A domains of TUN 1009. These are considered to be caused by partial dissolution of the A domains during the treatment with aqueous solution of OsO_4. The same phenomenon was observed for the quaternized film of a triblock copolymer of the SIA-type.[2] In this connection, it can be pointed out that the molecular arrangement of type e in Figure 11 is equivalent to that of triblock copolymers as shown in Figure 3a of ref 3, in which adjacent I domains are not chemically bound by A or S block chains. This may become the reason for the film weaknesses to swelling by water of quaternized films of such molecular arrangements.

Thus type b or d is probably the dominant molecular arrangement of samples with $M_k(I_1) = M_k(I_2) = M_k(I_3)$ and type c or e is that of samples with $M_k(I_1) = M_k(I_3) < M_k(I_2)$ when they give three-layer lamellar structures of the type -I-S-I-A-.

It can be concluded that an ISIAI-type pentablock copolymer with isoprene content of about 30-50% in weight, $M_k(S) \approx M_k(A)$, and $M_k(I_1) \approx M_k(I_2) \approx M_k(I_3)$, is required in order to obtain a film with the three-layer lamellar structure of -I-S-I-A-, which is stable to chemical modifications. The preparation of a charge-mosaic membrane from such a pentablock copolymer and its performance will be reported in a subsequent paper.

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Registry No. (Styrene)·(isoprene)·(4-VBDMA) (copolymer), 74418-57-8.

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Chelating Copolymers Containing Photosensitive Functionalities

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ABSTRACT: A series of azoaromatic polyureas was synthesized with incorporated pyridine moieties as polymeric ligands. The activation energies for cis-trans thermal isomerization of these polyureas suggest similar energy barriers to low molecular weight analogues, as well as to polymers with different molecular weights and chain segments. An increase in E_a values was observed upon complexation with cobalt and nickel. The photodecrease in viscosity was more pronounced in the (PU-MDI-DAP)-Co complex than in the PU-MDI-DAP. The viscosity of the solution increased after complexation. Preirradiated polymer solutions showed a greater increase in viscosity and slightly larger incorporation of metal ion compared to its behavior in the dark. This observation is attributed to conformational rearrangement of the macromolecular ligand prior to complexation.

Introduction

The combination of a chelating agent and a readily isomerizable group in a synthetic macromolecule, the physical and mechanical properties of which can be controlled, presents the possibility of a structurally modifiable photosensitive ion switch. Though many have studied the photochemistry and cis-trans isomerization of azobenzene and its derivatives[1] and several groups have studied the effect of this isomerization process on the stereochemistry and properties of macromolecules,[2-5] there are no examples of conformational changes induced by the absorption of a specific wavelength light quantum which have been used to drive a macromolecule's ability to complex metal ions of specific shape and stereochemical requirements.

This program was designed to establish the possibility of, and ground rules for, photochemically induced processes in macromolecules whose very change altered the metal ion chelation capabilities of an associated functionality.[6] Under the ideal circumstances, the goal would be to find a synthetic macromolecule whose conformational state at equilibrium absorbed a metal ion completely but which released that metal ion in its isomeric state, the latter being produced by a photochemical isomerization process.

Azobenzenes undergo a reversible photochemical isomerization reaction. Depending upon the associated conjugated functional groups, the photostationery state, i.e., the state at photochemical equilibrium, ranges from 70% to 100% cis isomer under conditions where the trans iso-

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mer is absorbing all the light. Quantum yields for this reaction are generally high and there are no competing reactions of significance. The reverse reaction occurs slowly at room temperature and thermal equilibrium generally favors the trans isomer. Therefore, the cis–trans isomerization of an azobenzene moiety represents virtually a model photochemical process in which one stereoisomer is favored thermally, the other stereoisomer is favored photochemically, and the conversion of one isomer to the other is virtually quantitative. These systems have another advantage and that is that there is no known evidence of emission from the excited states of azobenzene either in the cis or trans form. Therefore, there are no known processes of spectroscopic inefficiency competing with photochemical isomerization. As a result, a number of groups have used the azobenzene moiety to enforce conformational changes under appropriately controlled conditions. Azobenzenes have been used as caps for cyclodextrins,[7] to enforce selective metal ion complexation of crown ethers,[8–10] to alter the helical form in polypeptide chains,[11] to enforce conformational changes on synthetic polymers,[12] and to change the metal ion absorptivity of membranes.[13]

