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Chelating Copolymers Containing Photosensitive Functionalities. 2.

G. Sudesh Kumar, Patricia DePra,[†] Keda Zhang, and Douglas C. Neckers*

Department of Chemistry, Bowling Green State University, Bowling Green, Ohio 43403.

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ABSTRACT: A series of azoaromatic polyureas was prepared with incorporated bipyridine moieties as macromolecular ligands. The activation energies for cis–trans thermal isomerization, calculated from UV spectral changes, suggest similar energy barriers to low molecular weight analogues as well as to polymers with different molecular weight and chain segments. An increase in activation energy was observed upon complexation with cobalt and nickel. These polymers exhibited the now typical photoviscosity effect. Preirradiated polymer solutions showed a greater increase in viscosity upon complexation compared to the behavior of the same polymers in the dark. No trend has been observed, however, between the azo content of the polymer and the increase in solution viscosity. The observed effect is attributed to conformational rearrangement of the macromolecular ligands prior to complexation.

Introduction

The combination of a chelating agent and a readily isomerizable group in a macromolecule whose physical and mechanical properties can be controlled presents the possibility of a structurally modifiable photosensitive ion switch. Many have studied the photochemistry and cis–trans isomerism of azobenzene derivatives,[1] and several groups have studied the effect of this isomerization process on the stereochemistry and properties of macromolecules.[2–5] Investigation of conformational changes induced by the absorption of a specific wavelength light quantum being used to influence a macromolecule's ability to complex with metal ions or to form complexes of specific shape and stereochemistry is a recent phenomenon.[6–10]

In order to gain the basic knowledge to design a polymeric ligand which exhibits a reversible all-or-none ion-binding ability, we have selected the azobenzene unit as the photochromic group capable of photoinduced isomerization and built it into macromolecules containing ligand. The present work began with the following objectives: (1) to prepare various macromolecular ligands with the incorporation of photochromic azobenzene functionalities in the polymeric backbone, in the cross-links, and as pendant groups, (2) to investigate the binding ability of different ligands in the presence of a photochromic group, and (3) to determine the effect of photoisomerization on the binding ability of the ligands and of the binding of the ligands to metal ions on the isomerization process.

Earlier, we have reported template effects in bipyridine-based chelating polymers.[11] Diaminobipyridine–TDI polyureas were also reported as polymeric supports for metal catalysts.[12] Recently, we have investigated pyridine-based azoaromatic polyureas.[13] The present paper is an extension on these lines and deals with diaminobipyridine-based azoaromatic polyureas.

Experimental Section

4,4′-Diamino-2,2′-bipyridine (ABP) was prepared by the method described by Haginiwa[14] and that by Maenker and Case.[15] The methods were improved, as follows.[12] We used fuming HNO_3 rather than oleum/HNO_3 in nitrating the bipyridine *N*-oxide and the final yield improved to 40%. The product was white; mp 276–278 °C.

Polyureas I–VI (Figure 1) were synthesized by polyaddition reactions of diisocyanate and diamine monomers with Me_2SO in small amounts as the solvent. The ratio of NCO/(ABP) + (AA) was carefully kept to be 1.0 to ensure the linearity of the polymer chain.

Table I
Composition of Poly(azoureas)

sample	ABP, mol	AA, mol	diisocyanate, mol	% yield
PU-I		0.005	0.005	90.0
PU-II		0.005	0.00	85.5
PU-III		0.005	0.005	70.0
PU-IV	0.0025	0.0025	0.005	98.0
PU-V	0.0025	0.0025	0.005	96.2
PU-VI	0.0025	0.0025	0.005	85.0

Table II
Preparation and Characterization of Metallopolymers

polymer	$Co(OAc)_2$, mol	wt % ABP in feed	wt % Co^{2+}
PU-IV (0.3 g)	6.8×10^{-4}	14.2	1.02
PU-V (0.3 g)	5.8×10^{-4}	15.5	2.01
PU-VI (0.3 g)	4.5×10^{-4}	16.2	2.26
polymer	**$NiSO_4$, mol**	**wt % ABP in feed**	**wt % Ni^{2+}**
PU-IV	6.4×10^{-4}	15.5	1.15
PU-V	5.34×10^{-4}	14.2	1.73
PU-VI	4.9×10^{-4}	16.2	0.62

Polymers I–III were prepared by the reaction of an equal molar mixture of 4,4′-diaminoazobenzene (Eastman) and toluene 2,4-diisocyanate (TDI), 4,4′-methylenebis[phenyl isocyanate] (MDI), and hexamethylene diisocyanate (HMDI), respectively.

