Photoinduced Isomerization and Photoregulation of the Hydrodynamic Volume of Poly(α,ω-disubstituted 2,3-azabutadiene)

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More than 20 years ago, Kamachi et al. found that aldehyde azines (α,ω-disubstituted 2,3-azabutadienes) were polymerized by typical anionic initiators.[1] However, molecular weights of the polymers obtained were less than 3000, and no film could be formed from these polymers. Recently, we have succeeded in preparing highly crystalline polymers of molecular weights higher than 10 000 by anionic polymerizations of acetaldehyde azine ($CH_3CH{=}NN{=}CHCH_3$, AcAz), propionaldehyde azine ($C_2H_5CH{=}NN{=}CHC_2H_5$, PrAz), and *n*-butyraldehyde azine ($C_3H_7CH{=}NN{=}CHC_3H_7$, BuAz) with Grignard reagents.[2,3] We have also investigated the structures of these polymers by IR, Raman, UV-visible, ^{1}H-NMR, and ^{13}C-NMR spectroscopies and X-ray diffractions and concluded that the polymers are composed of 1,4-trans azo units in main chains, as shown in Scheme I.

Azo compounds are known to show cis-trans photoisomerization around the N=N bond. Although the cis-trans isomerization has been well-documented for aromatic azo compounds,[4] it has not been studied for the aliphatic series except a few cases.[5] The present paper reports on the photoinduced isomerization of N=N bonds in the main chain of the polyazines in solution and in film. To our knowledge, no paper has been reported on the photoisomerization of polymers containing aliphatic azo groups in their main chains.

Poly(AcAz), poly(PrAz), and poly(BuAz) were prepared as reported previously.[2,3] The results of the polymerizations are given in Table I. The polymers were obtained as pale yellow powders. Poly(AcAz) film was prepared by casting from a chloroform solution.

Monochromatized light from a 500-W xenon lamp was irradiated at the solutions or film of the polyazines at 25 °C. Hexane, cyclohexane, diethyl ether, tetrahydrofuran, 1,4-dioxane, benzene, toluene, chloroform, and dichloromethane were used for the solvents in the experiments of the light irradiation. Absorption spectra of the solutions or the film were recorded at given irradiation times. The hydrodynamic volumes of the irradiated polymers were estimated as weight-average molecular weights by GPC using THF as an eluent. Molecular weights were calibrated by using standard polystyrenes.

Poly(AcAz) in chloroform showed an absorption peak at 362 nm before irradiation (Figure 1), which was assigned to the n-π^* transition of the trans N=N bond by comparing the absorption spectrum with that of *trans*-diazomethane. The extinction coefficient of the 362-nm band ($\epsilon = 30$) was on the same order of magnitude as that of *trans*-diazomethane ($\epsilon = 25$, $\lambda = 343$ nm).[5]

Changes in the absorption spectrum of poly(AcAz) in chloroform by irradiation of 350-nm light are shown in Figure 1. Upon irradiation, the n-π^* absorption maximum red-shifted and the absorbance at the peak increased, giving isosbestic points at 345 and 418 nm. This is presumably due to photoinduced trans-to-cis isomerization of poly(AcAz). After irradiation of 350-nm light for 4 h, 400-nm light was irradiated in the sample solution. The absorption spectrum almost returned to the original spectrum (before irradiation at 350 nm; Figure 2) due to photoinduced cis-to-trans isomerization. The spectral change caused by irradiation of 400-nm light yielded no isosbestic points, implying that photochemical reactions take place along with isomerization from cis to trans. However, since the absorption spectrum almost returned to the original spectrum, the photochemical reaction seemed to be much slower than the isomerization from cis to trans.

In a separate experiment, a chloroform solution of poly(AcAz) was allowed to stand overnight in the dark at ambient temperature after a 4-h irradiation of 350-nm light. There was no change in the absorption spectrum of the solution in the dark, indicating that no thermal cis-to-trans backward isomerization occurred at ambient temperature.

Changes in absorbance at 380 nm as a function of irradiation (350 nm) time are shown in Figure 3, indicating

Scheme I

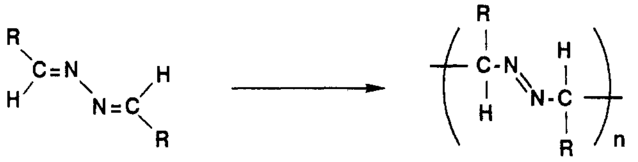

Table I
Polymerizations of Alkylaldehyde Azines[a]

azine (M)	initiator, mol %	solvent	temp, °C	yield,[b] %	$\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$[c]
AcAz (2.0)	2.0	1,4-dioxane	–20	32	46 000	2.47
PrAz (3.0)	1.3	hexane	0	49	17 000	1.88
BuAz (2.0)	2.0	toluene	–20	23	14 000	1.48
(2.0)	2.0	ether	–20	20	3 700	1.20

[a] Initiated by CH_3MgI, under argon; polymerization time 50 h. [b] Methanol-insoluble fraction: monomer conversion > 99%. [c] GPC.

