Conformational Analysis of Poly(propionaldehyde azine) in Dilute Solution

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ABSTRACT: The conformation of a photoresponsive polymer bearing azo units in the main chain, poly(propion-aldehyde azine) (PrAz), in tetrahydrofuran was investigated by viscosity measurements before and after *trans*-to-*cis* photoisomerization and also by the rotational isomeric state (RIS) model. Before photoisomerization (*i.e.*, in the case of *trans*-pPrAz), viscosity data indicated that pPrAz took a more extended conformation than did a diene polymer analog poly(butadiene). The RIS model analysis revealed that the extended conformation of pPrAz arose mainly from the difficulty of gauche conformation around the carbon-carbon bond in the main chain. After *trans*-to-*cis* photoisomerization (*i.e.*, in the case of pPrAz consisting of *trans* and *cis* units), viscosity data indicated that the photoisomerization led to a slight extension of the pPrAz chain. The RIS model analysis explained that the photoisomerization formed preferentially the anti-*cis* isomer, resulting in a larger characteristic ratio to avoid severe steric hindrance between the ethyl groups on neighboring main-chain carbon atoms.   [doi:10.1295/polymj.PJ2006066]
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Materials responsive to external stimuli may be useful for molecular machines and motors and thus they have been attracting increasing interest of researchers from the viewpoint of nanotechnological applications.[1] Among stimuli responsive materials, photoresponsive ones may be most promising because of their fast response.[2] Pioneering works by Irie *et al.*[3,4] have demonstrated that polymers bearing azobenzene moieties in their main chain undergo reversible *trans*-to-*cis* and *cis*-to-*trans* isomerization under photoirradiation to cause repetitive changes in their solution viscosity: *trans*-to-*cis* photoisomerization leads a decrease in solution viscosity whereas *cis*-to-*trans* photoisomerization returns the solution viscosity.

Kamachi *et al.*[5–7] have reported that azine compounds, diene analogs bearing C=N bond, are polymerized with Grignard reagents to form polymers consisting of 1,4-*trans* units. Their preliminary results have also indicated that these polymers of azine compounds undergo photoisomerization under UV irradiation, leading to changes in the polymer conformation in solution.[8]

To our best knowledge, however, there have been no detail studies on conformational change of photoresponsive polymers upon photoisomerization although it may be important for molecular design of photoresponsive polymers with high performance. Thus, we studied the conformation of poly(propion-aldehyde azine) (pPrAz) in solution before and after
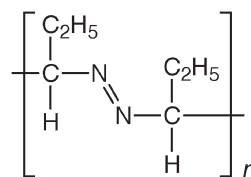
Scheme 1.   Chemical structure of pPrAz.

photoisomerization by viscometry and also by the rotational isomeric state model. Moreover, since azine polymers are diene polymer analogs, we compared the conformation of pPrAz with those of poly(butadiene) and poly(isoprene) with the *trans* and *cis* configurations to argue the effect of the replacement of the carbon double bond by the nitrogen one on the chain conformation.

EXPERIMENTAL

Materials

A commercially available solution of methylmagnesium iodide (CH$_3$MgI) (*ca.* 2 M solution in diethyl ether, TCI) was put into an ampule with a syringe under an argon atmosphere. Tetrahydrofuran (THF) used for measurements was purified by atmospheric distillation. Other reagents were used without further purification.

Propionaldehyde azine (PrAz) was prepared from propionaldehyde and hydrazine monohydrate according to the procedure of Curtius and Zinkeisen.[9] PrAz

was purified by successive distillations over calcium hydride under an argon atmosphere and stored under an argon atmosphere.

Polymer samples of PrAz (pPrAz) were prepared by anionic bulk polymerization initiated by CH_3MgI under an argon atmosphere according to the procedure of Kamachi *et al.*[5–7] The polymers obtained were purified by reprecipitation three times from THF solution to excess methanol. Polymers were recovered by freeze-drying from benzene solution.

Photoisomerization of pPrAz

Solutions of pPrAz in THF were irradiated with an Iuchi handy UV lamp SLUV-6 (365 nm). The distance between the sample cell and the lamp was fixed at *ca.* 11 cm. The polymers obtained were purified by reprecipitation three times from THF solution to excess methanol. Polymers were recovered by freeze-drying from benzene solution.

Measurements

Sedimentation equilibrium measurements were performed for solutions of pPrAz samples in THF at 25 °C using a Beckman-Coulter Optima XL-I ultracentrifuge equipped with a Rayleigh interferometer with a 675 nm light emitting from a diode laser. Aluminum 12 mm double-sector cells were used, and the height of the solution column was adjusted to *ca.* 2.5 mm. The rotor speed was fixed at 35,000 rpm.

The apparent molecular weight M_{app} was calculated by[10,11]

$$M_{app} = \frac{2RT(c_b - c_a)}{\omega^2(r_b^2 - r_a^2)c_0(1 - \bar{v}\rho_0)} \quad (1)$$

where r_a and r_b are the distances from the center of revolution to the meniscus and cell bottom, respectively, and c_a and c_b are polymer mass concentrations at r_a and r_b respectively, under the centrifugal field; ω is the angular velocity, c_0 is the mass concentration of the solution at $\omega = 0$, $\bar{v}$ is the partial specific volume, ρ_0 is the solvent density, and RT is the gas constant multiplied by the absolute temperature.