Terpolymers were prepared as shown in Table I. The polymerization in all cases was carried out at room temperature for 15 min by thoroughly mixing the monomers in small amounts of Me_2SO, whereupon the reaction mixture was poured into an excess of MeOH and the polymer was purified by reprecipitation from Me_2SO and vacuum-dried.

Preparation of Metallopolymers. Polyureas were complexed with $Co(OAc)_2{\cdot}4H_2O$ and $NiSO_4{\cdot}6H_2O$ according to the following procedure: THF solutions of the metal salts were added to the terpolymers IV–VI in given amounts (Table II) and stirred at room temperature for about 12 h. The reaction mixtures were then filtered and washed with THF and MeOH repeatedly until no traces of metal ions were detected in the filtrate and vacuum-dried. A model compound VII (Figure 1) was prepared by the reaction of *p,p*′-diaminoazobenzene and phenyl isocyanate in 1:2 molar ratio, washed with methanol, and dried. A similar model compound for the purpose of spectral comparison with the polymers was also prepared by the reaction of ABP and phenyl isocyanate in 1:2 molar ratio.

Absorption spectra were recorded with a Varian Cary 219 spectrophotometer. The temperature of the sample compartment was controlled with a thermostated circulating bath to within ±0.02 °C. Viscosity measurements were carried out in an Ubbelohde viscometer, at 30 °C with Me_2SO as the solvent. The concentrations were 0.8 g/dL throughout.

Solutions were irradiated by a GTE 400-W mercury lamp ($410 > \lambda > 350$ nm) suspended in proximity to the viscometer. The

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[†] PRF Summer Research Scholar, 1983.

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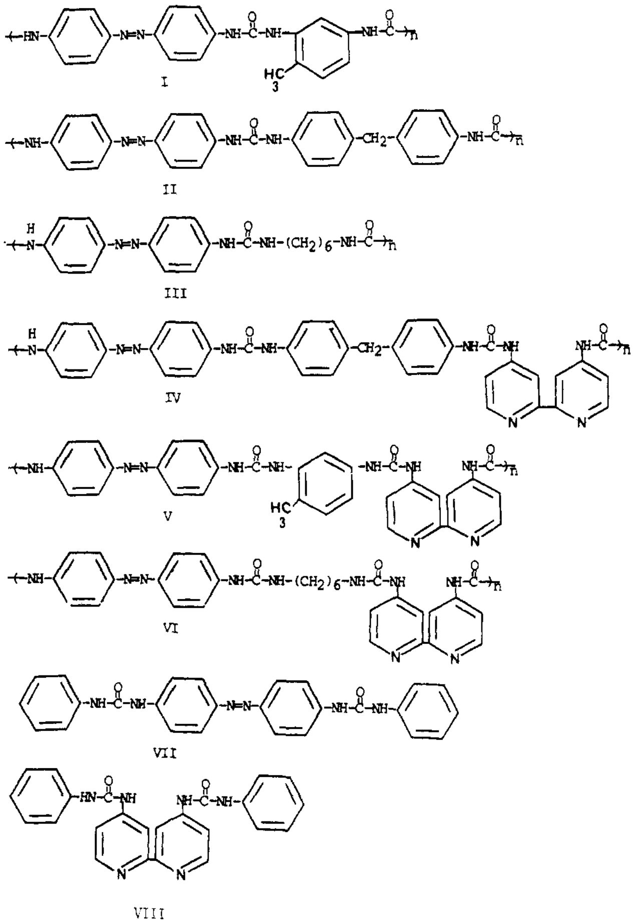

Figure 1. Structures of polyureas and model compounds.

intensity was 9.15 × 10^{17} quanta/min. The entire solution was maintained in a thermostated bath. For spectral studies, UV cells were irradiated with monochromatic light of 400 nm using a Bausch and Lomb monochromator.

Infrared spectra were obtained on a Perkin-Elmer 237 grating infrared spectrophotometer and atomic absorption spectra on a Perkin-Elmer 603AA spectrometer.

