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Photoresponsive Polymers. 3.[1] Reversible Solution Viscosity Change of Poly(methacrylic acid) Having Spirobenzopyran Pendant Groups in Methanol

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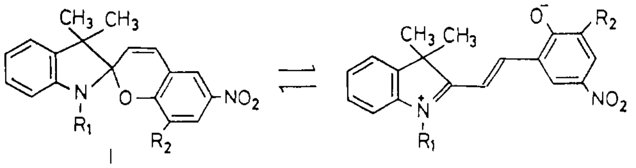
ABSTRACT: Reversible control of solution viscosity by as much as 50% has been achieved upon alternate irradiation with visible (λ >470 nm) and ultraviolet (410 nm > λ > 310 nm) light, using poly(methacrylic acid) having spirobenzopyran pendant groups in methanol. A large conformational change of the polymer chain was caused by the photoisomerization of the spirobenzopyran attached to the pendant groups. The disappearance/reappearance of the zwitterion structures (merocyanines) on the pendant groups upon visible/ultraviolet light irradiation is considered to alter the balance of the intrachain interactions, resulting in the expansion/contraction of the polymer chain.

Introduction

Although several attempts have been reported to control the conformation of synthetic polymers by photoirradiation, the studies are limited to polymer systems having covalently bound azobenzene residues in the pendant groups[2,4,5] or adsorbed azo dyes[2,3] and the observed effects are very small. Other photoisomerizable chromophores, such as spirobenzopyrans or indigos, are also considered to be useful as well. We have tried to attach spirobenzopyrans to the pendant groups of polymers as chromophores capable of transforming light energy into a change in main-chain conformation.[6]

Spirobenzopyrans are well-known photochromic molecules, which isomerize from the spiropyran to the intensely colored merocyanine form under ultraviolet irradiation; the merocyanines can return thermally or photochemically to the colorless spiropyrans as follows:[7]



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In polar solvents, such as alcohols, colored merocyanines form even in the dark and are in equilibrium with colorless spiropyrans. Photoexcitation of the merocyanines with visible light in alcohols brings about ring closure, with production of colorless spiropyrans; the red color disappears on irradiation with visible light.

In a previous paper,[6] we reported a reversible photodecrease of solution viscosity of poly(methyl methacrylate) having spirobenzopyran pendant groups in nonpolar solvents. The viscosity change was caused by intramolecular solvation by the ester side groups of the photogenerated polar merocyanines. In polar solvents we could not observe any appreciable viscosity decrease by photoirradiation of this polymer.

In this article, we report photoinduced conformational changes observed in poly(methacrylic acid) having spirobenzopyran pendant groups in polar solvents. Methanol solutions of the polymer have a red color, which indicates that merocyanines are formed in the pendant groups in equilibrium with spirobenzopyran in the polar solvent. Visible light irradiation of the solution displaces the equilibrium toward the formation of spirobenzopyran. The disappearance of the merocyanines is expected to alter the equilibrium conformation of the main chain, since the isomerization is associated with a large decrease of the dipole moment of the side chains.

Experimental Section

Polymers having spirobenzopyran pendant groups were synthesized by copolymerization of 1,3,3-trimethylindolino-6′-nitro-8′-[(methacroyloxy)methyl]spirobenzopyran (1, $R_1 = CH_3$; $R_2 = CH_2OCOC(CH_3){=}CH_2$) with methacrylic acid by radical initiation.[6] The content of spirobenzopyran in the polymers was

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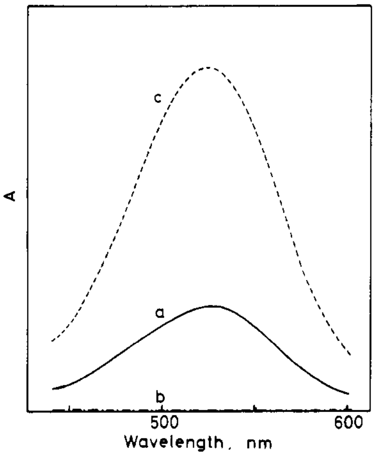

Figure 1. Absorption spectra of merocyanine bound to poly(methacrylic acid) in methanol at 20 °C: (a) under thermal equilibrium conditions; (b) under photostationary state of visible light ($\lambda > 470$ nm) irradiation; (c) under photostationary state of ultraviolet light ($410 \text{ nm} > \lambda > 310$ nm) irradiation.

determined by elemental analysis.