The weight-average molecular weight M_w and the second virial coefficient A_2 were determined from the plot of M_{app}^{-1} versus the average concentration $\bar{c} \equiv (c_a + c_b)/2$ in a low concentration region using[10,11]

$$\frac{1}{M_{app}} = \frac{1}{M_w} + 2A_2\bar{c} + \cdots \quad (2)$$

Densities ρ of pure THF and THF solutions of pPrAz with different concentrations were measured at 25 °C using an Anton-Paar DMA 5000 densitometer to determine $\bar{v}$ and ρ_0. The concentrations c_a and c_b under the centrifugal field were determined by interferometry along with the specific refractive index in-

crement $\partial n/\partial c$. Values of $\partial n/\partial c$ at 436 and 546 nm were measured at 25 °C using a modified Schultz-Cantow type differential refractometer, and extrapolated to obtain the $\partial n/\partial c$ value at 675 nm.

Viscosities of THF solutions of pPrAz samples were measured at 25 °C using a conventional capillary viscometer of the Ubbelohde type. The intrinsic viscosity $[\eta]$ and the Huggins coefficient k' were determined using the Huggins and Mead-Fuoss plots.

^{1}H NMR spectra were obtained on a JEOL JNM EX270 spectrometer in $CDCl_3$ at 30 °C. UV-vis absorption spectra were recorded on a JASCO UV-520 spectrophotometer in THF.

RESULTS AND DISCUSSION

Basic Characteristics of pPrAz Samples Used in This Study

The pPrAz samples employed in this study were prepared by anionic bulk polymerization initiated by CH_3MgI according to the procedure of Kamachi *et al.*[5–7] Kamachi *et al.*[5–7] have reported that polymers of alkyl aldehyde azines obtained using Grignard reagents are composed of 1,4-*trans* units, and also suggested that the azine polymers contain both erythro and threo units (Figure 1). Fractions of 1,4-*trans*, erythro, and threo units in the pPrAz samples used in this study were estimated by ^{1}H NMR spectroscopy (Figure 2a). While the *trans* fraction was almost unity, the fractions of erythro and threo units were *ca.* 0.65 and 0.35, respectively, for all the samples.[12]

Weight-average molecular weights M_w and second virial coefficients A_2 for the pPrAz samples were determined by sedimentation equilibrium. Figure 3a demonstrates M_{app}^{-1} as a function of $\bar{c}$. All the series of plots exhibit good linear relationships. From intercepts and slopes of the straight lines, M_w and A_2 values were determined as listed in Table I. All pPrAz
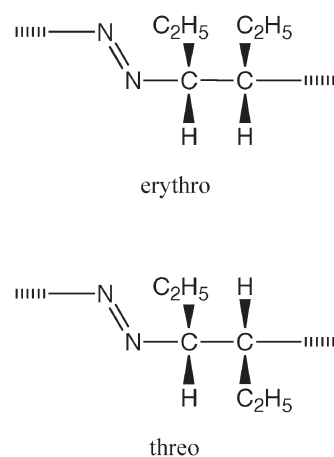

Figure 1. Molecular structures of erythro- and threo-*trans*-pPrAz.

samples possess rather low M_w, ranging (6.7–8.3) × 10³. The A_2 values obtained ((2.2–2.4) × 10⁻³ cm³ mol⁻²) indicate that THF is a good solvent for pPfAz at 25 °C.
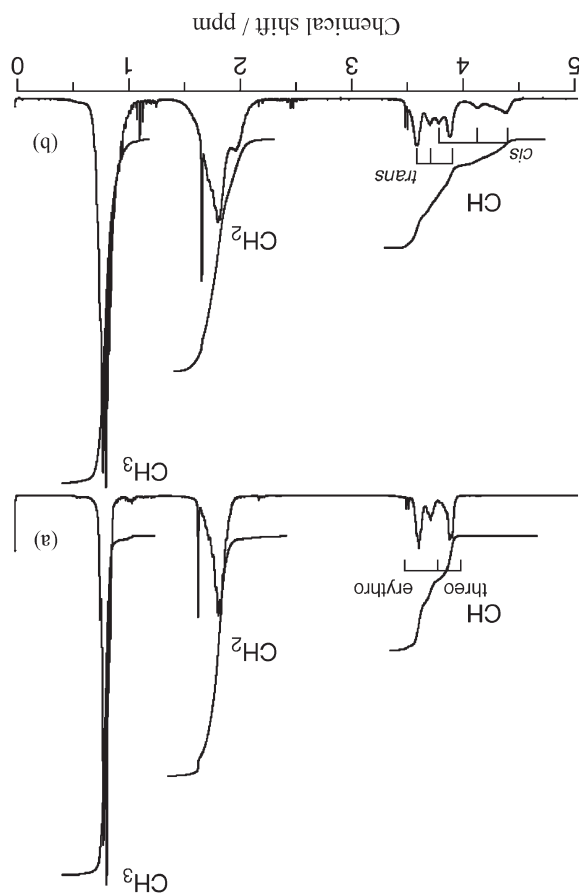
It has been also reported that the trans-polymers of alkyl aldehyde azines are isomerized to the cis config-uration under UV irradiation.[8] We irradiated a sample pPfAz-2 in THF with UV light (365 nm) for varying irradiation times (24–100 h) to prepare pPfAz samples with different cis contents. UV-vis absorption spec-troscopy confirmed trans-to-cis photoisomerization in the samples (cf. Figure S1 in the Supporting Infor-mation). Fractions f_{cis} of 1,4-cis unit in the pPfAz samples photoirradiated were determined by ^{1}H NMR spectroscopy (Figure 2b), as listed in Table II.[13] The