Results and Discussion

A. General. The properties of polyureas are given in Table I. All the polymers ranged from light yellow to dark brown in color. The polymerization reaction could be carried to completion but was stopped after 15 min to get soluble samples. The polymers were powdery and soluble in Me_2SO and DMF. The polymers obtained from HMDI were very sparingly soluble and hence were not studied in the same detail. Aliphatic diisocyanates do cross-link readily, which renders the resulting polymers insoluble.[16] Nitrogen analysis of the polymers is not very useful in defining the extent of incorporation of bipyridine units. The composition of the polymer–metal complexes is given in Table II. Model compound VIII gave an IR spectrum with the obvious peaks of urea, such as the carbonyl peak at 1695 cm^{-1}. The presence of this band and others at 1665, 1645, and 1530 cm^{-1} in the polymers (various vibrations of NH bonds) was taken as the evidence of polymer structure.[17] The solubility of the polymer–metal complexes was not different from the solubility of the parent polymer.

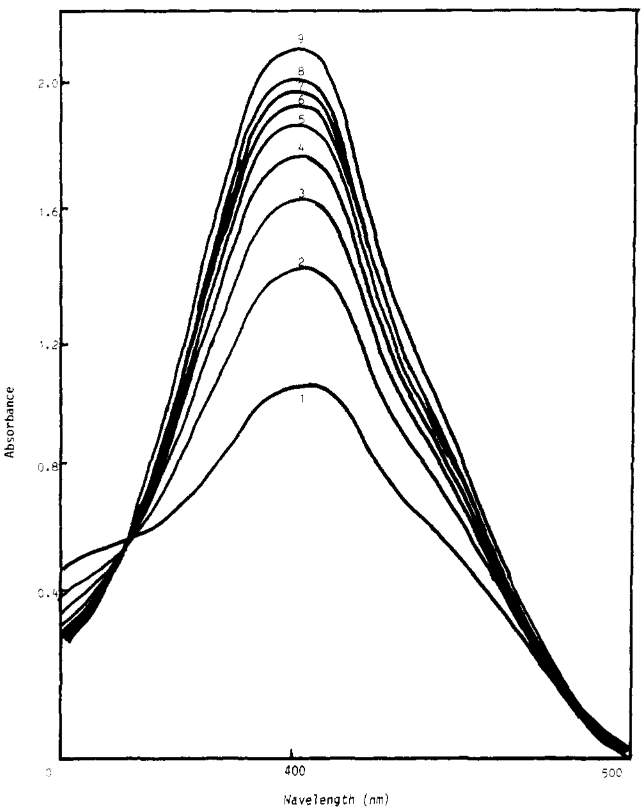

Figure 2. Absorption spectra of a polyurea (PU-IV) in Me_2SO showing thermal recovery after irradiation at 400 nm (temperature 35.5 °C): (1) photostationary state; (2) 30 min; (3) 60 min; (4) 90 min; (5) 120 min; (6) 150 min; (7) 180 min; (8) 210 min; (9) 240 min.

Table III
Activation Energies of Polyureas

sample	$[\eta]_{inh}^{30°C}$, dL/g	E_a, kcal/mol
1. model VII		19.0
2. PU-I	0.19	19.0
3. PU-II	0.20	19.0
4. PU-V	0.22	19.0
5. PU-IV	0.24	19.0
6. PU-V···Co	0.23	19.8
7. PU-V···Ni	0.22	19.8
8. PU-IV···Co	0.26	19.8
9. PU-IV···Ni	0.25	19.8
10. PU-TDI-DAP[a]		19.0
11. PU-MDI-DAP		19.0
12. PU-TDI-DAP···Co		19.8
13. PU-TDI-DAP···Ni		19.8
14. PU-MDI-DAP···Co		19.8
15. PU-MDI-DAP···Ni		19.8

[a] DAP = diaminopyridine.

B. Photochemical Isomerization Reactions. Azobenzenes are characterized by reversible transformations from the stable trans form to the less stable cis form on irradiation with ultraviolet radiation, accompanied by changes in the absorption spectrum. UV–vis spectroscopy has been extensively utilized for the study of photoisomerization. The spectroscopic method, by which isomerization around a well-defined bond is followed kinetically, provides an additional advantage because one can follow precisely the progress of the isomerization process so as to obtain a dispersion of the rate constants. Figure 2 presents a representative spectral profile of thermal reversal to trans form from photogenerated cis form. The thermal isomerization was followed at five different temperatures, i.e., 25.0, 29.5, 32.0, 35.5, and 38.0 °C. The isomerization follows first-order kinetics and the slope of a plot of log ($A_\infty - A_t$) against time gives the rates of isomerization. The activation energies (E_a) are summarized in Table III, and the correlation factor was 0.99 in each of the Arrhenius plots.

