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Photoresponsive Polymers. 2.[1] Reversible Solution Viscosity Change of Polyamides Having Azobenzene Residues in the Main Chain

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ABSTRACT: Polyamides having a photoisomerizable unsaturated linkage in the backbone of the polymer chain were synthesized in an attempt to construct photoresponsive polymer systems. Solution viscosity of polyamides composed of azobenzene and phenylenediamide residues under ultraviolet irradiation ($410 > \lambda > 350$ nm) was 60% lower than the viscosity in the dark in *N,N*-dimethylacetamide. The viscosity that was reduced by the irradiation returned to the initial value in 30 h at 20 °C after removing the light. The slow recovery of the viscosity in the dark was accelerated by visible light irradiation ($\lambda > 470$ nm). On alternate irradiation with ultraviolet and visible light, the solution viscosity was reversibly controlled by as much as 60%. Spectroscopic study and the effect of rigidity of chain segment on the photoviscosity behavior indicate that the photodecrease arises from the trans–cis photoisomerization of the azobenzene residues in the backbone of the semiflexible chain. Photocontrols of conductivity and pH value were also achieved by using photoresponsive polyamides having terephthalic acid groups.

Introduction

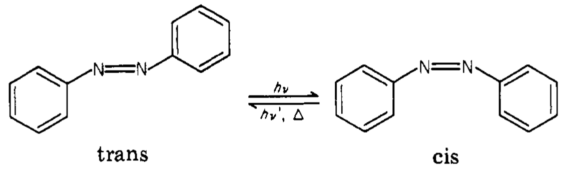
The photoinduced cis–trans isomerization of organic molecules about an unsaturated linkage is a well-known photochromic phenomenon that has been extensively studied. The isomerization process can be symbolized by

$$\text{trans} \underset{h\nu',\ \Delta}{\overset{h\nu}{\rightleftharpoons}} \text{cis}$$

A photosensitive chromophore in the trans form is converted under irradiation into the cis form, which returns to the initial state either thermally or photochemically. The isomerization is always accompanied by significant changes of physical properties such as dipole moment, melting and boiling points, and refractive index. In other words, we can photocontrol the physical properties of materials by using photoisomerizable molecules.

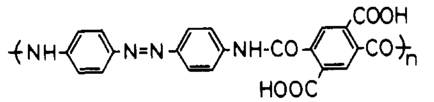
When we incorporate the photoisomerizable chromophores into the backbone of polymer chain, photoinduced isomerization of the chromophores is expected to induce a conformational change of the polymer chain. The photoinduced conformational change reversibly converts physical and chemical properties of the polymers and the polymer solutions.

In a previous paper[1] we reported the reversible photodecrease of solution viscosity of poly(methyl methacrylate) having spirobenzopyran side groups. The viscosity change is caused by intramolecular solvation by the ester side groups of the photogenerated polar merocyanines. This paper describes another type of photoresponsive polymers having a photoisomerizable unsaturated linkage in the backbone of the polymer chain. We adopted azobenzene as a photosensitive chromophore and synthesized polyamides having the azobenzene residues in the backbone of the polymer chain.[2,3] Azobenzene is a well-known photochromic molecule, which undergoes isomerization from the trans to the cis form under ultraviolet irradiation; the cis form can return thermally or photochemically to the trans form as follows:



Experimental Section

Polyamides I–V were synthesized by the condensation reaction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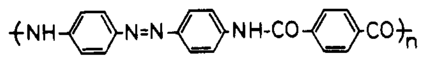
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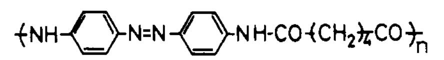
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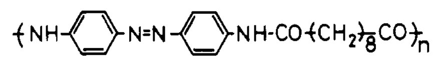
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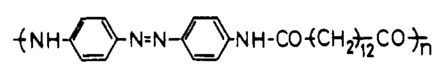
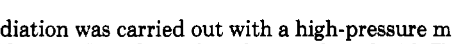

(V)

of *p,p'*-diaminoazobenzene with pyromellitic dianhydride, terephthaloyl dichloride, or ClCO–$(CH_2)_m$–COCl (m = 4, 8, and 12).[2,3] *p,p'*-Diaminoazobenzene was prepared by standard paths.[4] Pyromellitic dianhydride and terephthaloyl dichloride were purified by vacuum sublimation. The diacid chlorides (m = 4 and 8) were used as purchased. Dodecane-1,12-dicarbonyl dichloride (m = 12) was synthesized from the diacid and thionyl chloride. *N,N*-Dimethylacetamide used for polymerization as well as for conductivity measurement was purified as follows: The liquid was shaken with phosphorus pentaoxide, filtered through a glass filter, and vacuum distilled. This treatment was repeated three times. Hexamethylphosphoramide and *N*-methyl-2-pyrrolidone were purified by vacuum distillation over calcium hydride.