Table I. Weight average molecular weights M_w and the second virial coefficients A_2 for the pPfAz samples used in this study[a]

polymer code	$M_w/10^3$	$A_2/10^{-3}$ cm³ mol⁻²
pPfAz-1	6.7	2.4
pPfAz-2	7.5	2.2
pPfAz-3	8.1	2.4
pPfAz-4	8.3	2.2

[a]Determined by sedimentation equilibrium in THF at 25 °C.

Figure 2. ^{1}H NMR spectra for pPfAz-2 before (a) and after photoirradiation (b).

fraction gradually increases with the irradiation time, and reaches ca. a half after 100 h irradiation.

The M_w and A_2 values for the pPfAz samples pho-toisomerized were also determined by sedimenta-tion equilibrium (Figure 3b). The results are listed in Table II. The M_w value ((4.1–5.5) × 10³) for the pPfAz samples photoisomerized slightly decreases with irradiation time, indicating that the photoinduced decomposition occurred to some extent. On the other hand, A_2 values for the pPfAz samples photoisomer-ized are slightly larger than that for pPfAz-2. The effect of polymer chain ends[14] may contribute to the change in A_2.
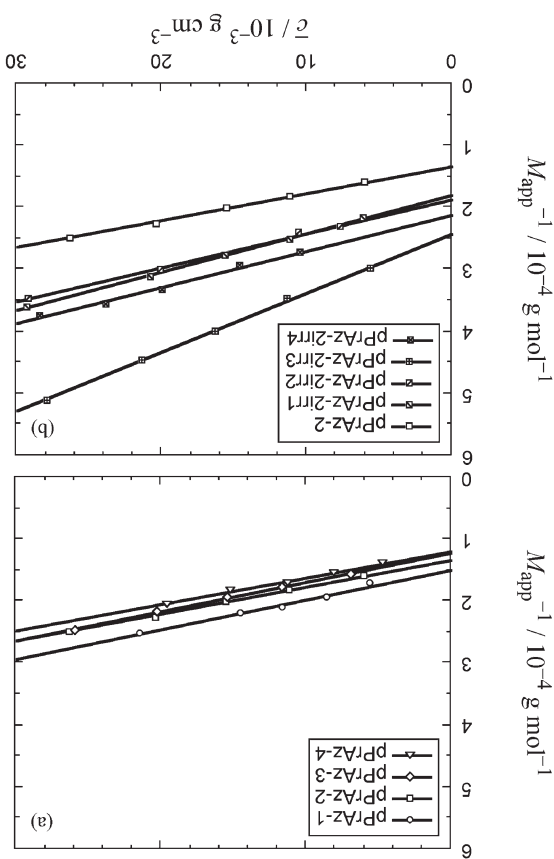
Table II. Weight average molecular weights M_w and the second virial coefficients A_2 for the pPfAz samples photoisomerized by UV irradiation[a]

polymer code	irradiation time /h	f_{cis}[b]	$M_w/10^3$	$A_2/10^{-3}$ cm³ mol⁻²
pPfAz-2irr1	24	0.33	5.5	3.1
pPfAz-2irr2	48	0.29	5.4	2.8
pPfAz-2irr3	60	0.38	4.1	4.8
pPfAz-2irr4	105	0.45	4.7	3.0

[a]Determined by sedimentation equilibrium in THF at 25 °C.
[b]The fraction of cis content in pPfAz determined by ^{1}H NMR.

Figure 3. Concentration dependencies of M_{app}^{-1} for the trans-pPfAz samples (a) and the photoirradiated pPfAz samples (b) measured in THF at 25 °C.
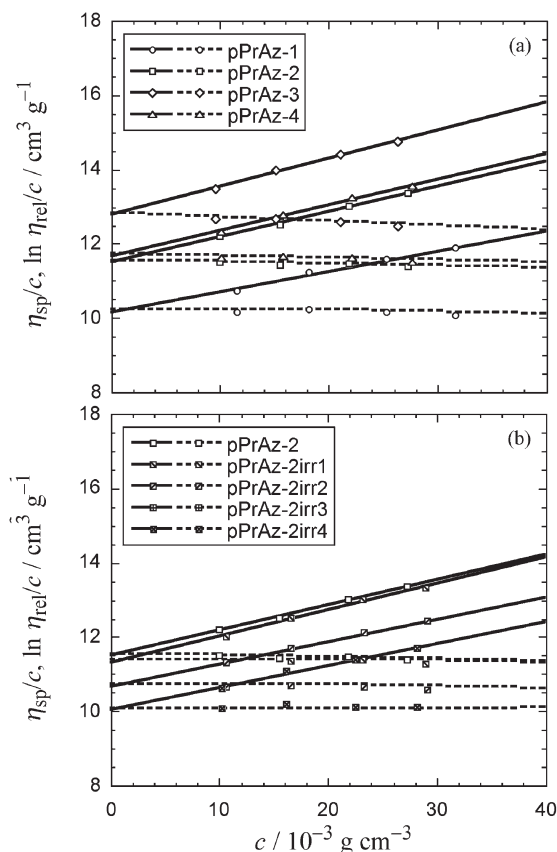
Figure 5. Comparison of $[\eta]$ for pPrAz before and after photoisomerization in THF as well as for pBD in the perturbed and unperturbed states. Triangles and the dotted line represent Colby *et al.*'s data[15] in cyclohexane and calculated values using Mark's characteristic ratio,[17] respectively.