It is well-known that the energy difference between the ground states of the trans and cis isomer is about 10

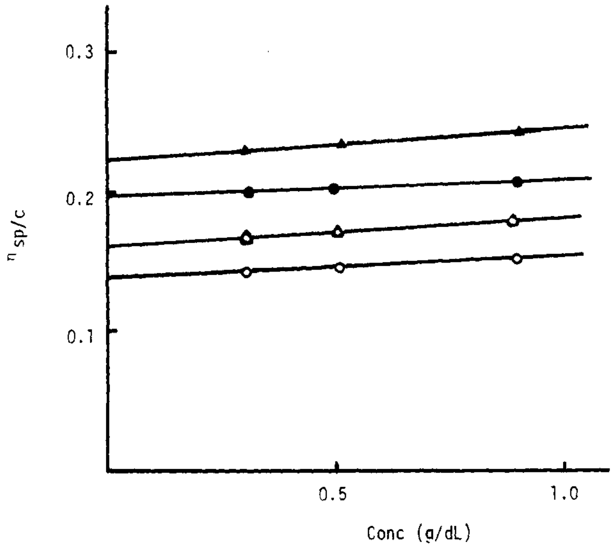

Figure 3. Photoviscosity effect in two different PU-IV samples at 30 °C: (●, ▲) in dark; (○, △) under irradiation. Concentration 0.8 g/dL.

kcal/mol.[18] In earlier work of Paik and Morawetz[19] and in more recent work by Eisenbach,[20] cis–trans thermal isomerization of azoaromatic chromophores as probes attached in small amounts to the side chain of polymers was utilized in order to follow a hindered rotation. Their results indicated that the thermal process involves a relatively high activation energy (≃20 kcal/mol) in dilute solutions. Chan and Morawetz[21] studied the photochemical isomerization in the main chains of the polyamides. Their results show that the rate is similar to that of the low molecular weight analogues. We have made similar observations in pyridine-based azopolyureas[13] and the data are presented in Table III for the purpose of comparison. The present results seem to reinforce our earlier inferences. The activation energies for the thermal isomerization process are essentially identical for all the polyureas with different chain segments and molecular weights. Also, the isomerism seems to be equally hindered in the model compound (VII). However, the activation energies for cobalt and nickel complexes are higher than those of their parent compounds. The invariance of the absorption maxima at 400 nm suggests that the increase in E_a cannot be due to electronic structural changes of azobenzene units. The increase in E_a is attributed instead to the formation of temporary chain cross-links which alter chain mobility and alter interchain interactions. As discussed in detail in later sections, it could also be due to alteration in relative stabilities of cis and trans forms after metal complexation.

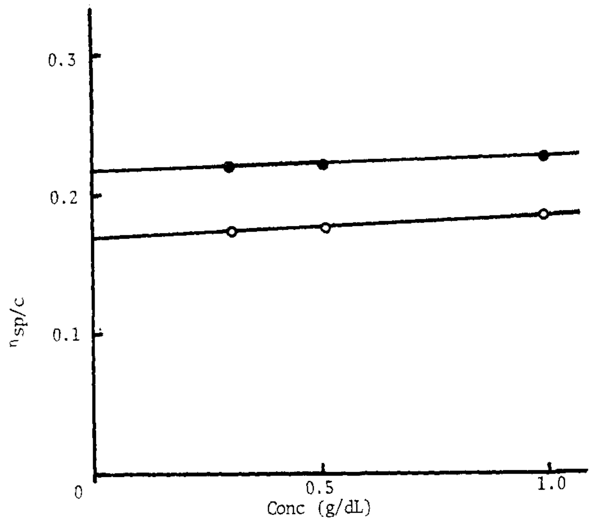

Figure 4. Viscosity of PU-IV···Co complex at 30 °C in the dark (●) and under irradiation (○) with mercury lamp (400 > λ > 350 nm).