Selecting a chelating agent to couple with azobenzene cis–trans isomerization has a number of requirements. First, if possible, the chelating agent must complex with a large variety of metals. Second, the equilibrium constant of complexation must not be too high, otherwise there is no hope of extrusion on a stereochemical basis of specific metals. Third, the complexing agent must be available in readily polymerizable form, either as a vinyl derivative for addition polymerization or as isocyanates as a means for condensation polymerization. Almost out of necessity one is forced to choose an aromatic complexing agent as the metal ion attractor for metal ion switch design. This is the first of a series of papers investigating the reactions of copolymers with metal ions as a function of the stereochemistry of a second azobenzene comonomer unit.

The present work was begun with the following specific objectives: (1) to prepare various macromolecular ligands with the incorporation of photochromic azobenzene functionalities in the polymeric backbone, (2) to investigate the possibility of controlling the nature and extent of complexation as the result of a photochemical isomerization reaction or photochemical change, the purpose of which was to design an on/off light metal ion complex switch, and (3) to investigate the possibility of template polymer syntheses[13] in which the polymer was synthesized in the presence of a specific metal so as to greatly increase the absorptivity of that metal in the thermally equilibrated form. This work was based on our previously reported template syntheses from 4-methyl-4′-vinyl-2,2′-bipyridine.[14]

Azoaromatic polyureas having 2,6-diaminopyridines in the backbone have been synthesized as macromolecular ligands in the present investigation. Their photochemical behavior has been compared for their nickel(II) and cobalt(II) complexes. The broad ramifications of this work will be extended to other chelating ligands in future publications.

Experimental Section

Polyureas I–VI (Figure 1) were synthesized by polyaddition reactions of diisocyanate and diamine monomers. Each 0.5 mol of diamine and diisocyanate monomer was mixed in 10 mL of Me_2SO, and the polymerization was carried out for 15 min at room temperature. The reaction mixture was precipitated in methanol and dried. Polymers I–III were prepared by the reaction of an equimolar mixture of *p,p*′-diaminoazobenzene[15] and toluene diisocyanate (TDI), methylenebis[phenyl isocyanate] (MDI), and hexamethylene diisocyanate (HMDI), respectively (Table I).

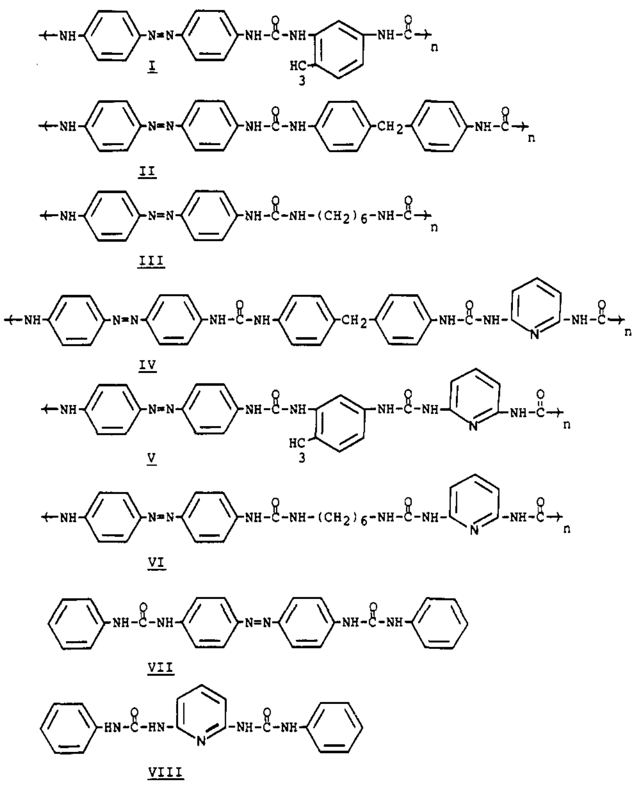

Figure 1. Structures of polyureas and model compounds.