Polymerization of polymer I was carried out in *N,N*-dimethylacetamide. A solution consisting of 0.636 g of *N,N'*-diaminoazobenzene, 0.654 g of pyromellitic dianhydride, and 14 mL of purified and dried *N,N*-dimethylacetamide was stirred for 20 h at about 50–60 °C. The reaction mixture was poured into a large volume of ethanol, yielding a fibrous precipitate. The polymer was purified by repeated reprecipitation from *N,N*-dimethylacetamide solution with ethanol and then dried in a vacuum oven. The absence of monomers and low molecular weight oligomers was confirmed with a gel permeation chromatograph spectrometer (Tōyōsoda HLC-801), using *N,N*-dimethylformamide as eluant. The molecular weight of the polymer was controlled by changing the ratio of the two monomers in the feed.

Polymerization of polymers II–V was carried out in a mixed solvent of hexamethylphosphoramide and *N*-methyl-2-pyrrolidone (2:1 by volume) by the same method as described in ref 2a–d). The polymers were washed several times with water, with acetone–water (1:1 by volume), and finally with acetone and dried in a vacuum oven.

Low molecular weight analogues VI and VII were also synthesized by using monofunctional acid chlorides and *p,p'*-diaminoazobenzene.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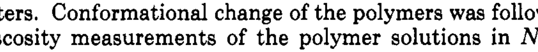
(VII)

Irradiation was carried out with a high-pressure mercury lamp (USHIO, 500 W), and wavelength was selected with Toshiba cutoff filters. Conformational change of the polymers was followed by viscosity measurements of the polymer solutions in *N,N'*-dimethylacetamide for polymer I or in *N*-methyl-2-pyrrolidone in the presence of LiCl for polymers II–V.

Absorption spectra were measured with a Cary 118 spectrophotometer. The temperature of the cell was controlled with a temperature-controlled circulating bath (Neslab LT-50). The sample temperature was monitored with a digital thermometer (Doric 410A) and was controlled to within ±0.5 °C.

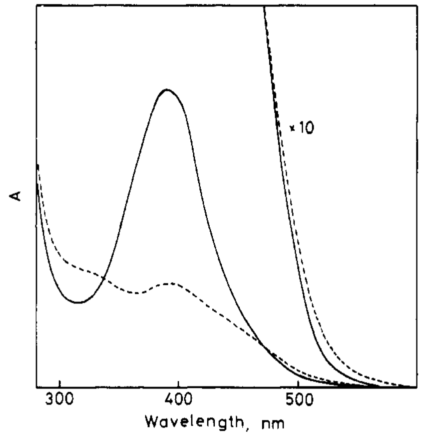

Figure 1. Absorption spectra of polyamide I in *N,N*-dimethylacetamide (—) in the dark before irradiation and (---) after irradiation with ultraviolet light (410 > λ > 350 nm).

Conductivity measurement was carried out with an autobalance universal bridge (Wayne Kerr, Model B642) at 25 °C. pH measurement of the aqueous solution of polymer I was performed at 20 °C under a nitrogen atmosphere. The aqueous solution was prepared by dissolving polymer I in water at room temperature, using a small amount of *N,N*-dimethylacetamide (less than 1%). The pH of the solution in the dark was adjusted to around 5.5 by the addition of a normal solution of sodium hydroxide.

The temperature of the cells used for viscosity, conductivity, and pH measurement was controlled to within ±0.05 °C by using a thermostated bath.

Results and Discussion

A. Photoisomerization. Azobenzene is known to change its absorption spectrum when the configuration changes from the trans to the cis form. Intense absorption at 320 nm due to $\pi-\pi^*$ transition decreases while absorption at 430 nm due to $n-\pi^*$ absorption increases.[5]

Similar spectral changes were observed for polyamides I–V and their analogues VI and VII. Figure 1 shows representative spectra of polymer I. The intense absorption band at 390 nm decreased when the *N,N*-dimethylacetamide solution of polymer I was irradiated with ultraviolet light (410 > λ > 350 nm), while the band at 510 nm increased. The intense band at 390 nm is ascribable to the trans form of the amide-substituted azobenzene in the backbone of the polymer chain and the band at 510 nm to the cis form. The red shift of the peak positions in comparison with unsubstituted azobenzene is attributable to the substituent effect. The interconversion of the 390-nm band to the 510-nm band is clear evidence of the photoisomerization of azobenzene residues in the chain backbone.

