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Photo-regulated metal coordination of azobenzene polymer having sterically controlled ion binding sites

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Summary

2,2'-Dimethylazobenzenes having metal chelating ligands at *meta*-positions were synthesized, and the interaction with metal ions were estimated for *syn*- and *anti*-ligands on thermal isomerization. The azobenzenes with the metal-interaction were transformed to vinyl azobenzenes and copolymerized with styrene. The metal extracting ability was found in photo-isomerized polymer having *syn*-bis(iminodiacetic acid) groups; the selectivity was high for Cu(II) ion.

Introduction

Azobenzene and many of its derivatives exhibit large conformational change by reversible *trans-cis* transformation. A number of polymer having azobenzene moieties have been synthesized; their photo-induced structure change has received much attention for functions as photoresponsive polymers, including the change of viscosity, pH, conductivity, solubility, wettability(1), and mechanical effects in monolayer system (2). Some azobenzene chromophores having chelating ability such as iminodiacetic groups (3,4) and a variety of crown ethers (5) at both 4,4'-position have been synthesized to mimic the behavior of ion binding affinity in biological systems and to modify a photosensitive ion switch; their ion binding properties have been controlled by photo-induced *trans-cis* isomerization.

Authors have previously reported the syntheses of side chain azobenzene polymers having ion binding sites and their metal extraction ability(6), in which metal binding ligands were connected at the 3,3'-position of both phenyl rings. However *meta*-substituent groups in azobenzene exist in both *anti*- and *syn*-configuration, therefore the interaction between two binding sites could not be kept constant when the azobenzene was isomerized to *cis*-form.

In this paper, two methyl groups were substituted at the 2,2'-position of azobenzene and the configuration of metal binding sites at *meta*-position were sterically controlled. The methyl groups at *ortho*-positions do not interfere with *cis-tans* isomerization and do not exist in *syn*-configuration by steric hindrance(7), so that two ligands at 3,3'- or 3,5'-position can be present in *syn*- or *anti*-configuration. The

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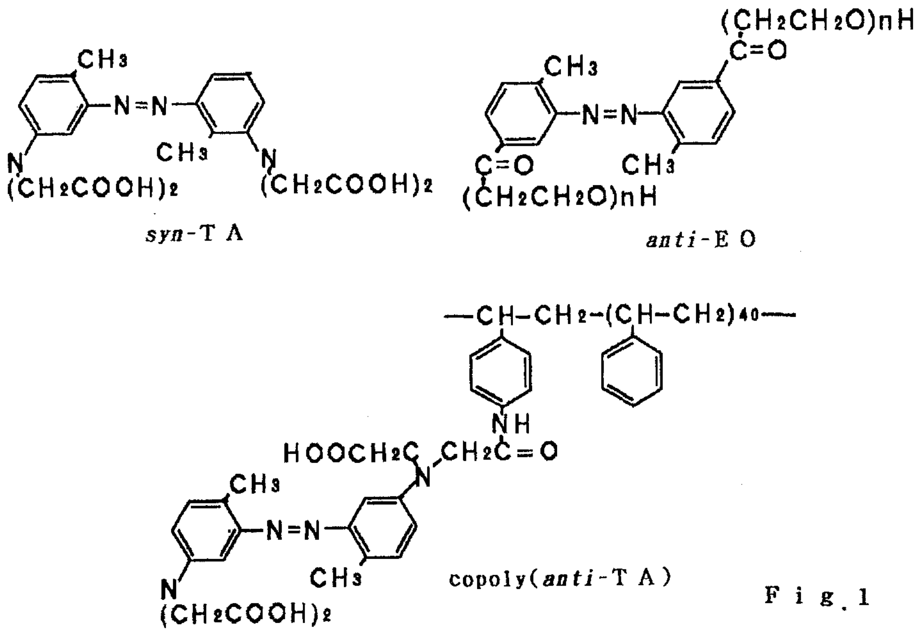

syn-T A

anti-E O

copoly(*anti*-T A)

Fig. 1

distance between 3,3'- or 3,5'-benzylic positions in azobenzene are estimated to be 10.0 Å and 9.5 Å in the *trans*-form, and 7.8 Å and 6.3 Å in the *cis*-form, respectively by space filling molecular model(8). Thus *meta*-substituent groups in the *cis*-form become feasible to interact each other compared with those in the *trans*-one. We synthesized low molecular weight azobenzenes, in which the chelating ligands at *meta*-positions could be brought close to metal ions enough to bind intramolecularly in *cis*-isomers. They were thermally isomerized with or without metal ions in order to estimate the spatial fitness between ligands and metal ions; the compounds which may interact with metal ions were transformed to vinyl-azobenzenes, and metal extracting efficiencies of the resulting polymers were investigated.