Irradiation was carried out with a 500-W high-pressure mercury lamp and wavelength was selected with Toshiba cutoff filters. Conformational change of the polymer was followed by viscosity measurements of the polymer solutions with an Ubbelohde viscometer specially designed for irradiation. Absorption spectra were measured with a Cary 118 spectrophotometer.

Results and Discussion

Absorption Spectra. Methanol solutions of the poly(methacrylic acid) having spirobenzopyran pendant groups have a red color under thermal equilibrium conditions at 20 °C. Figure 1a shows the absorption spectrum of the solution. It has an absorption maximum at 530 nm. The absorption spectrum is similar to the spectrum of 1,3,3-trimethylindolino-6′-nitro-8′-[[(isopropylcarbonyl)oxy]methyl]spirobenzopyran (1, $R_1 = CH_3$; $R_2 = CH_2OCOCH(CH_3)_2$) in methanol and is ascribable to the ring-opened form of the spirobenzopyrans, the merocyanine form.[7]

Visible light irradiation ($\lambda > 470$ nm) completely bleached the absorption, as shown in Figure 1b; after the light was removed, the absorption gradually reappeared in the dark. The photobleaching process corresponds to the ring-closing reaction of the merocyanine to the colorless spirobenzopyran.[7] Under photostationary state of visible light irradiation, the equilibrium completely shifted to the spirobenzopyran form. The reappearance of the red color indicates that the ring-opening reaction readily occurs in the dark at 20 °C in methanol, though the rate of appearance of the red color in the dark was not so fast as observed in the case of benzene solution of poly(methyl methacrylate) having spirobenzopyran pendant groups, where the photogenerated blue color disappeared in 3 min in the dark.[6]

Ultraviolet light irradiation ($410 \text{ nm} > \lambda > 310$ nm), on the other hand, enhanced the absorption around 530 nm, as shown in Figure 1c. The increase suggests that ultraviolet light displaced the equilibrium to the formation of the merocyanines, as observed for poly(methyl methacrylate) having spirobenzopyran pendant groups in benzene.[6] The intense absorption at 530 nm generated by ultraviolet light irradiation returned to the thermal equilibrium intensity after removal of the light. Under photostationary state of ultraviolet light irradiation at 20 °C, the concentration of the photogenerated merocyanines exceeded the concentration of merocyanines at thermal equilibrium before photoirradiation. The response of the absorption intensity to the ultraviolet and visible light irradiations suggests that the concentration of the merocyanine form in the pendant group of poly(methacrylic acid) can be controlled by the selection of the irradiating wavelength.

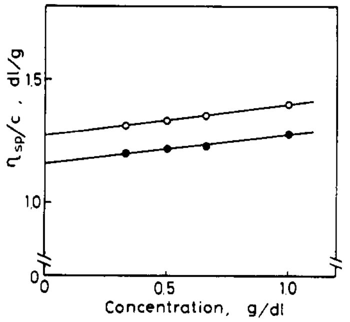

Figure 2. Viscosity of poly(methacrylic acid) having spirobenzopyran pendant groups (8.9 mol % of monomer unit) at 30 °C in methanol: (●) in the dark; (○) under visible light ($\lambda > 470$ nm) irradiation.