Thermal isomerization from the photogenerated cis form to the trans form was followed by the absorption spectrum. The absorption intensity at 390 nm of the polymer solutions increases gradually in the dark after removing the light at room temperature and reaches its maximum in 30 h. The isomerization proceeded exactly according to first-order kinetics. The slope of a plot of log $(A_\infty - A_t)$ against time t gives the rate of the thermal isomerization from the cis form to the trans form of the azobenzene residues in the backbone of the polymer chain; A_∞ and A_t are absorbances at 390 nm before photoirradiation and at time t, respectively. The rates and the activation energies are summarized in Table I. The rates of the low molecular weight analogues were also measured and are listed in Table I. The rates are identical for polyamides having

Table I
Kinetic Data of the Isomerization of Azobenzene Residues from Trans to Cis Form[a]

polymer or analogue[b]	$k \times 10^3$, min^{-1} 20 °C	25 °C	30 °C	35 °C	E_a, kcal/mol
polyamide II					
$[\eta] = 0.87$	2.3	4.4	7.8	15	22
polyamide III					
$[\eta] = 2.10$	2.2	4.1	7.6	13	22
$[\eta] = 0.50$	2.1	4.7	8.8	15	23
polyamide IV					
$[\eta] = 1.01$	2.3	4.3	8.4	14	22
polyamide V					
$[\eta] = 0.33$	2.4	4.7	8.1	16	22
analogue VI	2.4	4.8	8.7	14	22
analogue VII	2.2	4.0	7.6	13	22

[a] In *N*-methyl-2-pyrrolidone in the presence of LiCl (1.3 M). [b] Concentrations of the polymers and analogues are 2.0×10^{-5} (base-mol)/L.

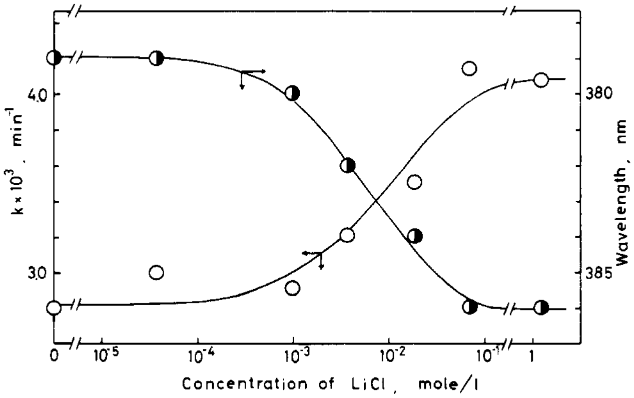

Figure 2. Effect of addition of LiCl on the thermal isomerization rate of low molecular weight analogue VII from the cis to the trans form and its absorption maximum in *N*-methyl-2-pyrrolidone at 25 °C. Concentration of the analogue is 2.0×10^{-5} mol/L.

different molecular weights and there is no significant difference in the activation energies between the polymer and the corresponding low molecular weight analogue. This observation for polymers having a high content of azobenzene residues in the chain backbone agrees with the results of Morawetz et al. for polymers containing small numbers of azobenzene residues that the rate of thermal isomerization of azobenzene in the polymer chain is identical with that of the corresponding low molecular weight analogue.[6] The nonvariance of the thermal isomerization rate on the molecular weight suggests the relaxation of the polymer conformation is rapid enough to follow the thermal isomerization.

The thermal isomerization rates of polyamides II–V and analogues VI and VII were accelerated by addition of LiCl. Figure 2 shows the effect of addition of LiCl on the rate of isomerization along with the absorption maximum of the low molecular weight analogue VII in *N*-methyl-2-pyrrolidone. The increase in the rate is accompanied by a red shift of the absorption peak. The red shift suggests that the increase of the rate arises from the electronic structure change of the azobenzene unit. The complexation mechanism proposed by Panar[2e] of LiCl to the amide group may account for the electronic structure change. In the experiments shown in Table I, concentrations of LiCl were kept to 1.3 M, at which concentration the complexation is considered to be complete.