Result and Discussion

Syntheses of 2,2'-Dimethylazobenzene Derivatives and the Effect of Metal Ion on Thermal Isomerization

2,2'-Dimethylazobenzenes having metal binding sites which were modified chelating agents such as ethylenediaminetetraacetic acid, and poly(ethylene glycol)(9). Both *anti*- and *syn*-azobenzene derivatives were synthesized by the bimolecular reduction of nitrobenzene derivatives. In the case of synthesis of 2,2'-dimethyl-3,5'-diaminoazobenzene(*syn*-diaminoazobenzene) by condensation with different nitrotoluidine, three major products were inevitably formed by self-condensation by-products and bimolecular reaction. *syn*-Diaminoazobenzene were purified by recrystallization from aqueous methanol and then hexane-ethyl acetate to afford pale orange crystal in 36 % yield. Although aromatic protons of isolated compound could not be distinguished from two by-products by ^{1}H-NMR spectrum, two methyl signals with equal integral values appeared at 2.5 and 2.6 ppm, and a higher field peak could be assigned as methyl group

Table 1. Pseudo first order rate constant for isomerization of azobenzene derivatives

	Isomerization						
Azobenzene	*trans-cis* a)	*cis-trans* b)					
			Zn	Cu	Ca	Pb	UO_2
syn-TA	2.2	1.5	0.6	0.8	1.4	-0.4	-0.1
anti-TA	3.3	2.5	2.0	1.5	1.5	-0.4	-0.7
syn-EO-2	1.4	3.1	1.6	1.6	3.1	1.9	2.0
anti-EO-2	3.2	2.1	1.3	1.7	2.0	1.8	1.8
syn-EO-3	0.8	3.0	1.9	1.3	1.9	1.7	1.9
anti-EO-3	2.9	2.8	1.8	1.5	1.9	2.1	2.5

a) Photo-isomerization at 25 C(x10^{-2}/s). b) Thermal isomerization with or without metal ion at 45 C(x10^{-1}/h)

existing between amino- and azo-group. The possibility that the isolated product was a 1:1-mixture of self-condensed by-products yet remained, while its melting point was at 85-88 C which was much lower than that of symmetric *anti*-diaminoazobenzene, thus the isolated compound was confirmed as asymmetric *syn*-diaminoazobenzene.

Photo-isomerization reached a stationary state within a couple of minutes and pseudo first order constants are given in Table 1. The effect of metal addition on the rate of photo-isomerization could not be determined quantitatively, presumably due to the catalytic effect of metal ions(10,11) and each ligand might act independently to form intermolecular 2:1 or 1:1 metal-complexes to some extent(12). The degrees of thermal isomerization were small even at 45 C in the case of azobenzene having large molecular weight substitution and there was no regularity for the rate between *syn*- and *anti*-azobenzenes. When the solution of Pb^{2+} or UO_2^{2+} ions was added to *cis*-isomerized azobenzene, the absorption maxima decreased without UV-irradiation. Two ligands in *trans*-azobenzene might coordinate with metal ions possessing relatively large ionic length to induce *trans-cis* isomerization. The inhibitory effect of metal ions on thermal isomerization was observed for TA, EO-2, and EO-3 (structure in Fig.1); its efficiencies for *syn*-configuration were large. In the case of EO-3, there was small difference in inhibitory effect between *syn*- and *anti*-configuration. The 3,3'-ligands possessing long molecular size might be possible to close each other even in *anti*-configuration.

Metal Extraction with Azo-polymers

Vinyl polymers having TA- and EO-2-moieties which exhibited some interaction with metal ions on thermal isomerization were synthesized by condensation with p-aminostyrene and by acylation with p-vinylbenzoyl chloride; they were copolymerized with styrene. Metal extracting efficiencies were evaluated from distribution equilibria of picrate ions between aqueous phase and organic phase(13). The transfer of picric acid from the aqueous phase was little by EO-copolymers. Rigid azobenzene

Table 2. Metal extracting efficiency of azopolymers

Polymer			Metal extraction(%) b)		
	Isomer	*cis*-% a)	Ca	Zn	Cu
syn-TA	*trans*		4.1	6.6	7.9
	cis	35	4.9	22	43
anti-TA	*trans*		1.9	5.9	8.3
	cis	37	1.8	20	23
syn-EO-2	*trans*		3.6	7.5	10
	cis	59	3.7	7.0	13
anti-EO-2	*trans*		5.3	8.6	12
	cis	66	8.6	9.0	12

a) Percentage of pendant *cis*-azobenzene. b) Extracted metal picrate with azopolymer; *cis*-ext.%, calculated by the equation: (ext.% with *cis*-polymer - *trans*-% x *trans*-ext.%)/*cis*-%.

rings in EO-moieties might interfere to form the cyclic structure suitable for metal ionic radius and/or to give hydrophilic circumstance of polyether ring(9).