Table I
Composition of Polyazoureas

sample	DAP, mol	diisocyanate, mol	aminoazobenzene, mol	% yield	% N calcd	% N obsd
PU I		0.005	0.005	90.0	21.76	20.5
PU II		0.005	0.005	85.5	18.18	18.0
PU III		0.005	0.005	70.0	22.10	22.5
PU IV	0.0025	0.005	0.0025	85.5	21.10	21.0
PU V	0.0025	0.005	0.0025	80.1	24.18	24.1
PU VI	0.0025	0.005	0.0025	75.2	24.48	24.3

Terpolymers IV–VI were prepared from 0.5 mol of *p,p*′-diaminoazobenzene, 0.5 mol of 2,6-diaminopyridine, and 1 mol of the desired isocyanate. The polymerization in all cases was carried out by thoroughly mixing the monomers in small amounts of Me_2SO. The polymerizations were carried out at room temperature for 15–30 min, whereupon the reaction mixture was poured into an excess of methyl alcohol and the polymer purified by reprecipitation and then vacuum dried. The molecular weight of the terpolymer was controlled by adding an excess of diisocyanate in the monomer feed.

Preparation of Metallopolymers. Polyureas IV–VI were complexed with $Co(OAc)_2 \cdot 4H_2O$ and $NiSO_4 \cdot 6H_2O$ according to the following procedure: tetrahydrofuran solutions of the metal salts were added to the terpolymers IV–VI in appropriate stoichiometric amounts and stirred at room temperature for 24 h. The reaction mixture was then filtered and washed with THF and methanol repeatedly until no traces of metal ions were detected in the filtrate. The polymers were vacuum dried. A model compound (VII) was prepared by the reaction of *p,p*′-diaminoazobenzene and phenyl isocyanate in a 1:2 molar ratio, washed with methanol, and dried. A similar model compound (VIII) was prepared by the reaction of 2,6-diaminopyridine and phenyl isocyanate in a 1:2 molar ratio.

Absorption spectra were recorded with a Varian Cary 219 spectrophotometer. The temperature of the spectrometer sample compartment was controlled with a thermostated circulating bath to within ±0.02 °C. Viscosity measurements were carried out in a Ubbelohde viscometer at 35 °C with Me_2SO as the solvent. The concentrations throughout were 0.8 g/dL.

Solutions were irradiated by a GTE/Sylvania mercury lamp, 500-W 120-V light, suspended in close proximity to the viscometer.

Table II
Preparation and Characterization of Metallopolymers

polymer	$Co(OAc)_2$, mol	wt % DAP in feed	wt % Co^{2+}	rel % loading of metal
PU-TDI-DAP (0.3 g)	4.5×10^{-4}	14.27	1.61	11.3
PU-MDI-DAP (0.304 g)	3.6×10^{-4}	15.32	1.00	14.32
PU-HMDI-DAP (0.3 g)	4.5×10^{-4}	18.2	2.00	17.65

	$NiSO_4$, mol	wt % DAP in feed	wt % Ni^{2+}	rel % loading of metal
PU-TDI-DAP (0.3 g)	5.3×10^{-4}	14.27	1.65	15.77
PU-MDI-DAP (0.3 g)	5.7×10^{-4}	15.30	1.39	14.67
PU-HMDI-DAP (0.25 g)	5.3×10^{-4}	18.0	1.25	11.03

The entire solution was maintained in a thermostated bath at 35 °C.

Infrared spectra were obtained on a Perkin-Elmer 237 grating infrared spectrophotometer, nuclear magnetic resonance spectra on a Varian CFT 20 spectrometer, and atomic absorption spectra on a Perkin-Elmer 603AA spectrometer.

Results and Discussion

A. General. The properties of the polyureas I–VI are given in Table I. All the polymers ranged from light yellow to dark brown and all showed the characteristic absorption spectra associated with typical azobenzene chromophores. The yields of the polymerization processes in all cases were high, and the polymers obtained were powdery and insoluble in most organic solvents. In general, the polymers were soluble in both DMF and Me_2SO. In the event the polymerization process produced an insoluble polymer, the polymerization reaction was repeated and the polymerization stopped at an earlier stage to obtain soluble samples. The polymers prepared from HMDI were in general insoluble and hence were not studied in the same detail as were the other polymers. As is well-known, aliphatic diisocyanates cross-link easily and render polymers made from them generally insoluble.[16] Nitrogen analysis of the polymers is not useful in defining the extent of incorporation of the pyridine moiety, although it generally agrees favorably with the calculated quantities.