Figure 4. Huggins and Mead-Fuoss plots for (a) *trans*-pPrAz samples and (b) pPrAz sample photoirradiated in THF. Here, η_{sp} and η_{rel} are the specific and relative viscosities of the solution.

Table III. Intrinsic viscosities $[\eta]$, Huggins constants k', and charateric ratios C_N for the pPrAz samples

polymer code	$[\eta]/\text{cm}^3\,\text{g}^{-1}$	k'	C_N
pPrAz-1	10.2	0.49	8.42
pPrAz-2	11.5	0.48	8.78
pPrAz-3	12.8	0.44	9.20
pPrAz-4	11.7	0.48	8.60
pPrAz-2irr1	11.4	0.51	9.69
pPrAz-2irr2	10.7	0.49	9.34
pPrAz-2irr3	11.2	0.52	10.56
pPrAz-2irr4	10.1	0.54	9.40

Viscosity Measurements

Figure 4 demonstrates Huggins and Mead-Fuoss plots for the pPrAz samples in THF at 25 °C. For all the pPrAz samples, plots exhibit good linear relationships. From intercepts and slopes of the straight lines, $[\eta]$ and k' values were determined as listed in Table III. Values of k' for all the pPrAz samples are within a normal range.

Figure 5 plots those $[\eta]$ results against the degree of polymerization N_w calculated by M_w/M_0 with the molar mass M_0 of the monomer unit. Although $[\eta]$ values are not so different before and after photoisomerization, the data points (filled circles) after photo-
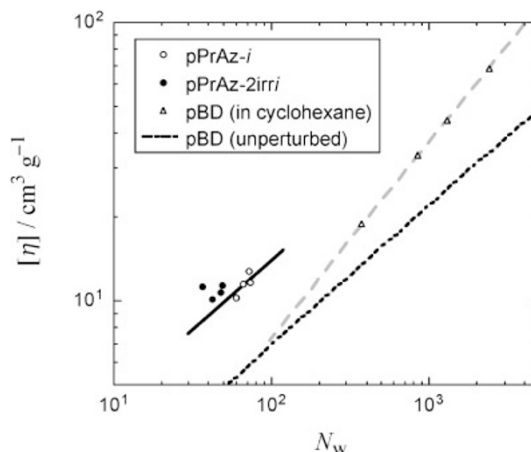
isomerization locate appreciably above the line passing through the data points (unfilled circles) for *trans*-pPrAz with a slope of 0.5. This indicates that the *trans*-to-*cis* photoisomerization extends the pPrAz chain. (If the chain dimension of pPrAz might be affected by the excluded volume effect, the filled circles should obey a steeper line, which deviates more from the triangles.)

The change in the chain dimension upon photoirradiation for this azine polymer is much less remarkable than that for polymers bearing azobenzene moieties in their main chain.[3,4] Moreover, it is amazing that the *trans*-to-*cis* photoisomerization changes the chain dimension oppositely between the azine and azobenzene polymers.

In Figure 5, triangles represent $[\eta]$ data for poly-(butadiene) (pBD) with a *cis* content of *ca.* 0.4 in cyclohexane (a good solvent) reported by Colby *et al.*[15] To compare the chain dimension for the two different polymers, Colby *et al.*'s $[\eta]$ were multiplied by the ratio of M_0 of pBD to that of pPrAz in the plot. Though N_w ranges investigated for the two polymers do not overlap, the extrapolation of Colby *et al.*'s data definitely indicates that the chain dimension of pPrAz is larger than that of pBD at the same N_w.

The dotted line in the same figure indicates $[\eta]$ (multiplied by the M_0 ratio) for pBD with $f_{cis} = 0.4$ in the unperturbed state, calculated by the equation

$$[\eta] = \Phi(C_N \cdot 4N\overline{b^2})^{3/2}/M \tag{3}$$

where Φ is the Flory viscosity constant, C_N is the characteristic ratio, $\overline{b^2}$ is the square average bond length of the polymer main chain, and M and N are the polymer molecular weight and degree of polymerization, respectively; for pBD $\overline{b^2} = 0.0221$ nm^2. The characteris-

tic ratio C_N for pBD with $f_{cis} = 0.4$ was calculated to be 5.2 at infinite N, using the rotational isomeric state (RIS) model with parameters used by Mark[16,17] (see below), and Φ was chosen to be $2.5 \times 10^{23}\,\text{mol}^{-1}$.[18] Using this theoretical line, the viscosity expansion factor α_η^3 for Colby *et al.*'s lowest molecular weight pBD sample ($N_w = 370$) in cyclohexane was estimated to be as small as 1.4, and the extrapolation of Colby *et al.*'s $[\eta]$ data implies that the excluded volume effect vanishes around $N_w = 100$.