When a benzene solution of Copoly(TA)s having ionic iminodiacetic ligands was vigorously stirred in an aqueous solution of metal picrate, an insoluble polymer complexed with metals appeared in both phases except calcium ion. Extraction of calcium ion was only in a small amount by four kinds of Copoly-(TA)s presumably as consequence of a low complex stability against hydroxy anion (9). The extraction of Zn^{2+} and Cu^{2+} ions with *cis*-isomers were larger than those of *trans*-ones, and a selectivity (ratio of extraction efficiency of *trans* to *cis*) was significant in *syn*-azobenzene polymer. Two ligands in *syn*-azobenzene are close to each other by *cis*-isomerization, the resulting co-ordination with metal ions increased compared with those in *anti*-one. The selectivity for Cu^{2+} ion is slightly higher than that for Zn^{2+} ion. The phenomenon was quite different to the results for 4,4'-bis[bis-(carboxymethyl)iminomethyl] azobenzene(3) and 3,3'-bis[bis(carboxymethyl)amino] azobenzene polymer (6). Distance of two ligands in *syn*-*cis*-azobenzene is appropriate with Cu-ionic radius compared with Zn ion possessing large ionic radius.

Although it is impossible to attain 100%-selectivity, that is, all or nothing change in ion binding ability because of the occurrence of coordination by the mono-iminodiacetic acid groups, the amount of immiscible cis-azobenzene polymer complexed with metal ions slowly decreased with stirring. This indicates that the moderately binded metal ions are released by thermal isomerization of azobenzene moieties. The reversibility suggests possible applications for photo-regulated macromolecular ionophores.

Experimental

Synthesis of 2,2'-dimethylazobenzene derivatives

3,3'-Bis[bis(carboxymethyl)amino]-2,2'-dimethylazobenzene(*anti*- TA): 3,3'-diamino-2,2'-dimethylazobenzene(*anti*-diamino-azobenzene) was prepared by reductive coupling reaction of 4-methyl-3-nitro-aniline with zinc powder in 75% aqueous methanol containing sodium hydroxide(14), and purified by recrystallization from 90% aqueous ethanol. Yield, 76%. mp, 126-128 C. ^{1}H-NMR($CDCl_3$): δ, 2.6(s,6H, CH_3), 3.7(s, 4H, NH_2), 6.6, 6.8 (d, 4H, 3,4-ArH), 7.2(d, 2H, 6-ArH)ppm.

anti-TA was prepared by carboxymethylation of *anti*-diaminoazobenzene with bromoacetic acid in an aqueous alkaline ethanol(6), Yield, 77%. mp 220-224 C(decomp.). IR(KBr): 3600-2500(OH), 1700(C=O) cm^{-1}. ^{1}H-NMR(DMSO d_6), δ: 2.6 (s, 6H, CH_3), 4.1(s, 8H, CH_2), 5.9(bs, OH), 6.8(d, 4H, 3,4-ArH), 7.2(d, 2H, 6-ArH)ppm. α_{max}= 327 nm, ε=9400(ethanol). Found: C, 55.79; H, 5.21; N, 11.91%. Calcd for $C_{22}H_{24}N_4O_8$: C, 55.93; H, 5.12; N, 11.81%.

syn-Diaminoazobenzene: recrystallized from 50% aq. methanol and then a mixture of hexane-ethyl acetate(95:5). Yield, 36%. mp 85-88 C. ^{1}H-NMR ($CDCl_3$), δ: 2.5(s, 3H, 2-CH_3), 2.6(s, 3H, 2'-CH_3), 6.7-7.2(m, 6H, ArH)ppm.

3,5'-Bis[bis(carboxymethyl)amino]-2,2'-dimethylazobenzene(*syn*-TA): Yield, 20%. mp 202-210 C(decomp.) ^{1}H-NMR(DMSO, d_6), δ, 2.6(t, 6H, CH_3), 4.0(s, 8H, CH_2), 6.6(bs, OH), 6.6-7.4(m, 6H, ArH)ppm. α_{max}= 327 nm, ε= 9600(ethanol). Found: C, 56.17; H, 5.34; N, 11.40%.