For the metal binding studies, the amount of diaminopyridine incorporated was calculated on the basis of the feed composition (Table II). The solubility of the polymeric metal complexes was not different from the solubility of the parent polymer, and the compositions of these complexes are also given in Table II. The complexes all gave essentially similar infrared spectra with the obvious peaks of the urea, such as the carbonyl peak at 1695 cm^{-1}. The presence of absorption bands at 1665, 1645, 1555, and 1530 cm^{-1} (various vibrations of the NH bonds) indicate the absence of significant cross-links.[17]

B. Photochemical Isomerization Reactions. The absorption spectrum of azobenzene is known to change when the configuration changes from trans to cis upon irradiation.[18] The intense absorption at 320 nm due to the π–π^* transition decreases while the absorption maximum due to the cis isomer at 430 nm which is due to the n–π^* transition increases.

We observe similar spectral changes from model compound VII and all the polyureas I–VI. These compounds exhibit an absorption maximum at approximately 400 nm and the ϵ value is 6.43×10^4. These values of λ_{max} are shifted toward the red from the peak positions of unsubstituted azobenzenes. However, there was no color change associated with cis–trans isomerization.

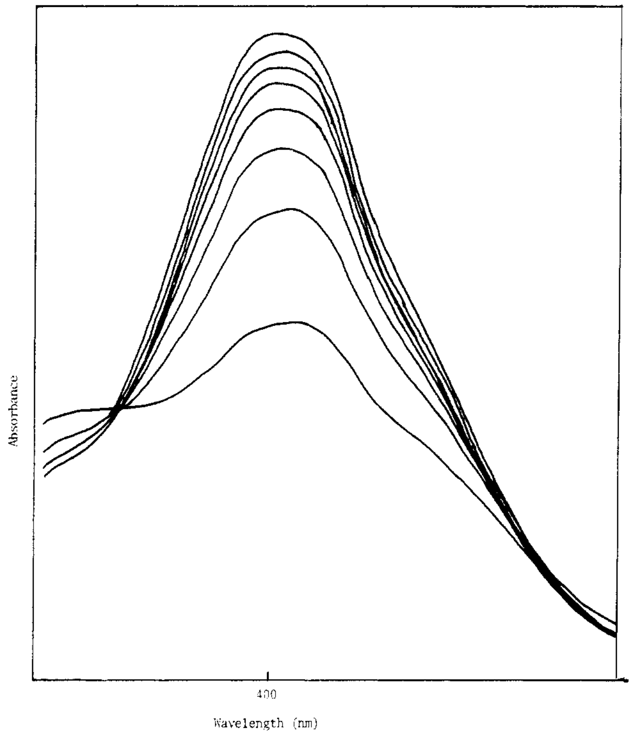

Figure 2. Absorption spectra of polyurea IV in Me_2SO showing thermal recovery after irradiation with ultraviolet light ($410 > \lambda > 350$ nm).

Table III
Activation Energies of Polyureas

sample	η_{inh}(35 °C), dL/g	E_a, kcal/mol
1. model (VII)		19.0
2. PU-TDI	0.1885	19.0
3. PU-MDI	0.206	19.0
4. PU-TDI-DAP	0.1442	19.0
5. PU-MDI-DAP	0.1229	19.0
6. (PU-TDI-DAP)-Co	0.1933	19.8
7. (PU-TDI-DAP)-Ni	0.1702	19.8
8. (PU-MDI-DAP)-Co	0.1476	19.8
9. (PU-MDI-DAP)-Ni	0.1520	19.8

C. Thermal Reorganization. Thermal isomerism from the photogenerated cis form to the trans form was followed from the absorption spectrum (Figure 2). The intensity at 400 nm of the polymer solutions increased gradually in the dark and reached its maximum after 8 h at 26 °C. The isomerization follows first-order kinetics, and the slope of a plot of log $(A_\infty - A_t)$ against time gives the rate of the thermal isomerization of the cis to the trans isomeric form of the azobenzene residues in the polyurea backbone.