Since we can expect that the strength of the excluded volume for pPrAz in THF is similar to that of pBD in cyclohexane from A_2 data, and moreover that the more extended conformation of pPrAz weakens the excluded volume effect, our pPrAz samples with $N_w < 100$ used in this study may be free from the excluded volume effect. Thus, eq 3 for the unperturbed chain can be applied for $[\eta]$ data of our pPrAz samples. For pPrAz, $\overline{b^2}$ is $0.0210\,\text{nm}^2$ (see below), and we can estimate C_N from eq 3 and experimental $[\eta]$ for *trans*-pPrAz and photoisomerized one. The results, listed in Table III, are larger than C_∞ (C_N at infinite N) not only for *trans*-pBD ($= 5.8$) but also for *trans*-poly(isoprene) (pIP) ($= 7.35$).

Analysis Using the Rotational Isomeric State (RIS) Model

Mark[16,17] calculated characteristic ratios for diene polymers, pBD and pIP, on the basis of the RIS model, and compared these calculated values with experimental results. We here calculated C_N for pPrAz, referring to the procedure of Mark. Let us first consider *trans*-pPrAz. Figure 6 shows the chemical structure of the repeat unit of erythro-*trans*-pPrAz, where the skeletal atoms N, N, C, C, and N are defined as atoms 0, 1, 2, 3, and 4, respectively, the bond length between atoms $i - 1$ and i are denoted as b_i, and an angle formed by bonds i and $i + 1$ as θ_i. This numbering is the same as Mark's for the diene analogues. Bond lengths and angles in Figure 6 were estimated using a CambridgeSoft Chem3D Ultra software (version 10.0) as follows: $b_1 = 0.125\,\text{nm}$; $b_2 = b_4 = 0.149\,\text{nm}$; $b_3 = 0.155\,\text{nm}$; $\theta_1 = \theta_4 = 113.4°$; $\theta_2 = \theta_3 = 107.3°$. These parameters are slightly different from the correspond-
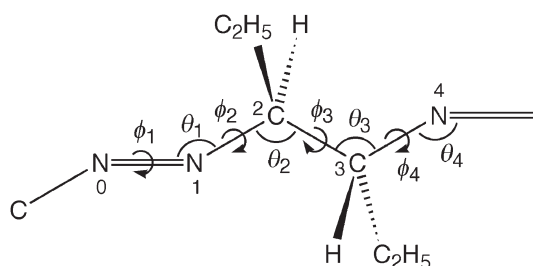
ing parameters for the diene polymer analogues.

In the RIS approximation, each skeletal bond adopts one of a small number of discrete rotational states, where the rotational angle about bond i is defined as ϕ_i measured from the trans state of $0°$. Here, we consider the same rotational isomers as those Mark considered for the diene polymer analogues, explained as follows. Since bond 1 is double bond, ϕ_1 is fixed at $0°$. Bonds 2 and 4 are single bonds lying between double and single bonds, and thus ϕ_2 and ϕ_4 can be assumed to be $\pm 60°$ and $180°$ by its chemical bond nature.[19–21] The single bond 3 between two single bonds may adopt trans and gauche states (*i.e.*, $\phi_3 = 0°$, $\pm 120°$) to avoid the steric repulsion between atoms attached to C^2 and C^3. Thus there are 27 ($= 3^3$) rotational isomers per monomer unit in the RIS model for *trans*-pPrAz.

For the rotational states for bond 2, statistical weights of $\phi_2 = \pm 60°$ and $180°$ are defined as 1 and α, respectively. Mark[17] introduced the following two statistical weight matrices with respect to rotations around bonds 3 and 4 of *trans*-diene polymers,

		ϕ_3		
		0°	120°	−120°
ϕ_2	60°	1	σ	σ
	180°	1	$\sigma\beta$	$\sigma\beta$
	−60°	1	σ	σ

		ϕ_4		
		60°	180°	−60°
ϕ_3	0°	1	α	1
	120°	1	$\alpha\beta$	1
	−120°	1	$\alpha\beta$	1

where statistical weights of $\phi_3 = 0°$ and $120°$ are defined as 1 and σ, respectively. When bond 2 or 4 is in the cis state ($\phi_i = 180°$, $i = 2$ or 4), bond 3 may take less favorably the gauche states, which is taken into account by a factor $\beta(< 1)$ in the above matrices.