B. Photoviscosity Effect. Figure 3 shows the solution viscosity of polymer I in *N*,*N*-dimethylacetamide in the dark as well as during irradiation with ultraviolet light (410 > λ > 350 nm). The intrinsic viscosity during irradiation is 60% lower than the viscosity in the dark. The absence of a concentration effect suggests that the photodecrease arises from the conformational change of the polymer chain and not from interchain interaction.

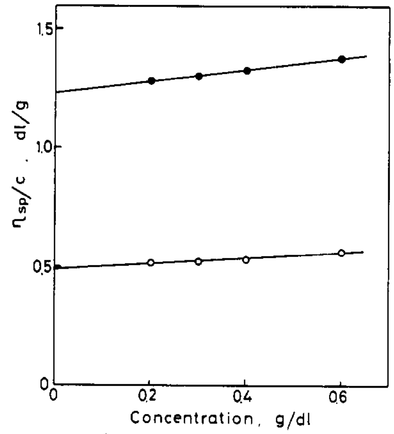

Figure 3. Viscosity of polyamide I in *N*,*N*-dimethylacetamide at 20 °C (●) in the dark before irradiation and (○) under irradiation with ultraviolet light (410 > λ > 350 nm).

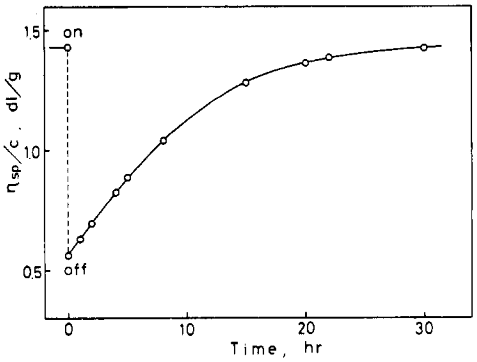

Figure 4. Recovery of viscosity of polyamide I in *N*,*N*-dimethylacetamide at 20 °C in the dark. Concentration of the polymer is 0.9 g/dL.

The viscosity reduced by photoillumination returns to the initial value in 30 h in the dark at 20 °C, as shown in Figure 4. Thermal recovery of the viscosity occurs at a rate similar to that at which the absorption intensity at 390 nm increases. The correlation between the viscosity and the absorption intensity at 390 nm implies that the shrinkage of the polymer conformation is induced by the isomerization of the azobenzene residues from the trans to the cis form, and the thermal recovery from the cis to the trans form expands the chain conformation.

The slow recovery of the viscosity in the dark was accelerated by visible light irradiation (λ > 470 nm). Figure 5b shows the decrease of viscosity of a polymer I solution by irradiation with ultraviolet light (410 > λ_1 > 350 nm) and the recovery with visible light (λ_2 > 470 nm). The viscosity returns to the photostationary value with visible light, which is slightly less than the thermal equilibrium value, in 10 min, though the thermal recovery takes 30 h in the dark. The rate of the acceleration depends on the light intensity, the time necessary for the recovery becoming less than 3 min when a high-intensity superhigh-pressure mercury lamp is used (Philips SP-500).

The cis form of the substituted azobenzene in the main chain has weak absorption around 510 nm due to n–π* transition (Figure 1). Photobleaching of this band with visible light (λ > 470 nm) accelerates the recovery of the absorption at 390 nm due to the trans form from 30 h

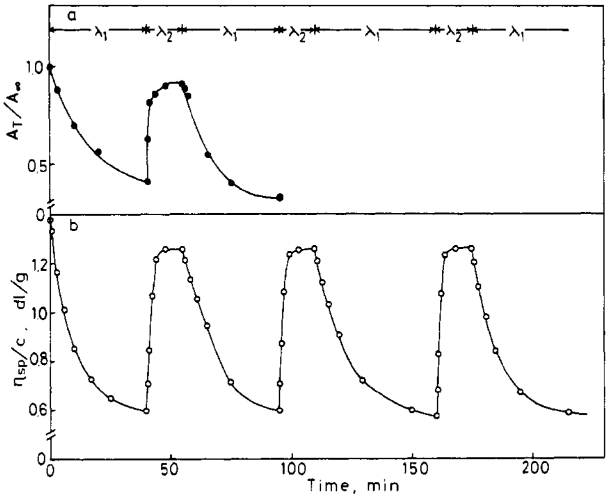

Figure 5. Changes of (a) content of the trans form of azobenzene residues in the polyamide I backbone and (b) viscosity of polyamide I in *N*,*N*-dimethylacetamide on alternate irradiation with ultraviolet (410 > λ_1 > 350 nm) and visible (λ_2 > 470 nm) light at 20 °C. Concentration of the polymer is 0.9 g/dL.