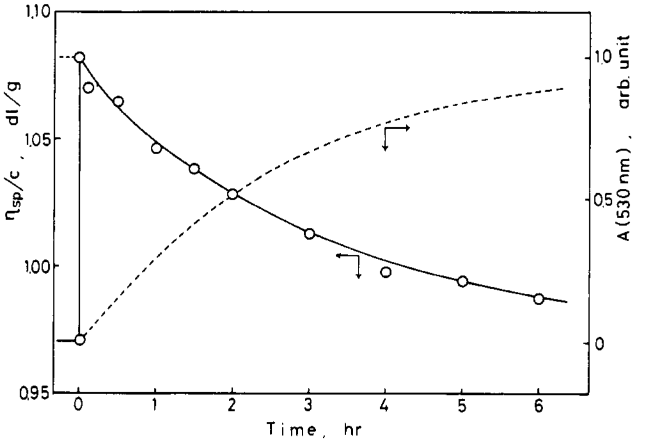

Figure 3. Recovery of the viscosity of poly(methacrylic acid) having spirobenzopyran pendant groups (8.9 mol % of monomer unit) and reappearance of the absorption at 530 nm due to merocyanine in methanol at 20 °C. Concentration of the polymer is 0.25 g/dL.

Photoviscosity Effect. Figure 2 shows the viscosity of poly(methacrylic acid) having spirobenzopyran pendant groups (8.9 mol % of monomer unit) in methanol in the dark as well as under visible light ($\lambda > 470$ nm) irradiation. The intrinsic viscosity under visible irradiation was 10% higher than the viscosity in the dark. The possibility that thermal effects from photoirradiation are responsible is readily excluded since the photoviscosity effects observed are the reverse of those expected if heating from light absorption were the source of the changes. The increase of the viscosity shows that the light energy absorbed by the merocyanine form is utilized to expand the polymer conformation.

The viscosity increased by visible light irradiation returned to the initial value in several hours at 20 °C after the light was removed. Figure 3 shows the return of the viscosity along with the reappearance of the absorption at 530 nm. The recovery behavior of the viscosity correlates well with the return of the absorption to the thermal equilibrium state.

Although it takes a long time for the merocyanines in the polymer pendant groups to return to the thermal equilibrium concentration in polar methanol, the rate was accelerated by adding less polar dioxane. The addition of 30 vol % of dioxane accelerated the rate of the recovery of the absorption at 530 nm about 2.5 times. In less polar

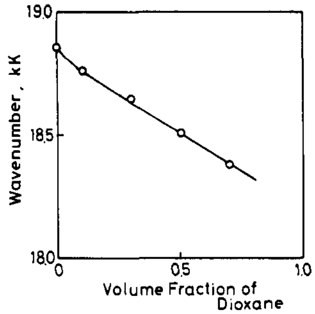

Figure 4. Shift of the absorption maximum of merocyanine bound to poly(methacrylic acid) in methanol by the addition of dioxane.

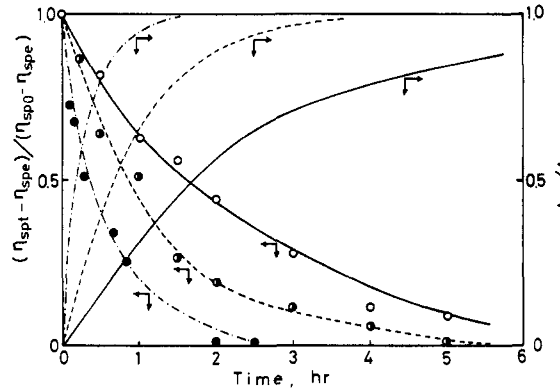

Figure 5. Effect of the addition of dioxane on the recovery of the viscosity of poly(methacrylic acid) having spirobenzopyran pendant groups (8.9 mol % of monomer unit) and reappearance of the absorption at 530 nm due to merocyanine at 20 °C in methanol. Volume ratios of dioxane to methanol are (—) 0%, (---) 30%, and (-·-) 70%. η_{spt}, η_{spo}, and η_{spe} are specific viscosities at time t, under photostationary state of visible light (λ >470 nm) irradiation, and under thermal equilibrium conditions, respectively. A_t and A_e are absorbances at time t and under thermal equilibrium conditions, respectively. Concentration of the polymer is 0.25 g/dL.