On the other hand, the monomer unit of *trans*-pPrAz has two ethyl groups on the neighboring C^2 and C^3 atoms which affect the rotation around bond 3. As shown in Figure 7, the two ethyl groups come closer at $\phi_3 = \pm 120°$ for the erythro unit and at $\phi_3 = 0°$ and $120°$ for the threo unit (the R,R-form), so that statistical weights for such rotational states should be multiplied by a factor $\gamma(< 1)$, which was not necessary for diene polymers. As a result, the above upper matrix for *trans*-diene polymers should be replaced by

erythro		ϕ_3		
		0°	120°	−120°
ϕ_2	60°	1	$\sigma\gamma$	$\sigma\gamma$
	180°	1	$\sigma\beta\gamma$	$\sigma\beta\gamma$
	−60°	1	$\sigma\gamma$	$\sigma\gamma$

Figure 6. Molecular structure of erythro-*trans*-pPrAz.
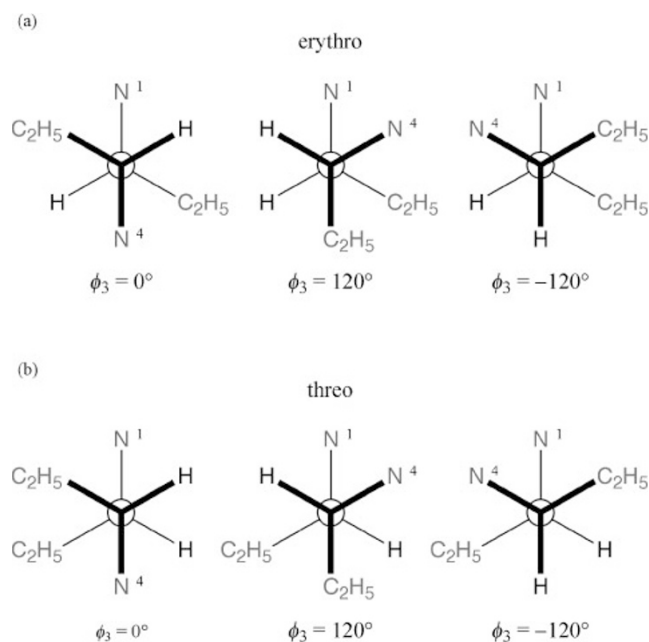
Figure 7. Molecular structures of rotational isomers of erythro- (a) and threo-*trans*-pPrAz (b).

or

threo		ϕ_3		
		0°	120°	−120°
ϕ_2	60°	γ	$\sigma\gamma$	σ
	180°	γ	$\sigma\beta\gamma$	$\sigma\beta$
	−60°	γ	$\sigma\gamma$	σ

Here, σ is the statistical weight due to the steric hindrance between N^1 and N^4, which corresponds to the steric hindrance between C^1 and C^4 for diene polymers. (We do not consider the S,S-form of the threo unit because it is identical with the R,R-form in the calculation of C_N.) On the other hand, the above lower matrix for *trans*-diene polymers can be used as it is for *trans*-pPrAz. Thus, statistical properties of the rotational isomers for *trans*-pPrAz are described by the four parameters, α, β, γ, and σ.

The population of the rotational isomers in each monomer unit of diene and azine polymers is independent of the state of the neighboring monomer units along the chain. In such a case, the characteristic ratio C_N can be calculated by eq A·1 in Appendix. Mark[17] demonstrated that the experimental characteristic ratio of *trans*-pBD is favorably compared with the RIS model with the statistical weights $\sigma = 1$, $\alpha = 0.96$, and $\beta = 0.24$.

To calculate the C_N for *trans*-pPrAz, eq A·1 must be extended for copolymers composed of the erythro and threo units. If the sequence of the erythro and threo units is random, the average with respect the erythro and threo isomers can be done independently along the copolymer chain, and eq A·1 is simply modified to eq A·7.
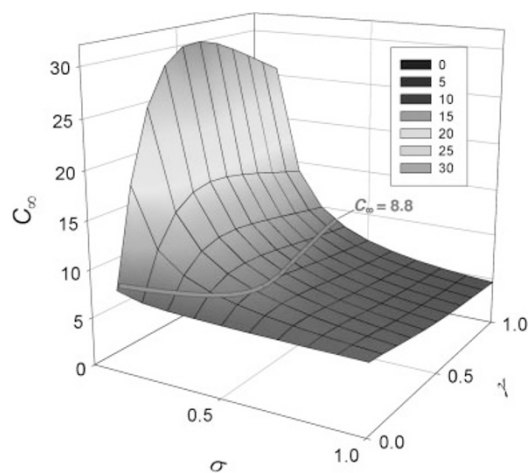
Figure 8. The characteristic ratio C_∞ calculated by eq A·7 for *trans*-pPrAz as a function of σ and γ at fixed $\alpha = 0.96$ and $\beta = 0.24$ (see text).

It can be demonstrated that C_N calculated by eq A·7 using reasonable values of the statistical weights quickly approaches to the asymptotic value C_∞ with increasing N (*cf.* Figure S2 in the Supporting Information). Thus, we compare theoretical C_∞ with experimental C_N for *trans*-pPrAz with $N > 50$ in what follows. Moreover, C_∞ is dependent on α and β relatively weakly as shown in Figure S3 in the Supporting Information, so that we may approximate the statistical weights α and β for *trans*-pPrAz to those for *trans*-pBD.