(Figure 4) to 10 min, as shown in Figure 5a. The content of the trans form of the azobenzene residues estimated from the absorption spectrum is plotted against photoillumination time in Figure 5a. The content can be expressed by $(A_t/A_\infty)[\epsilon_t/(\epsilon_t - \epsilon_c)] - \epsilon_c/(\epsilon_t - \epsilon_c)$, where A_t and A_∞ are the absorbances at 390 nm at time t and before irradiation and ϵ_t and ϵ_c are the extinction coefficients of the trans form at 390 nm and that of the cis form. The values of A_t/A_∞ are plotted instead of $(A_t/A_\infty)[\epsilon_t/(\epsilon_t - \epsilon_c)] - \epsilon_c/(\epsilon_t - \epsilon_c)$ in Figure 5a because precise ϵ_c and ϵ_t values are not known and the ϵ_c value is considered to be very small compared with ϵ_t.

It appears from inspection of Figure 5 that a photodecrease and -increase of the viscosity occur concomitantly with the changes of the trans form content; the fast recovery of the viscosity arises from the photoinduced fast isomerization of the azobenzene residues from the cis to the trans form. The acceleration effect also supports a mechanism in which the photochange of viscosity is caused by isomerization of the azobenzene residues in the backbone of the polymer chain. The decrease/recovery cycle of the viscosity can be repeated many times without any noticeable fatigue.

C. Effect of Rigidity of Chain Segments. The backbone of polyamide I is composed of azobenzene and phenylenediamide residues. These stiff residues suggest the polymer behaves as a semiflexible rod in solution. The extended rodlike shape of the semiflexible chain is expected to shrink readily to a compact conformation when the configuration of the constituent azobenzene residues changes from the trans to the cis form. The large photodecrease of viscosity of polyamide I is interpreted by this mechanism.

The effect of flexible segments between the azobenzene residues on the photodecrease was examined to support further the photoshrinkage mechanism. Polyamides having a phenylene residue (II) and methylene chains with different lengths (III–V) between azobenzene residues were prepared.

Polyamide II has a structure similar to that of polymer I, except it has no carboxylic groups. Although polyamides II–V are hardly soluble in pure amide solvents, the addition of LiCl salt enhances the solubility of the polymers in several amide solvents, such as *N*-methyl-2-pyrrolidone or *N*,*N*-dimethylacetamide. Figure 6 shows the decrease of viscosity of polyamide II in *N*-methyl-2-pyrrolidone in the presence of LiCl (1.3 M) with ultraviolet light (410 > λ_1 > 350 nm) and the recovery with visible light (λ_2 > 470 nm). The viscosity returns to the photostationary value and the decrease/recovery cycles can be repeated many times. The amount of the photodecrease, 63%, is very close to the value observed for polymer I in *N*,*N*-dimethylacetamide (Figure 3). The result suggests the added LiCl does not affect the photoviscosity much, though the mechanism of association of LiCl to the polyamides may be complex. The photodecrease mainly depends on the backbone structure of the polymer.

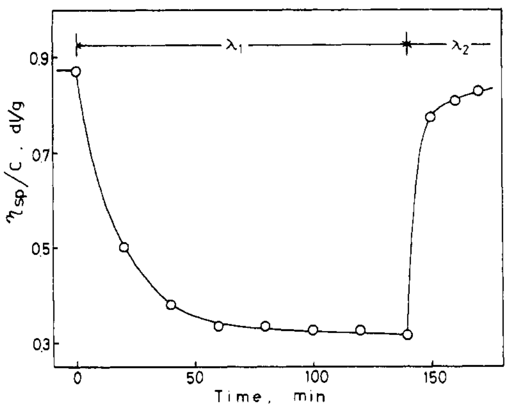

Figure 6. Changes of viscosity of polyamide II in *N*-methyl-2-pyrrolidone in the presence of LiCl (1.3 M) on alternate irradiation with ultraviolet (410 > λ_1 > 350 nm) and visible (λ_2 > 470 nm) light at 25 °C. Concentration of the polymer is 0.3 g/dL.