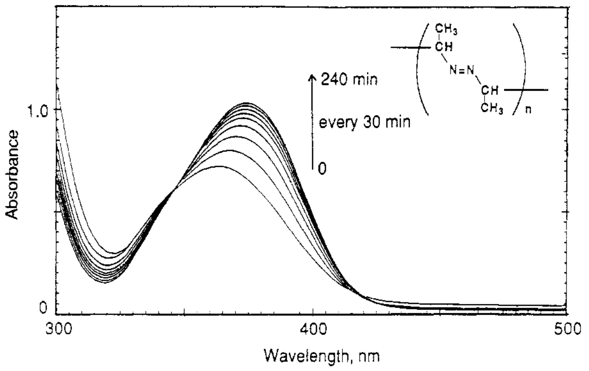

Figure 1. Change in the absorption spectra of poly(AcAz) in chloroform (25 mM) during 350-nm light irradiation at 25 °C.

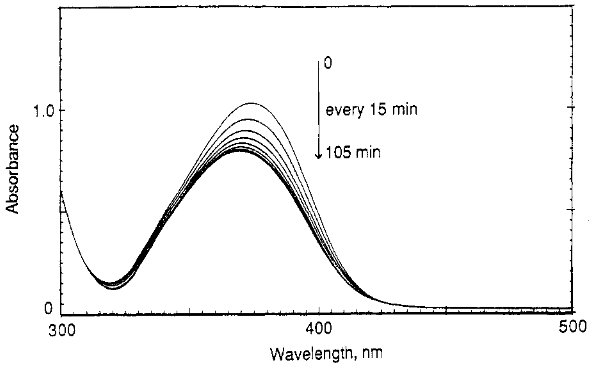

Figure 2. Change in absorption spectra of poly(AcAz) in chloroform (25 mM) during 400-nm light irradiation at 25 °C.

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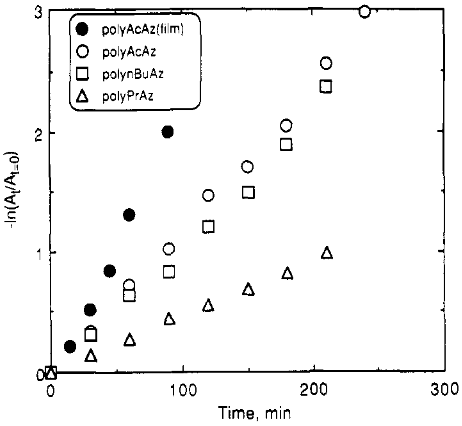

Figure 3. First-order plots for the absorbance change observed at 380 nm at 25 °C caused by 350-nm light irradiation.

that they obey first-order kinetics. The apparent rates of the spectral change due to the trans-to-cis photoisomerization varied for varying α,ω-disubstituted groups of the azine compounds. The rate was found to be independent of the molecular weight of the polymers and of the solvent employed. The photoisomerization was also examined for the film of poly(AcAz). The apparent rate of the spectral change for the poly(AcAz) film was faster than that in solution, probably due to the strain of the azo groups in the film.

The photoinduced trans-to-cis isomerization of the azo groups in the main chain of the polyazines probably causes a significant change in their chain conformations. Thus, a change in the apparent hydrodynamic volumes of polyazines upon irradiation of light was investigated by GPC. A typical example of the change of the hydrodynamic volume is shown in Figure 4. A significant decrease in the apparent molecular weight which corresponds to a decrease in the hydrodynamic volume was observed when the trans-to-cis interconversion occurred at an irradiation of 350-nm light and an irradiation of 400-nm light restored the hydrodynamic volume due to the regeneration of the trans configuration. Similar changes in the hydrodynamic volume were observed at repeated irradiations of 350- and 400-nm light, respectively. These changes in the hydrodynamic volume are consistent with those in absorption spectra at repeated irradiations of 350- and 400-nm light.

Aromatic azo compounds such as azobenzene are known to photoisomerize easily, while aliphatic azo compounds are easily decomposed by light and/or heat as in the case of α,α'-azobis(isobutyronitrile) (AIBN). Polyazines, despite the aliphatic azo compounds, showed no weight loss at 100 °C in pyrolysis,[2,3] which indicated that polyazine compounds were thermally more stable than low molecular weight aliphatic azo compounds.

In summary, (1) the polyazines showed photoisomerization in their main-chain N═N groups without thermal back isomerization. (2) The direction of the isomerization (cis-to-trans and trans-to-cis) depends on the wavelength of light (350-nm light for trans-to-cis and 400-nm light for cis-to-trans). (3) A change in the hydrodynamic volume of the polymer in solution was observed upon irradiation with light. Photoregulation of the apparent coil size of the polyazines may be utilized as a light-controlled "on–off" switching system.

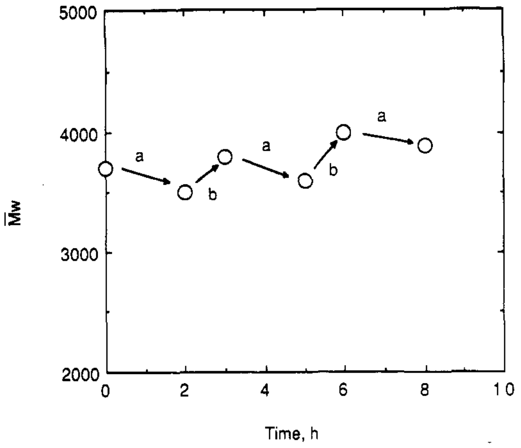

Figure 4. Change in the size of poly(BuAz) in tetrahydrofuran (25 mM) caused by photoirradiation at 25 °C: (a) 350-nm light irradiation, (b) 400-nm light irradiation. The weight-average molecular weight ($\bar{M}_w$) was calibrated with polystyrene standards.

We are continuing detailed studies of the nature and the mechanism of the photoinduced isomerization of the polyazines.

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