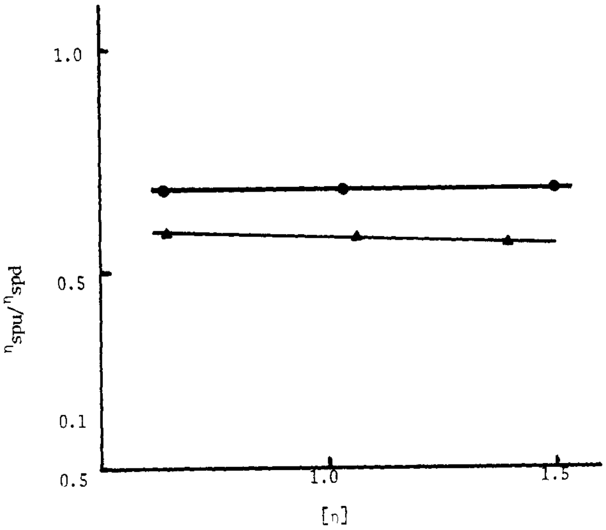

Figure 5. Dependence of the photodecrease of viscosity of PU-IV (▲) and PU-IV···Co complex (●) on molecular weight.

C. Photoviscosity Effect. The backbone of polyureas I–III 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 rodlike 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.[22] Figure 3 shows the intrinsic viscosity of PU-IV in Me_2SO at different concentrations both in the dark and under irradiation. The solutions were irradiated to the photostationary state. The intrinsic viscosity of the PU-IV solution during photoirradiation is reduced by about 40% compared to the corresponding sample in the dark. The photodecrease in viscosity for PU-IV···Co complex is shown in Figure 4. The relative content of the cis form of azobenzene residues at the photostationary state was calculated by using the following relationship: $(1 - \epsilon_c/\epsilon_t)\gamma$, where ϵ_c, ϵ_t, and γ are extinction coefficients of the cis and trans forms and cis content, respectively. These data from spectral measurements suggest that relative cis contents for the polymer and its metal complex were in the range 0.65–0.70. Hence, the difference in photodecrease of viscosity in both these cases seems to be due to differing conformational changes induced by light. The effect is less pronounced in this case. Since, in both the cases, there is no effect of concentration on the viscosity of the sample, this photodecrease should arise from a conformational change of the polymer chain and not from interchain interactions.

Molecular weight dependence on the photodecrease in viscosity of PU-IV and its cobalt complex is shown in Figure 5. Intrinsic viscosity was used as the index for molecular weights, and $\eta_{sp}^{UV}/\eta_{sp}^{d}$ is plotted against intrinsic viscosity, where η_{sp}^{UV} and η_{sp}^{d} are intrinsic viscosities under irradiation and in the dark, respectively. In the molecular weight range examined, the molecular weight does not seem to influence photochemically induced chain contraction. The deviations are ascribable to chain-end effects. The photoisomerization of azobenzene at the chain terminals would not contribute to the chain deformation

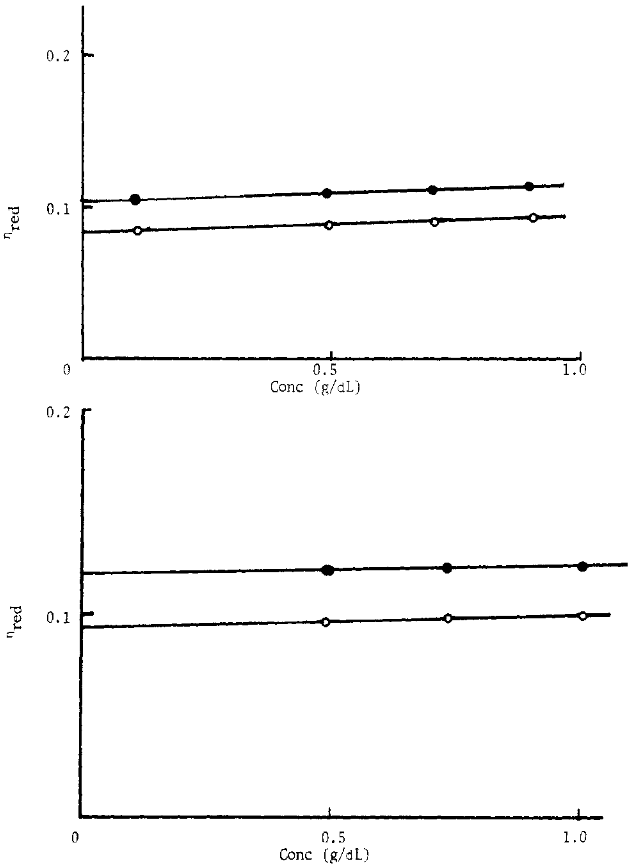

Figure 6. Photoviscosity effect in PU-V (above) and PU-V···Co complex (below): (●) viscosity in the dark; (○) viscosity under irradiation.