Figure 8 shows C_∞ for *trans*-pPrAz with the erythro fraction of 0.65 as a function of σ and γ at fixed α (= 0.96) and β (= 0.24). This figure exhibits that σ must be less than *ca.* 0.5 to attain to the experimental values of C_N (= 8.8 ± 0.4) in Table III. This is a contrast to the σ value (= 1) of *trans*-pBD,[17] and we can say that the more extended conformation of pPrAz arises from the difficulty of gauche conformation around bond 3.

The characteristic ratio for photoisomerized pPrAz samples can be also calculated using eq A·7, where the samples are regarded as random copolymers of the *trans* and *cis* isomers. Quantities relating to the *cis* isomer in eq A·7 are estimated more simply using virtual bonds defined in Figure 9, as for *cis*-diene polymers.[16] Since extensions of bonds 4 and 2 meet at a cross point P in the figure for the *cis* polymer, we can define two virtual bonds between C^3 and P (bond a) and between C^2 and P (bond b), in place of bonds 4 and 2 in Figure 9. Bond 1 is not necessary to consider, and bond 3 is renamed as bond c. The bond length b_a (= b_b) and the bond angle θ_a were estimated to be 0.310 nm and 46.8° by the Chem3D software.

In *cis*-pPrAz, ethyl groups attaching to C^2 and C^3 on both sides of the N=N bond are close each other,
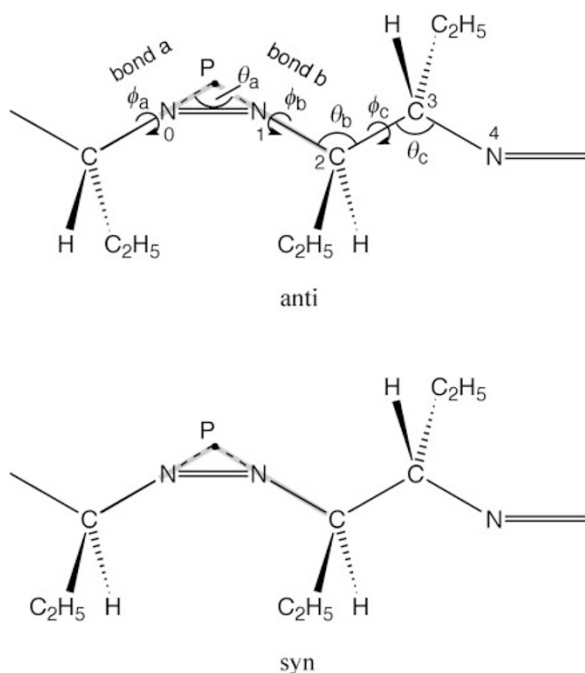
Figure 9. Molecular structures of anti- and syn-*cis*-pPrAz.

and restrict severely the rotations around bonds a and b; this effect was not necessary to be considered for *cis*-diene polymers. There are two stereo isomers with respect to the configuration of the two ethyl groups as also shown in Figure 9.[22] For the anti unit, only two rotational states $(\phi_a, \phi_b) = (60°, 60°)$ and $(-60°, -60°)$ are feasible to avoid severe steric hindrance between the ethyl groups. On the other hand, the feasible rotational state for the syn unit may be only $(60°, -60°)$ or $(-60°, 60°)$. We can expect that bond c is independent of the rotational state of bond b, and the statistical weights for bond c are the same as those for bond 3 in *trans*-pPrAz. For pPrAz with $f_{cis} = 0.33$, eq A·7 provides $C_\infty \approx 10.2$ and 4.7, if the *cis* unit is anti and syn ones, respectively. The experimental C_N for photoisomerized pPrAz samples is close to the former. This indicates that the irradiation of 365 nm light preferentially produces the anti-*cis* unit, presumably because of the steric hindrance between ethyl groups on both sides of the N=N bond.

Kamachi *et al.*[8] studied the variation in the chain size of poly(butyraldehyde azine) (pBuAz) with the *trans*-to-*cis* photoisomerization by size exclusion chromatography (SEC). Their result that the elution volume of photoirradiated pBuAz is larger than that of *trans*-pBuAz was opposite to our viscosity result for pPrAz. This implies that C_N for azine polymers can sensitively depend on the chemical structure of the side chain. Unfortunately, Kamachi *et al.* did not measure absolute molecular weights of their pBuAz sample before and after photoisomerization, which is required to make a quantitative argument of C_N for pBuAz.

Irie *et al.*[3,4] reported the drastic effect of photoisomerization in polymers of which main chain is comprised of azobenzene units. The RIS model analysis demonstrates that the characteristic ratio C_N of *cis*-azine polymers strongly depends on the chemical structure of the side chains on both sides of azo group. Since the chemical structure on both sides of azo group is very much different between azine and azobenzene polymers, it is little wonder that the photoisomerization gives rise to the opposite change in the chain size of azobenzene polymers. The rigid phenylene unit attaching to azo group may enhance the change in the chain size by photoisomerization of azobenzene polymers. This effect is not expected for azine polymers.