A_∞ and A_t are the absorbances at 390 nm before irradiation and at time, t, respectively. The activation energies of the thermal isomerizations from cis to trans are given in Table III. These activation energies are compared with those of low molecular weight analogues also measured under the same conditions for the purpose of comparison. The activation energies for the thermal isomerization processes are essentially identical for all the polyureas with different chain segments and molecular weights. There is no significant difference in the activation energies among polyureas I, II, IV, and V, and the model compound. However, the activation energies for the Co and Ni complexes differed from their parent compound. The invariance of the absorption maximum suggests that the increase in activation energy cannot be due to electronic

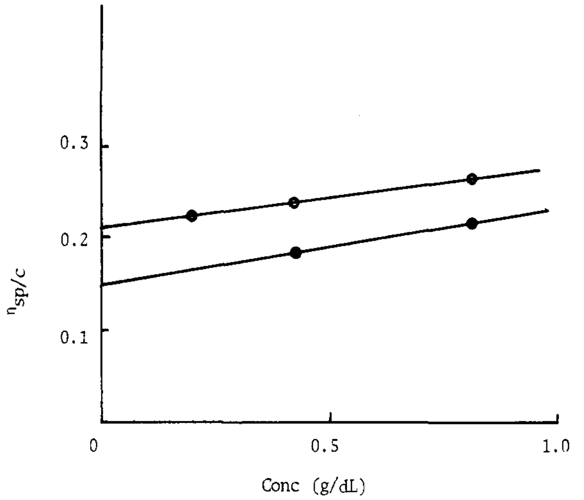

Figure 3. Viscosity of PU-MDI-DAP at 35 °C (○) in the dark before irradiation and (●) under irradiation with ultraviolet light (410 > λ > 350 nm).

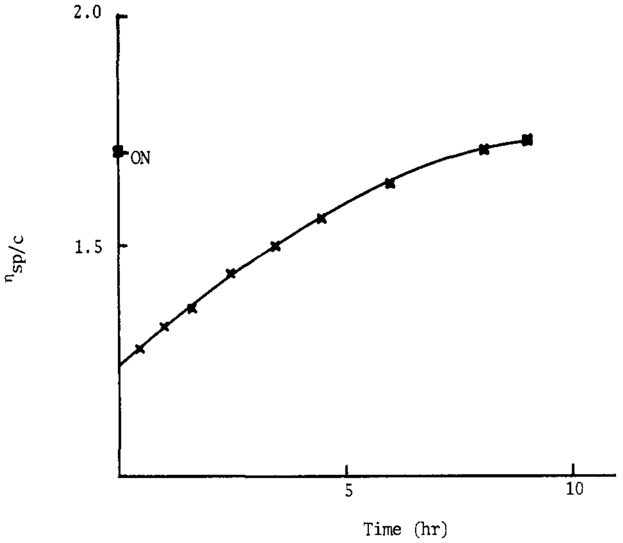

Figure 4. Recovery of viscosity of PU-MDI-DAP in Me_2SO at 20 °C in the dark. Concentration of polymer was 0.8123 g/dL.

structural changes of the azobenzene units. The increase in the activation energy is instead attributed to the formation of temporary cross-links through the metal ion which would inhibit chain mobility and alter interchain interactions. It may also be possible that, when complexed, the trans form of the polymer is more stable than the cis form.

The backbone of polyureas (I–VI) is composed of azobenzene and other aromatic residues. The constitution of these stiff segments suggests that the polymer would behave like a semiflexible rod in solution. The extended rod-like shape of the semiflexible chain is expected to shrink readily to a compact conformation when the configuration of the constituent azobenzene residue changes from the trans to the cis form. It results in the change in viscosity of polymer solutions and is termed as photoviscosity effect.[19] Figure 3 shows the solution viscosity of PU-MDI-DAP (terpolymer of diaminopyridine, *p,p′*-diaminoazobenzene, and MDI in 1:1:2 ratio) in Me_2SO in the dark as well as during irradiation with a mercury resonance lamp. The viscosity during irradiation is reduced by about 30% when compared with the intrinsic viscosity of the same sample in the dark. Since there is no effect of concentration on the viscosity of the sample, this photodecrease must arise from a conformational change of the polymer chain and not from interchain interactions. It is also observed that the viscosity decrease after illumination completely recovers to the initial viscosity value after 8 h in the dark at 20 °C (Figure 4). Thermal recovery of the original viscosity as well as the recovery of the absorption intensity (cis → trans) is compared in Figure 5. These two plots superimpose well and indicate that contraction of the macromolecular volume is indeed induced by the isomerization of the azobenzene residues and that slow thermal recovery expands the chain conformation. The decrease in solution viscosity upon irradiation is much more pronounced in the case of the (PU-MDI-DAP)-Co complex (Figure 6). Conformational changes induced by light facilitate inner chain coordination which might favor isomerization to the cis form. This is also evidenced in the higher values of activation energies for thermal rearrangement of the azobenzene/pyridine metal complexes. A mechanism was proposed by Tolmachev et al.[20] to deal with processes of complex formation involving macromolecules, which better conforms to the polymer nature of macro ligands. Although there is substantial literature on the preparation of poly(vinylpyridine) complexes of various transition-metal ions,[21–23] there are relatively few systems which can be said to be well characterized. The problem of complex characterization is especially acute for PVP complexes of the simple transition-metal halides,