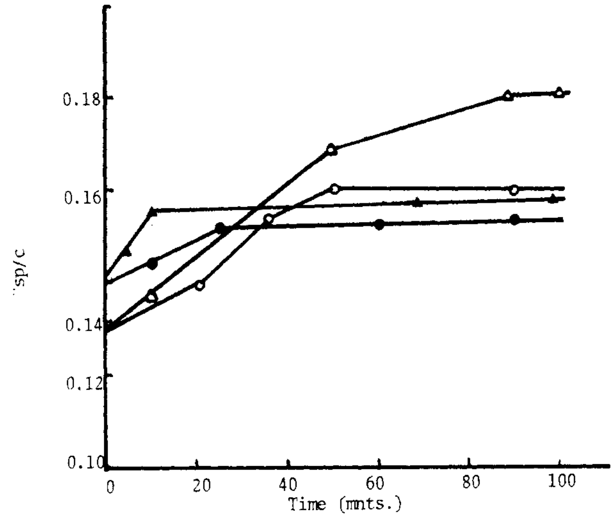

Figure 7. Change in solution viscosity of PU-IV upon complexation with (△) $Co(OAc)_2$ (1×10^{-4} mol) and with (○, △) $Ni(OAc)_2$ (1×10^{-4} mol): (●, ▲) in the dark; (○, △) under preirradiation conditions. Temperature 30 °C.

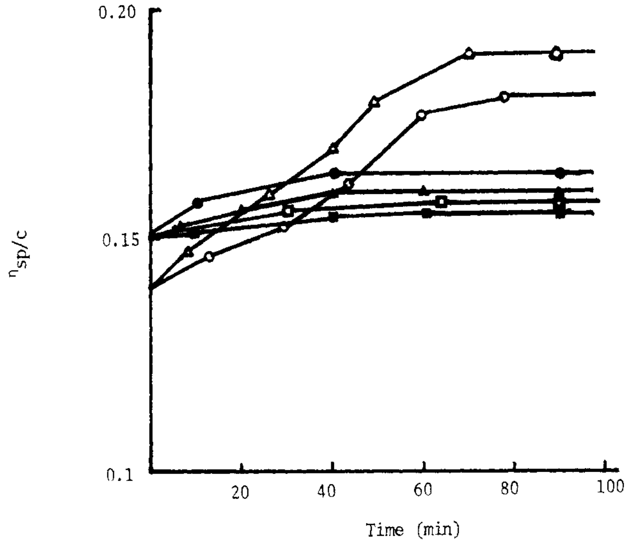

Figure 8. Progressive change in solution viscosity of (□) PU-AZO-I, (△) PU-AZO-II, and (○) PU-AZO-III upon complexation with $Co(OAc)_2$ (1×10^{-4} mol) in the dark (●, ▲, ■) and under preirradiated (○, △, □) conditions. Solvent Me_2SO, temperature 30 °C.

Table IV
Preparation of PU-IV Samples with Various Azo Contents

sample	ABP	AA	MDI	% yield
PU-AZO-I	0.0025	0.0075	0.010	90.0
PU-AZO-II	0.005	0.005	0.010	86.5
PU-AZO-III	0.0075	0.0025	0.010	93.5

as much as a group in the middle contributes. In fact, this argument is especially valid when there is no linear methylene chain to act as a strain absorber.

Figure 6 represents the data obtained with PU-V system and its cobalt complex. The low shrinkage in viscosity is possibly due to the fact that the isomerization of helical-type meta polymer (because of TDI connecting group) results in lesser alteration in molecular dimensions. The photodecrease in the case of PU-V···Co is also quite small. It is interesting to note that although the E_a values are identical for MDI-interconnected linear polymer and TDI-interconnected helical-type polymer, the decrease in molecular dimensions is far more felt in the former case and quite less in the latter.