Table II
Effect of Backbone Structure of the Polymers on the Photodecrease of the Solution Viscosity

polymer	R	η_{sp}(UV)/ η_{sp}(dark)[a]	$(1 - \epsilon_c/\epsilon_t)y$[b]
polyamide II $[\eta] = 0.87$	$-(p\text{-}C_6H_4)-$[c]	0.37	0.47
polyamide III $[\eta] = 1.5$	$-(CH_2)_4-$[c]	0.59	0.79
polyamide IV $[\eta] = 1.01$	$-(CH_2)_8-$[c]	0.80	0.69
polyamide V $[\eta] = 0.33$	$-(CH_2)_{12}-$[c]	0.96	0.52

[a] η_{sp}(UV) and η_{sp}(dark) are specific viscosities under irradiation with ultraviolet light (410 > λ > 350 nm) and in dark before irradiation in *N*-methyl-2-pyrrolidone in the presence of LiCl (1.3 M), respectively. Concentration of the polymer is 0.3 g/dL. [b] Relative content of the cis form of the azobenzene residues in the photostationary state under ultraviolet irradiation (410 > λ > 350 nm). ϵ_c, ϵ_t, and y are extinction coefficients of the cis and trans forms at 390 nm and the content of the cis form in the photostationary state. [c] R group in

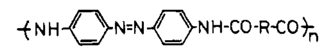

Table II shows the effect of backbone structure of the polymers on the photodecrease of the viscosity in *N*-methyl-2-pyrrolidone in the presence of LiCl (1.3 M) and the relative content of the cis form of the azobenzene residues in the photostationary states under ultraviolet irradiation (410 > λ > 350 nm). The value of $(1 - \epsilon_c/\epsilon_t)y$ was used as a measure of the apparent cis content, where y is the cis content.

The amount of photodecrease of the viscosity decreased with increasing number of methylene chains in the backbone of the polymers. The stiffest polymer, that having a phenylene residue, gave a large photodecrease relative to the amount observed for polyamide I, while the viscosity

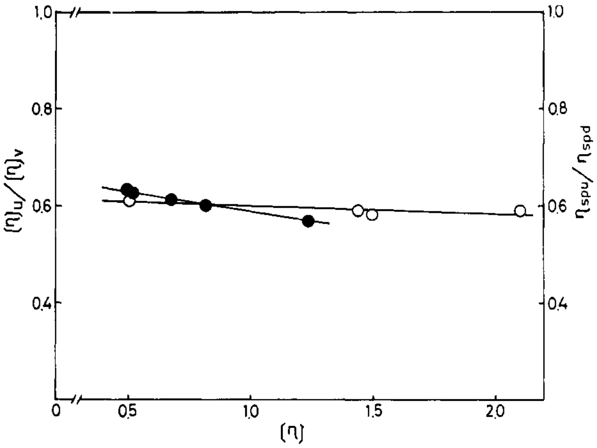

Figure 7. Dependence of the photodecrease of the viscosity of (●) polyamide I and (○) polyamide III on the molecular weight. $[\eta]_v$ and $[\eta]_u$ are intrinsic viscosities of polyamide I under irradiation with visible ($\lambda > 470$ nm) and ultraviolet ($410 > \lambda > 350$ nm) light at 20 °C in *N,N*-dimethylacetamide, respectively. η_{spd} and η_{spu} are specific viscosities of polyamide III in the dark before irradiation and under irradiation with ultraviolet ($410 > \lambda > 350$ nm) light at 25 °C in *N*-methyl-2-pyrrolidone in the presence of LiCl (1.3 M), respectively. Concentration of the polymer is 0.3 g/dL.

of polymers having flexible long methylene chains was hardly reduced by photoillumination.

The cis content in the photostationary state under ultraviolet light irradiation also has a tendency to decrease with increasing number of methylene chains, though the decrease of the cis content from polymer III to polymer V is only 34%, which cannot explain the large decrease of photoviscosity effect, 90%. The absence of the photodecrease of the viscosity in polymer V solution suggests that the flexible methylene chain acts as a strain absorber. The conformational change induced by the isomerization of azobenzene residue is relaxed in the connecting flexible methylene chains, resulting in no change of shape of the polymer.

Molecular weight dependence on the photodecrease of the viscosity is shown in Figure 7 for polymers I and III. In this figure intrinsic viscosity was adopted as a measure of molecular weight, and $[\eta]_u/[\eta]_v$ is plotted against the intrinsic viscosity, where $[\eta]_v$ and $[\eta]_u$ are intrinsic viscosities under the photostationary state of visible and ultraviolet light irradiations, respectively. In the molecular weight range examined, the molecular weight scarcely affects the amount of photodecrease of viscosity. The trend in the decrease of photoviscosity effect with decreasing molecular weight is ascribable to a chain-end effect. Isomerization of the azobenzene unit at the end positions of the chain hardly contributes to a change of shape of the polymer, while isomerization in the middle position is expected to change the shape of the polymer to a large extent.

