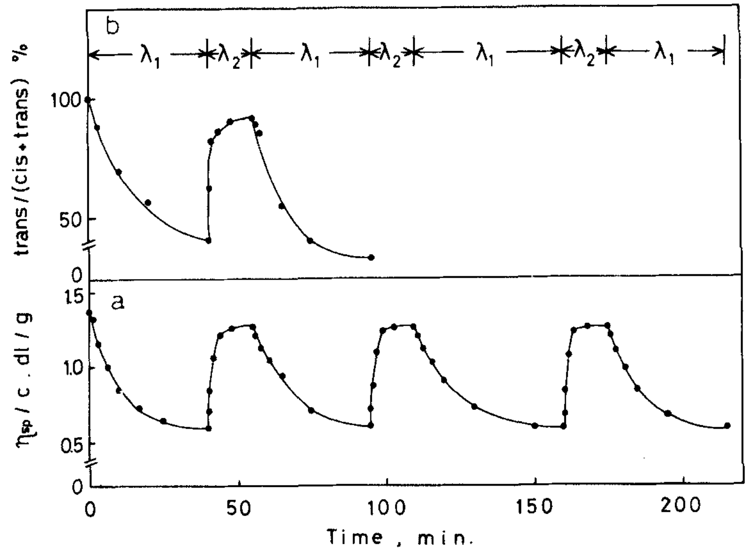

FIG. 7. Changes on alternating irradiation with ultraviolet (400 nm $> \lambda_1 >$ 330 nm) and visible ($\lambda_2 >$ 470 nm) light of a polyamide containing azobenzene in the main chain in dimethylacetamide: (a) viscosity change; (b) content of trans form of azobenzene unit (estimated from absorption spectrum).

was incorporated into the main chain by the condensation reaction of p-diaminoazobenzene and pyromellitic dianhydride [6]. The azobenzene unit in the polymer in the trans form has strong absorption at 385 nm. Photoexcitation by ultraviolet light reduced the absorption, and a new band appeared around 500 nm. This spectrum change can be attributed to trans-cis isomerization of the azobenzene unit.

Figure 7 shows the viscosity of the polymer in dimethylacetamide under alternate irradiation by ultraviolet and visible light along with content of trans-form of azobenzene unit estimated from the absorption spectrum. The decrease/recovery cycles of the viscosity of this polymer unambiguously correlate directly with the trans-cis isomerization of azobenzene unit in the main chain of the polymer.

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