D. Viscosity: Macromolecular Complex Formation. Another series of experiments was carried out to follow the change in the viscosity of these polymer solutions upon complexation and their response to the external light source. Figures 7 and 8 show that the intrinsic viscosity increases as the complexation proceeds with Co and Ni salt solutions. These experiments were carried out in the dark where the polymer rests in its stable trans-azo configuration. In fact, a parallel set of experiments was also carried out with polyureas I–III to make sure that the increase in viscosity is, indeed, due to the presence of bipyridine ligand sites. As expected, there was no change in the intrinsic viscosities of these solutions. We have made similar observations in pyridine-based systems reported earlier.[13] These observations are in contrast to the synthetic muscle model case suggested by Teyssie et al.,[23] who reported strong chain contractions due to the formation of coordination centers in the binding of poly(vinylamine) to metals such as Cu^{2+}, Ni^{2+}, and Zn^{2+} ions. Similar results in the case of poly(4-vinylpyridine) was explained as due to the twisting of positively charged alkylated pyridine groups in the conformational arrangement associated with the formation of tetrapyridine complexes.[24,25] We attribute these differences to the rigid backbone of polyureas, in contrast to the flexible carbon-chain backbone in those reported systems, where the conformational rearrangement is less feasible.

The PU-IV, which was irradiated till the photostationary state (preirradiated) prior to the addition of metal salt solution, exhibits a very interesting behavior. For this purpose we have prepared polymers as shown in Table IV with varying azo contents in their backbone, designated as PU-AZO-I, PU-AZO-II, and PU-AZO-III. The ratio of ABP:MDI:aminoazobenzene in the feed was 1:4:3, 1:2:1, and 3:4:1 in PU-AZO-I, PU-AZO-II, and PU-AZO-III, respectively. The intensity of the absorption maxima at 400 nm also decreased in the same order. In the dark the increase in the intrinsic viscosity upon complexation was in the following order: PU-AZO-I > PU-AZO-II > PU-AZO-III. Preiiradiated solutions exhibited the following order (Figure 8): PU-AZO-II > PU-AZO-I > PU-AZO-III.

A similar trend was not observed with nickel salt solution. These results may mean that the complexing groups in the macromolecular ligand exist in conformations different from that required in the preferred stereochemistry of the given metal ion complex before irradiation. The photostationary state may provide a given spatial structure required by the electronic configuration of a metal ion M^{n+} at least in some coordination sites. The bipyridine moieties belonging to two different chains thus are likely to coordinate to the same metal ion in this new conformation and this may serve to enhance the intrinsic viscosity. The higher E_a values for metal complexes, the increase in viscosity upon complexation, and enhancement of the same in preirradiated samples seem to point to the presence of temporary cross-linking by the complexing metal ion. The polymer samples after the viscosity measurements were precipitated and metal content and trans-azo content were determined, but no noticeable difference could be observed.

In summary, when compared to the pyridine-based systems we have reported earlier, there are various important similarities. The activation energies for the thermal cis–trans isomerization processes of the polymers are the same. In both the case of the pyridine and the bipyridine polymer, macromolecular complex formation seems to occur with an increase in solution viscosity. However, the preirradiated solutions in the present case exhibit a greater increase in viscosity upon complexation than in pyridine-based azopolyureas. This is because of the much stronger complexes formed with bipyridine relative to pyridine. The photochemical behavior also seems to be dependent upon the metal ion. While the Co^{2+} exhibits pronounced effects, Ni^{2+} seems to exhibit these effects in a less marked fashion. The characterization of these polymeric ligand complexes is especially acute because of the fact that the metal ion coordination sphere could be occupied by ligand, acetate, or solvent. The participation of more than one polymer chain is reflected in the viscosity studies.

Conclusions

A series of azoaromatic polyureas was synthesized from 4,4′-diaminobipyridines, the latter to serve as ligand sites. The activation energies of the thermal reversal from photogenerated cis to stable trans form suggest a similar energy barrier to low molecular weight analogues. The polyurea–metal complexes did have higher E_a values. The polymers exhibited the photoviscosity effect to varying degrees. Preirradiated polymer solutions showed a greater increase in viscosity upon complexation when compared to their behavior under similar experimental conditions in the dark. Our observations on the complexing behavior of these macromolecular ligands with Co^{2+} and Ni^{2+} in their trans and cis conformations also may be indicative of the possibility of photocontrol of chelation.

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