D. Conductivity and pH Measurements. Figure 8 shows the response of conductivity of an *N,N*-dimethylacetamide solution containing polyamide I under alternate irradiation with ultraviolet and visible light. The specific conductivity increased with ultraviolet irradiation ($410 > \lambda_1 > 350$ nm), while it decreased with visible irradiation ($\lambda_2 > 470$ nm). The amount of change was about 3% of the conductivity of the polymer solution under the experimental conditions used. The response of the conductivity correlates well with the isomerization of the azobenzene residue in the polymer backbone shown in Figure 5a. The correlation suggests that dissociation equilibrium of amide-substituted terephthalic acid residues in the polymer backbone is influenced by conformational change of the polymer chain. Dissociation of the acid is stimulated in the compact or shrunken conformation, while the extended conformation depresses the dissociation. A possible explanation for the increase of the dissociation in the compact conformation is that the azobenzene residue in the cis form in the compact conformation has a polar structure compared with the trans form and that the polar structure assists in dissociation of the acid. The change of the polymer mobility due to the shrinkage may not contribute to a change of conductivity because solution conductivity is mainly controlled by mobility and numbers of the low molecular ions and not by the polymer ions.

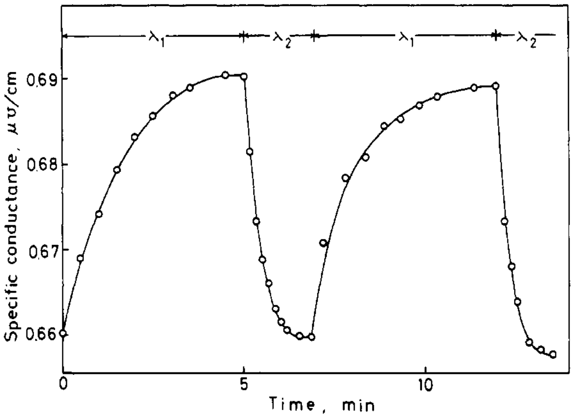

Figure 8. Changes of specific conductance of an *N,N*-dimethylacetamide solution of polyamide I at 25 °C on alternate irradiation with ultraviolet ($410 > \lambda_1 > 350$ nm) and visible ($\lambda_2 > 470$ nm) light. Concentration of the polymer is 0.04 g/dL.

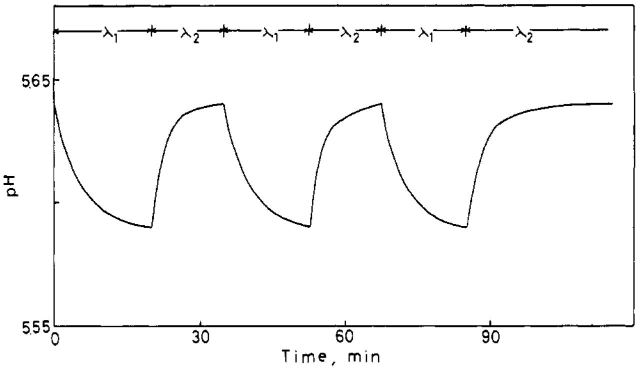

Figure 9. Changes of pH of an aqueous solution of polyamide I at 20 °C on alternate irradiation with ultraviolet ($410 > \lambda_1 > 350$ nm) and visible ($\lambda_2 > 470$ nm) light. Concentration of the polymer is 0.05 g/dL.

The change of the equilibrium constant of the dissociation of the acid in organic solvent by photoirradiation suggests the possibility of pH control in aqueous system. The photocontrol of pH by using a synthetic polymer has special interest from the viewpoint of constructing a photoreceptor analogue.[7]

Figure 9 shows the response of pH in aqueous solution of polyamide I by alternate irradiation with ultraviolet and visible light. pH decreased under the ultraviolet light irradiation ($410 > \lambda_1 > 350$ nm) and returned to the initial value under visible light ($\lambda_2 > 470$ nm) as the conductivity response in *N,N*-dimethylacetamide predicts. Although the amount of the change in pH is very small, the decrease/increase cycle can be repeated many times without any noticeable fatigue.

Viscosity, conductivity, and pH value are only a few examples of physical and chemical properties of polymer solutions which can be controlled. We can expect to control reversibly many aspects of the properties of polymer solutions and solid by using photoresponsive polymers.