APPENDIX: CALCULATION OF THE CHARACTERISTIC RATIO

When the monomer unit consists of four different kinds of main-chain bonds and the population of the rotational isomers is independent of the state of neighboring monomer units, the characteristic ratio C_N can be calculated by

$$C_N = 1 + (s + N^{-1}\boldsymbol{S}_1\boldsymbol{U}_N\boldsymbol{S}_2)/2\overline{b^2} \qquad (A·1)$$

where

$$s \equiv \boldsymbol{b}_1^T\langle\boldsymbol{T}_1\rangle\boldsymbol{b}_2 + (\boldsymbol{b}_1^T\langle\boldsymbol{T}_1\boldsymbol{T}_2\rangle + \boldsymbol{b}_2^T\langle\boldsymbol{T}_2\rangle)\boldsymbol{b}_3$$
$$+ (\boldsymbol{b}_1^T\langle\boldsymbol{T}_1\boldsymbol{T}_2\boldsymbol{T}_3\rangle + \boldsymbol{b}_2^T\langle\boldsymbol{T}_2\boldsymbol{T}_3\rangle + \boldsymbol{l}_3^T\langle\boldsymbol{T}_3\rangle)\boldsymbol{b}_4$$
$$(A·2)$$

$$\boldsymbol{S}_1 \equiv \boldsymbol{b}_1^T\langle\boldsymbol{T}_1\boldsymbol{T}_2\boldsymbol{T}_3\boldsymbol{T}_4\rangle + \boldsymbol{b}_2^T\langle\boldsymbol{T}_2\boldsymbol{T}_3\boldsymbol{T}_4\rangle$$
$$+ \boldsymbol{b}_3^T\langle\boldsymbol{T}_3\boldsymbol{T}_4\rangle + \boldsymbol{b}_4^T\langle\boldsymbol{T}_4\rangle \qquad (A·3)$$

$$\boldsymbol{S}_2 \equiv \boldsymbol{b}_1 + \langle\boldsymbol{T}_1\rangle\boldsymbol{b}_2 + \langle\boldsymbol{T}_1\boldsymbol{T}_2\rangle\boldsymbol{b}_3 + \langle\boldsymbol{T}_1\boldsymbol{T}_2\boldsymbol{T}_3\rangle\boldsymbol{b}_4 \quad (A·4)$$

$$\boldsymbol{U}_N \equiv [(N-1)\boldsymbol{E} + (\boldsymbol{E} - \langle\boldsymbol{T}_1\boldsymbol{T}_2\boldsymbol{T}_3\boldsymbol{T}_4\rangle^{N-1})$$
$$\times (\boldsymbol{E} - \langle\boldsymbol{T}_1\boldsymbol{T}_2\boldsymbol{T}_3\boldsymbol{T}_4\rangle^{-1})^{-1}]$$
$$\times (\boldsymbol{E} - \langle\boldsymbol{T}_1\boldsymbol{T}_2\boldsymbol{T}_3\boldsymbol{T}_4\rangle)^{-1} \qquad (A·5)$$

with the vector $\boldsymbol{b}_i$ of bond i (a column vector), the unit matrix $\boldsymbol{E}$, and the transformation matrix $\boldsymbol{T}_i$ defined by

$$\boldsymbol{T}_i \equiv \begin{pmatrix} \cos\phi_i\cos\theta_i & \sin\phi_i & \cos\phi_i\sin\theta_i \\ \sin\phi_i\cos\theta_i & -\cos\phi_i & \sin\phi_i\sin\theta_i \\ \sin\theta_i & 0 & -\cos\theta_i \end{pmatrix} \quad (A·6)$$

The superscript T indicates the transposition and $\langle\cdots\rangle$ means the statistical average taken with statistical weight matrices (see the text).

Similarly, C_N for the independent chain composed of 3 different kinds of main-chain bonds can be made by substituting $\boldsymbol{b}_4 = 0$ in eqs A·2–A·4 and taking out $\boldsymbol{T}_4$ from eqs A·3 and A·5.

For random copolymers, the average with respect the kind of the monomer unit can be done independently along the copolymer chain, and eq A·1 is simply modified to

$$C_N = 1 + (s_{av} + N^{-1}\boldsymbol{S}_{1,av}\boldsymbol{U}_{N,av}\boldsymbol{S}_{2,av})/2\overline{b^2} \quad (A\cdot7)$$

Here, the averaged quantity X_{av} ($X = s$, $\boldsymbol{S}_1$, $\boldsymbol{U}_N$, or $\boldsymbol{S}_2$) is calculated for copolymers by $\sum_j f_j X_j$ with the fractions f_j ($\sum_j f_j = 1$) and the quantities X_j for j units (*i.e.*, the erythro-*trans*, threo-*trans*, erythro-anti-*cis*, erythro-syn-*cis*, threo-anti-*cis*, and threo-syn-*cis* units). At infinite N, $\boldsymbol{U}_N$ given by eq A·5 can be reduced to $N(\boldsymbol{E} - \langle \boldsymbol{T}_1\boldsymbol{T}_2\boldsymbol{T}_3\boldsymbol{T}_4 \rangle)^{-1}$, and the calculation of eq A·7 becomes much simpler.

Electronic Supporting Information Available: Figures S1, S2 and S3. These materials are available *via.* the Internet at http://www.spsj.or.jp/c5/pj/pj.htm

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