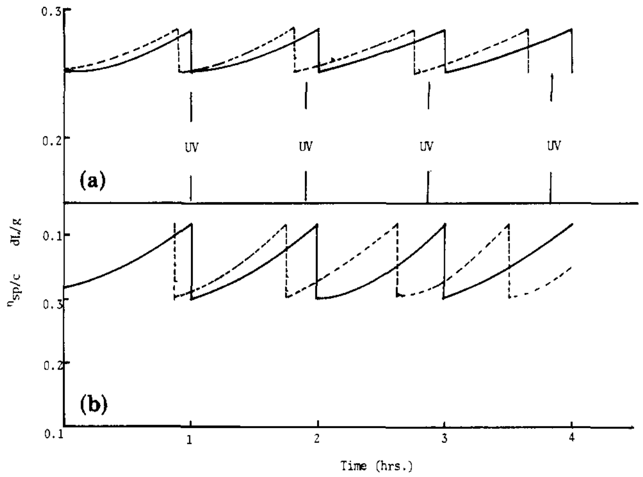

Figure 5. Changes of (a) trans form of azobenzene residues in PU-MDI-DAP backbone and (b) viscosity of PU-MDI-DAP solution upon alternate irradiation at 35 °C. Concentration of the polymer was 0.8123 g/dL: (—) in dark, (- - -) in visible light.

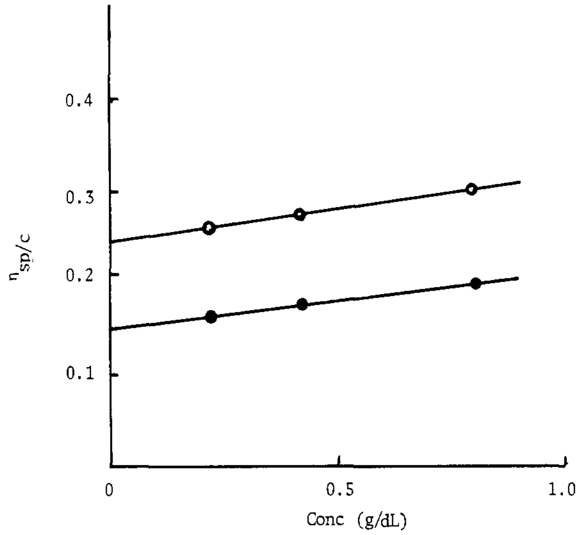

Figure 6. Viscosity of (PU-MDI-DAP)-cobalt complex at 35 °C (○) in the dark before irradiation and (●) under irradiation.