3,5'-Bis(2-hydroxydiethoxycarbonyl)-2,2'-dimethylazobenzene(*syn*-EO-2)) : 3,5'-Dicarboxy-2,2'-dimethylazobenzene was synthesized by a coupling reaction of 2- and 5-methyl-3-nitrobenzoic acid(mp, 270-275 C, decomp.), and then converted to 3,5'-bis(chlorocarbonyl)-2,2'-dimethylazobenzene with thionyl chloride(mp. 118-122 C). Bis(acyl chloride) was condensed with diethylene glycol in the presence of triethylamine. Yield, 32%. IR (KBr): 3400(OH), 1710(C=O)cm^{-1}. ^{1}H-NMR($CDCl_3$), δ= 2.6(s, 3H, 2-CH_3), 2.9 (s, 3H, 2-CH_3), 3.5-3.9(m, 12H, -$CH_2OCH_2CH_2OH$), 4.4(t, 4H, ArCOO-CH_2), 7.0-8.1(m, 6H, ArH). α_{max}= 325 nm, ε= 10000(ethanol). Found: C, 60.95; H, 6.61; N, 6.04%. Calcd for $C_{22}H_{28}N_2O_8$: C, 60.75; H, 6.37; N, 5.90%.

Syntheses of Azobenzene Polymers

3-Bis(carboxymethyl)amino-5'-[N-carboxymethyl-N-(4-vinylphenylcarbamoylmethyl)amino]-2,2'-dimethylazobenzene(*syn*-vinyl-TA): A solution of *syn*-TA(1.0 g, 2.1 mmol) and dicyclohexylcarbodiimide(DCC, 0.63 g, 3 mmol) in 100 ml of DMAc was stirred at room temperature overnight, and then added p-aminostyrene (1.2 g, 10 mmol) and a small amount of hydroquinone to the solution. The reaction mixture was stirred at 50 C for 5 h, and then poured into water containing 2 g of NaOH. DCC-urea was separated by filtration and unreacted p-aminostyrene was extracted with benzene. The solution was acidified to pH 2.5; the product thus precipitated was filtered, washed with water, and recrystallized from ethanol. Yield. 35%, mp. 155-157 C(decomp.) IR: 1680(amide)cm^{-1}. ^{1}H-NMR: 5.5-5.8 (q, 2H, vinyl)ppm. Found: C, 62.16; H, 6.27; N, 11.84%. Calcd for $C_{30}H_{31}N_5O_7$: C, 62.80; H, 5.27; N, 12.21%.

Vinyl monomer of *syn*-EO-2 was synthesized by acylation of *syn*-EO-2 with p-vinylbenzoyl chloride in acetone. Yield 66%. Found: 64.83; H, 6.65; N, 4.68%. Calcd for $C_{31}H_{34}N_2O_9$: C, 65.56; H, 6.00; N, 4.63 %.

Copoly(*anti*-TA): A solution of *anti*-TA(0.1 g), styrene(0.72 g, 40 molar equivalent to *anti*-TA), and AIBN(0.02 g) in DMF(5 ml) was heated at 55 C for 50 h, and poured into methanol(100 ml). Copoly(*anti*-TA) thus precipitated was filtered, and thoroughly washed with methanol. A pend-

ant azobenzene unit was calculated from an absorbance at 325 nm. Copoly(*anti*-TA): Yield, 46%. Azobenzene unit, 1.41%. $[\eta]$= 0.064 dlg^{-1} in benzene at 25C.
Copoly(*syn*-TA): Yield 48%. Azobenzene unit, 0.95%. $[\eta]$=0.062 dlg^{-1}
Copoly(*anti*-EO-2): Yield, 45%. Azobenzene unit, 2.8%. $[\eta]$=0.059 dlg^{-1}.
Copoly(*syn*-EO-2): Yield, 48%. Azobenzene unit, 2.9%. $[\eta]$=0.083 dlg^{-1}.

Isomerization and Metal Extracting Efficiency

A solution of azobenzene derivative(1.25 x $10^{-4}Ml^{-1}$) in 10% aq. ethanol containing 1.2 equivalent of NaOH was irradiated at 25 C using a 75W-high pressure Hg lamp with UV-cut filter(Toshiba UV-310)(15). The rate constants was calculated by monitoring the absorption maxima of trans-isomer(π-π^*-band); the first order plots were generally linear for a half period to reach a stationary state. The degree of isomerization was calculated on the assumption that an absorption of *cis*-isomer would be negligible at the π-π^*-band of *trans*-isomer(16).

Metal extraction was conducted by vigorous stirring a benzene solution of *cis*-isomerized polymer(concentration of azobenzene unit, 10^{-3} Ml^{-1}) in an aqueous picric acid solution ($10^{-3}Ml^{-1}$) containing metal hydroxide(2.5 x $10^{-3}Ml^{-1}$) for 30 min. An insoluble metal complexed with polymer was separated by centrifugation; the concentration of picrate ion in the aqueous phase was determined spectrophotometrically.

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