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Inter- and Intramolecular Interactions of Polymers As Studied by Fluorescence Spectroscopy. 7. Allosteric Self-Association of an Exciplex-Forming Polymer under Extremely Dilute Conditions

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ABSTRACT: Allosteric self-association was found in poly[oxy[2-(1-pyrenylmethyl)propylene]oxy[4-(*N*,*N*-dimethylamino)benzyl]malonyl] (PE(Py-1D)) having an appropriate degree of polymerization under extremely dilute conditions. The polymer (PE(Py-1D)) was prepared by bulk polycondensation of the corresponding 1,3-propanediol with the corresponding diethyl malonate. Comparison of the absorption spectra of PE(Py-1D) with that of monomer model (I) indicated the presence of a weak ground-state interaction between chromophores. The ratio of exciplex emission (F_e) to monomer emission from the local excited state of pyrenyl groups (F_m) increased allosterically with concentration, suggesting interpolymer association in the concentration region below 10^{-5} M. The driving force of interpolymer association was attributed to the weak ground-state interactions between the electron donor (*N*,*N*-dimethylanilino group) and the electron acceptor (pyrenyl group). No exciplex emission was detected in reference experiments mixing monomer model compounds (I and II) containing pyrenyl and *N*,*N*-dimethylanilino groups in the concentration region below 10^{-5} M. Qualitative explanations for the above results are presented on the basis of solvent and molecular weight effects on emission and absorption spectroscopy.

The solution theory of polymers postulates that polymer molecules in dilute solutions are independent of each other. However, polymers containing groups whose interactions are undetectably weak in model monomer systems can exhibit prominent interpolymer association. A typical example is found in antigen–antibody interactions. The driving force for enhanced intermolecular interactions in polymers is attributed to zipping or cooperative effects.

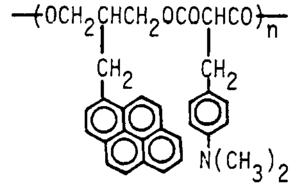
Since 1975, we have been demonstrating the association of weakly interacting groups in synthetic polymers by means of fluorescence spectroscopy.[1-5] Although exciplex-forming electron-donor (D)–electron-acceptor (A) pairs do not generally exhibit observable ground-state interactions in the case of monofunctional compounds, the weak interactions are sufficient to bring about polymer association in which the degree of association depends on the degree of polymerization.[2] Polymer association often accompanies changes in conformation, which affect further association. Consequently, polymer association is not expected to be a simple function of concentration.

Now we have found allosteric self-association of the relatively simple polymer PE(Py-1D) at a unit segment concentration below 10^{-5} mol dm^{-3}.

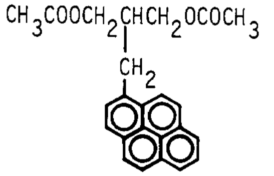
Experimental Section

Materials. Monomer Models. 2-(1-Pyrenylmethyl)-1,3-propylene diacetate (I) and diethyl [4-(*N*,*N*-dimethylamino)-benzyl]malonate (II) were prepared by methods already reported.[5,6]

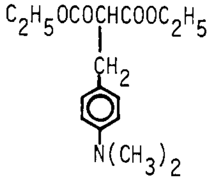
Chart I
Structure of Exciplex-Forming Polymer and the Monomers



PE(Py-1D)



I



II

Poly[oxy[2-(1-pyrenylmethyl)propylene]oxy[4-(*N*,*N*-dimethylamino)benzyl]malonyl] (PE(Py-1D)). Equimolar amounts of 2-[(1-pyrenyl)methyl]-1,3-propanediol and II were heated to produce bulk polycondensation, using calcium acetate as catalyst. Polycondensation was conducted under a nitrogen atmosphere at normal pressure and at an initial temperature of 160 °C. The reaction vessel was then heated to 210 °C and evacuated gradually to 10^{-2} mmHg over a period of 18 h. IR (KBr disk) 1732 cm^{-1} (>C=O); NMR (Me$_2$SO-d_6, 90 °C) δ 3.04 (6 H, s, N(CH$_3$)$_2$), 6.2–6.7 (4 H, m, phenylene), 7.3–8.3 (9 H, m, pyrenyl). Anal. Calcd for $C_{32}H_{29}O_4N$ (repeat unit): C, 78.19; H, 5.95; N, 2.85. Found: C, 77.0; H, 6.25; N, 2.53. The polymer sample was

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