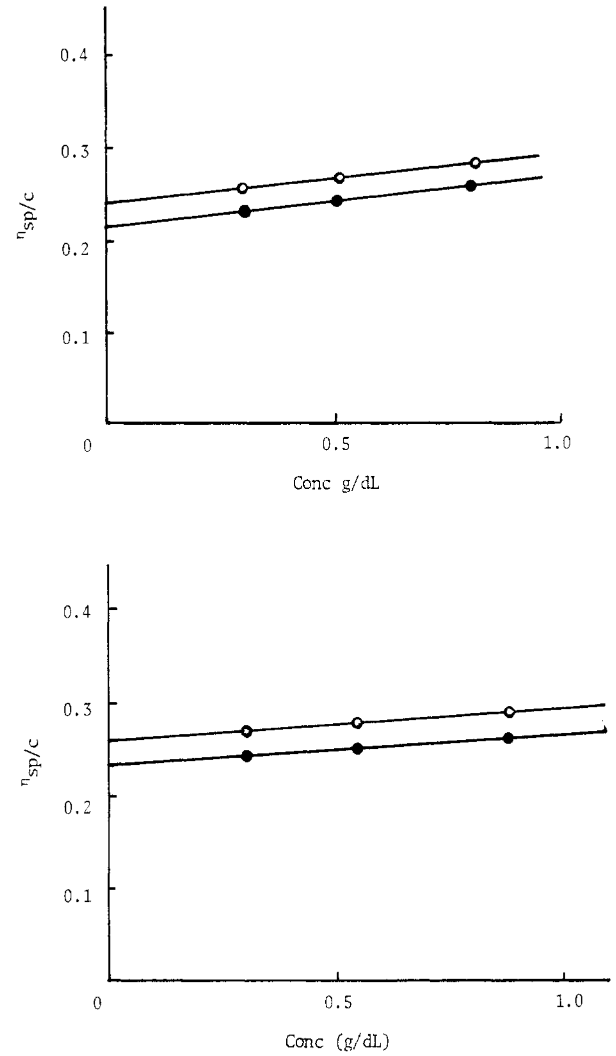

Figure 7. Viscosity of PU–TDI–DAP (above) and (PU–TDI–DAP)–cobalt complex (below) at 35 °C (○) in the dark and (●) under irradiation.

MeX_n, because in these compounds the metal ion usually has six coordination sites which must be occupied by the pyridine moiety, halide, or the solvent. A further complication is that when the metal ion is bound to more than one pyridine ligand in polymeric systems, these ligands may be attached to one, two, or three different polymer chains. The metal center, thus, acts as a cross-linking agent with a consequent effect on both the viscosity and the solubility of the material.

After the irradiation was completed, the polymer was precipitated and the amount of metal ion in the polymer was estimated by atomic absorption spectroscopy. We found that there was no detectable difference in the metal ion concentration before and after irradiation.

The recovery from cis to trans may also be accelerated to some extent by visible light (Figure 5). The decrease/recovery cycle can be repeated many times without noticeable fatigue.

Figure 7 shows the photoviscosity effect observed with PU–TDI–DAP. The effect with this polymer is less marked when compared to PU–MDI–DAP. Because the para polymer structure is linear whereas the meta polymer more likely has a helical-type structure, this is to be expected. Isomerization of the linear polymer causes much larger changes in molecular dimension, giving less extended and more compact molecules, with a consequently larger decrease in the viscosity than does the meta polymer in which the change in molecular dimensions is expected to be substantially less. There is essentially no photodecrease in the viscosity of the (PU–TDI–DAP)–Co complex (Figure 7).

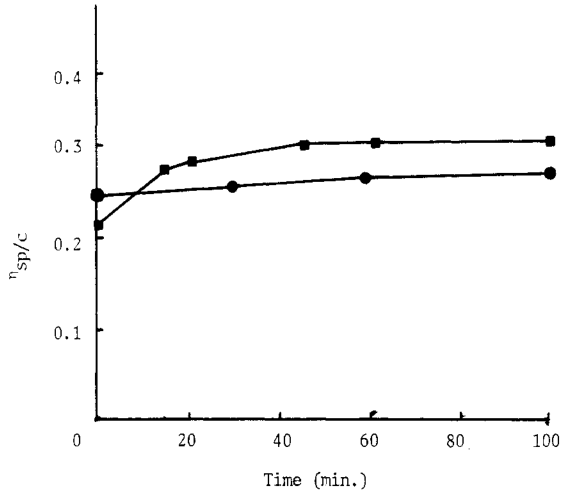

Figure 8. Changes in viscosity of PU–MDI–DAP solution with progressive complexation (●) in the dark (■) when the solution is preirradiated. Concentration of polymer is 0.8123 g/dL. Concentration of $Co(OAc)_2$ is 1×10^{-4} mol.

In spite of the differences in viscosity in the polymers in the cis and the trans forms, there was no essential change in solubility of any of the polymer–cobalt complexes when they were irradiated. No precipitation was observed with the polymers nor with the polymer–metal complexes.