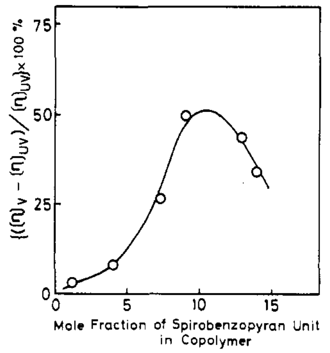

Figure 6. Dependence of the photoinduced viscosity change of a methanol solution of poly(methacrylic acid) having spirobenzopyran pendant groups on the content of the spirobenzopyran unit at 20 °C. $[\eta]_V$ and $[\eta]_{UV}$ are intrinsic viscosities under photostationary state of visible light (λ >470 nm) irradiation and under photostationary state of ultraviolet light (410 nm > λ > 310 nm) irradiation, respectively.

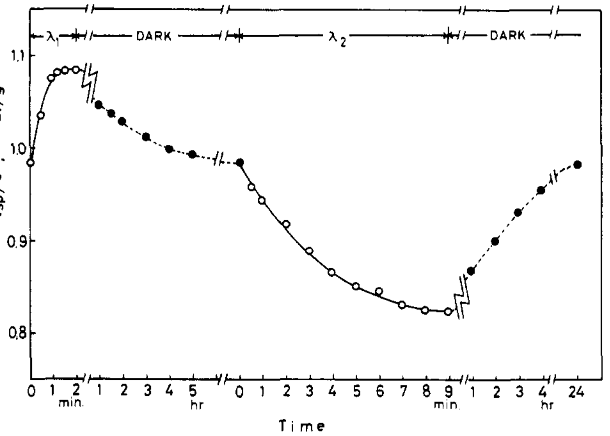

Figure 7. Changes of the viscosity of a methanol solution of poly(methacrylic acid) having spirobenzopyran pendant groups (7.4 mol % of monomer unit) on visible light (λ_1 >470 nm) irradiation and ultraviolet light (410 nm > λ_2 > 310 nm) irradiation at 20 °C. Concentration of the polymer is 0.25 g/dL.

solvents the visible maximum of the merocyanine form shifted to longer wavelength (Figure 4), and the merocyanine form became less stable compared with the spirobenzopyran form. The decrease of solvation energy in less polar solvents of the zwitterion structure results in the destabilization and the shift.[7] The increase of the absorption intensity recovery rate was accompanied by an increase in the rate of the return of the viscosity, as shown in Figure 5. The correlation between the behavior of merocyanine concentration in the pendant groups and the viscosity indicates that expansion or contraction of the polymer conformation is unambiguously caused by the photoisomerization of the spirobenzopyran pendant groups.

The merocyanine has a zwitterion structure.[7] The destruction of the zwitterion structure from the pendant groups by visible light irradiation is considered to alter the balance of intrachain interactions. Electrostatic attractive forces between the zwitterions and the charges on carboxylic acid residues of the polymer chain[8] tend to contract the polymer chain, while the charges on the carboxylic acid residues, at the same time, generate repulsive forces which tend to expand the polymer. The polymer conformation depends on the balance of the two forces. In the dark before photoirradiation the attractive forces overcome the repulsive forces and the polymer chain has a contracted conformation. Upon visible light irradiation, the attractive force considerably decreases because of the disappearance of the zwitterion structures, unbalancing the system until electrostatic forces cause the polymer chain to expand. Under photostationary state of visible light irradiation, the conformation of the polymer is mainly determined by the repulsive forces between the charges on the carboxylic acid residues.

The dipole–dipole interaction between the zwitterion structures is considered to make an insignificant contribution to the attractive forces. The viscosity change of the methanol solution of the poly(methacrylic acid) having spirobenzopyran pendant groups has a maximum at a spirobenzopyran content of 10 mol % of monomer unit, as depicted in Figure 6. The appearance of the maximum at a rather low content of spirobenzopyran implies that the viscosity change is not due to the intrazwitterion structure interaction but due to the intramolecular interaction between the zwitterion structures and the carboxylic acid residues in the side groups. A large viscosity effect should be observed with high spirobenzopyran content if the intramolecular interaction between the zwitterion structures contributed to the attractive forces to a large extent. A high content of spirobenzopyran groups, on the contrary, suppressed the photoviscosity effect.