D. Viscosity–Macromolecular Complexation. A series of experiments was also carried out to follow the change in the viscosity of a solution of the chelating polymers upon complexation. Figure 8 shows the slight increase in viscosity of PU–MDI–DAP as complex formation progresses. There is a sharp contrast to the "synthetic muscle model" case suggested by Teyssie et al.,[24] who reported strong chain contractions caused by the formation of coordination centers in the binding of poly(vinylamine) to metals such as Cu^{2+}, Ni^{2+}, or Zn^{2+} ions. These workers reported at least a fourfold decrease in the viscosity of solutions of polymer complexes. A notable reduction in the volume of the macromolecule was shown to occur upon complex formation. In the case of poly(4-vinylpyridine), the limiting value of the intrinsic viscosity was as low as that observed in the presence of an adequate quantity of a divalent metal ion which cannot bind to the ligand.[25] This result has been explained as being caused by the twisting of the positively charged alkylated pyridine groups in the conformational arrangement associated with the formation of tetrapyridine complexes. The sharp differences we observed seem to be due to the rigid backbone of polyureas in contrast to the flexible carbon-chain backbone found in these reported systems.

The viscosity of the PU–IV solution which had been irradiated prior to the addition of the metal salt solution exhibits a very interesting behavior. The viscosity of this sample increases rapidly and levels off at a value higher than the value observed for the same sample which has not been irradiated. This likely means that the complexing groups in the macromolecular ligand may exist in conformations different from that required by the preferred stereochemistry of a given metal ion before irradiation. Because functional groups are sometimes statistically distributed over a macromolecular chain, both favorable and less favorable conformations for complexation can occur. Hence, the formation of a given spatial structure required by the electronic configuration of a metal ion M_n^+

is followed or preceded by a conformational rearrangement in the ligand which may assume an appropriate orientation. The higher activation energies of the polyurea–metal complex, the increase in the viscosity of the solution upon complexation, and the enhancement of viscosity in the complexation of the preirradiated sample when taken together may point to the presence of temporary cross-linking by the complexing metal ion. The pyridine moieties belonging to two different chains thus may coordinate to the same metal ion and serve to enhance the solution viscosity.

The polymer samples from the viscosity experiments were precipitated in methanol, and the metal ion content was determined by atomic absorption spectroscopy. There was a 0.2% by weight increase in the cobalt content of the preirradiated sample. Thus, there is a greater incorporation of Co^{2+} in the polymeric ligand when the latter is preirradiated, but when the polymer–metal complex was irradiated after the complex had formed, there was no change in metal ion content.

E. Conclusions. A series of azoaromatic polyureas were synthesized from aminopyridines, the latter to serve as polymeric ligands. The activation energies of the thermal isomerization process of *cis*-azobenzene to *trans*-azobenzene in these polyureas suggest they have the same activation energy barrier as do low molecular weight analogues as well as polymers of varying molecular weights and dissimilar chain segments. An increase in the activation energy values was observed when these polymers were complexed with various metal ions. There was a photodecrease in viscosity which was more pronounced in (PU–MDI–DAP)–Co than in the corresponding PU–MDI–DAP. The photodecrease was also less prominent in PU–TDI–DAP. Preirradiated polymer solutions showed a greater increase in viscosity upon complexation as well as slightly larger incorporations of metal ions during complexation when compared to their behavior under similar experimental conditions in the dark.

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Registry No. VII, 74261-74-8; VIII, 91928-52-8; poly(*p,p'*-diaminoazobenzene–TDI) (copolymer), 91928-47-1; poly(*p,p'*-diaminoazobenzene–TDI) (SRU), 91928-53-9; poly(*p,p'*-diaminoazobenzene–MDI) (copolymer), 36088-77-4; poly(*p,p'*-diaminoazobenzene–MDI) (SRU), 36088-70-5; poly(*p,p'*-diaminoazobenzene–HMDI) (copolymer), 91928-48-2; poly(*p,p'*-diaminoazobenzene–HMDI) (SRU), 91928-54-0; (*p,p'*-diaminoazobenzene)·(2,6-diaminopyridino)·(TDI) (copolymer), 91928-49-3; (*p,p'*-diaminoazobenzene)·(2,6-diaminopyridine)·(MDI) (copolymer), 91928-50-6; (*p,p'*-diaminoazobenzene)·(2,6-diaminopyridino)·(HMDI) (copolymer), 91928-51-7.

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