The photoviscosity mechanism that the intramolecular attractive forces between the zwitterions of merocyanines and the charges on the carboxylic acid residues contract the polymer chain suggests that the complete conversion of the pendant spirobenzopyrans to the merocyanine form

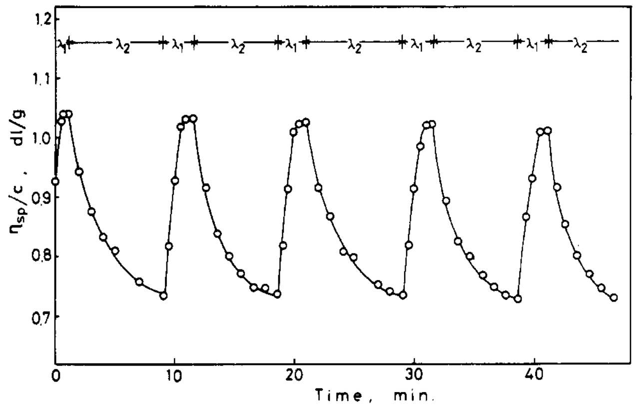

Figure 8. Changes of the viscosity of a methanol solution of poly(methacrylic acid) having spirobenzopyran pendant groups (8.9 mol % of monomer unit) on alternate irradiation with visible (λ_1 >470 nm) and ultraviolet (410 nm > λ_2 > 310 nm) light at 20 °C. Concentration of the polymer is 0.25 g/dL.

causes large shrinkage of the polymer chian. The shift of the equilibrium to the merocyanine form can be achieved by ultraviolet light irradiation as already shown in Figure 1. Figure 7 shows the effect of ultraviolet light irradiation on the solution viscosity of the poly(methacrylic acid) having spirobenzopyran pendant groups. Ultraviolet light irradiation (410 nm > λ > 310 nm) after the viscosity returns to the thermal equilibrium state caused a decrease of the viscosity. The viscosity reduced by ultraviolet light irradiation returned to the thermal equilibrium value in the dark after the light was removed. The amount of the decrease was larger than the increase observed under visible light irradiation. This suggests that the conformation of the polymer chain under thermal equilibrium conditions is a loosely contracted form and not a densely compact one. The amount of the viscosity change is related to the merocyanine concentration difference between the thermal equilibrium state and the two photostationary states achieved with visible and ultraviolet light irradiation. The photoinduced concentration change is larger for the ultraviolet light irradiation as shown in Figure 1, resulting in a larger photoviscosity effect under ultraviolet light irradiation.

Ultraviolet or visible light irradiation accelerated the slow return of the viscosity in the dark after the photostationary state had been reached. High viscosity generated by visible light irradiation was reduced in less than 10 min, by as much as 40%, under ultraviolet light irradiation, though comparable thermal recovery takes several hours. Visible light, on the other hand, accelerated the recovery of the viscosity reduced by ultraviolet light irradiation. Figure 8 shows the viscosity of poly(methacrylic acid) having spirobenzopyran pendant groups in methanol under alternate irradiation with visible and ultraviolet light. Alternate irradiation brings about viscosity changes as much as 40% and the increase/decrease cycle of the viscosity can be repeated many times without noticeable fatigue. The rate of the viscosity change depended on the light intensity, concentration of the polymer, and the shape of the cell, the time becoming less than 3 min with a high-intensity superhigh-pressure lamp (Philips SP-500).

Summary

Poly(methacrylic acid) having spirobenzopyran pendant groups has been prepared in an attempt to construct photoresponsive polymer systems. The pendant spirobenzopyran isomerized from the merocyanine to the spiropyran form under visible light (λ >470 nm) irradiation, whereas ultraviolet light (410 nm > λ > 310 nm) irradiation caused isomerization from the spiropyran to the merocyanine form. Alternate irradiation with visible and ultraviolet light induced a polymer solution viscosity change by as much as 50% in methanol. The disappearance/reappearance of the zwitterion structure (merocyanine form) in the pendant groups by visible/ultraviolet irradiation altered the balance of the intrachain interaction, resulting in an increase/decrease of the solution viscosity. This is a typical example of the control of solution viscosity by selection of irradiating wavelength. We can expect to control not only solution viscosity but other physical properties of the polymer and the polymer solutions by selection of irradiating wavelength.

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