

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Polymeric Metal Catalysts and Reagents

D. C. Neckers<sup>a</sup>

<sup>a</sup> Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio

**To cite this Article** Neckers, D. C.(1987) 'Polymeric Metal Catalysts and Reagents', Journal of Macromolecular Science, Part A, 24: 3, 431 — 448

**To link to this Article:** DOI: 10.1080/00222338708074459

**URL:** <http://dx.doi.org/10.1080/00222338708074459>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## POLYMERIC METAL CATALYSTS AND REAGENTS

D. C. NECKERS

Department of Chemistry and Center for Photochemical Sciences  
Bowling Green State University  
Bowling Green, Ohio 43403

### ABSTRACT

This paper reviews the author's work in polymeric metal catalysts and reagents. The discussion focuses on polymeric bipyridines and on polymer-protected  $\text{AlCl}_3$ .

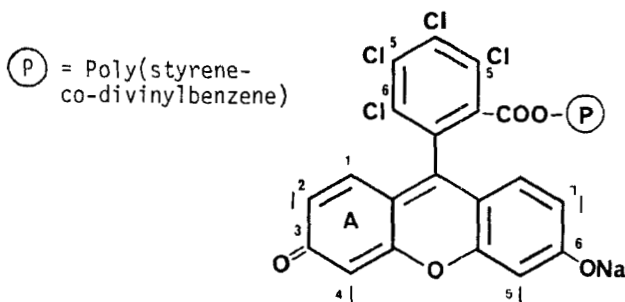
### INTRODUCTION

Solid-phase synthesis is a term introduced by Merrifield [1] to describe the technique of immobilizing a chemical reagent to a polymer support for the purpose of separation. In catalytic applications, the catalyst is anchored to the support and the reagents are passed through a bed of the polymer-supported catalyst. Under appropriate conditions, theory says, conversion to product takes place in-stream, and elution of product from the supported column of catalyst follows.

Merrifield, according to his personal reports [2], searched extensively to find the proper polymeric support in his initial studies of the synthesis of a tetrapeptide [3]. As a biochemist, he was inclined toward hydrophilic supports like Sephadex or agarose. When these proved difficult to functionalize, he resorted to the ion-exchange literature and to crosslinked polystyrene beads. In fact the first report of the chloromethylation of poly(styrene-co-divinylbenzene) beads is that reported by Merrifield in his first *Journal of the American Chemical Society* publication on polypeptide synthesis [4].

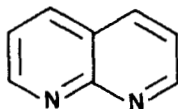
Photosensitizers are molecules which absorb radiation from a source and

transfer the energy absorbed to other acceptor molecules whose excited state manifolds lie at lower energy levels. Work in our group centered, at the outset [5], on the synthesis of polymer based photosensitizers. The idea was to immobilize an energy transfer donor to a polymer support for the purpose of designing a heterogeneous energy transfer catalyst. This was the genesis of the author's extensive work on polymeric sensitizers for the formation of singlet oxygen, in particular polymer Rose Bengal. Polymer Rose Bengal remains the most successful heterogeneous energy transfer donor yet prepared, but this work has been reviewed in other contexts [6].



Polymer Rose Bengal

This paper reviews work in two separate areas of macromolecular metal complexes. Work is outlined which led to the development of polymeric derivatives that include aluminum chloride. These were termed "polymer protected reagents" in our earliest paper on the subject [7]. The other subject reviewed in this paper is in the area of polymeric derivatives based on bipyridine.



Bipyridine

## POLYMER-PROTECTED REAGENTS

Polymer-protected aluminum chloride was a mistake. It resulted from the use of Vogel's description of Friedel-Crafts chemistry [8] to attempt to synthesize of the first polymer-immobilized photosensitizer. In that old chemistry, an acylation was carried out in either one of two preferred solvents; carbon disulfide or nitrobenzene. Carbon disulfide was the low-boiling solvent and nitrobenzene was used for more difficult Friedel-Crafts acylations. One of the classic solvent effects in the organic chemistry of 30 years ago, for example, was the acylation of naphthalene, which occurred at the 1-position in  $\text{CS}_2$  and at the 2-position in nitrobenzene.

Using Friedel-Crafts chemistry and carbon disulfide as the solvent, we attempted the acetylation of poly(styrene-*co*-divinylbenzene) beads. After the appropriate reflux period, the beads were dumped into ice water and washed with copious quantities of polar solvents. Though the beads yellowed during the preparation, they showed the expected carbonyl stretching frequency ( $5.92 \mu\text{m}$ ) for an acetophenone-like acetylated polystyrene.



The UV absorption of the beads could not be obtained at the time because there was no suitable way to handle the absorption of insoluble solids. It was expected to be that of a typical acetophenone, however, with an  $n-\pi^*$  absorption maximum at 315 nm.

The actual discovery of polymer aluminum chloride came because polymer acetophenone was so totally useless as a triplet sensitizer. In triplet-sensitized processes as studied at the time [9], aromatic carbonyl compounds were tested either by energy transfer to polyenes, such as butadiene or piperylene, or as hydrogen atom abstractors from carbinols [10], such as benzhydrol or cyclohexanol. Thus, the aromatic carbonyl compound was irradiated through Pyrex glass with a mercury-resonance lamp in the presence of the carbinol, and formation of either residual alcohol or ketone (aldehyde) oxidation product was measured chromatographically. The polyene method was preferred by most workers of the Hammond school active in the field at the time because it was introduced in an early paper from Hammond's group [11] as a method for counting the number of triplet states an aromatic carbonyl compound formed per unit time. Hydrogen abstraction, however, was the earliest photochemical reaction known for aromatic carbonyl compound triplet states [12] and, thus, it had been

studied by various workers in photochemistry who were not trained by George Hammond. Such was the author's wont.

Therefore, to test the formation of triplet states from polymer acetophenone, our group used hydrogen abstraction from alcohols as a qualitative indicator for formation of the triplet state of the ketone. Had we used the Hammond test procedure, it is unlikely that polymer aluminum chloride would have been discovered. Triplet-state sensitizers based on polystyrene to which acetophenone is immobilized is a fundamentally flawed idea. All the triplet excited state tends to engage in is accelerated degradation of the polymeric support by hydrogen abstraction [13]. Heterogeneous energy transfer in the UV region of the spectrum has never really become an acceptable procedure for the formation of triplet states though others have investigated it in some detail.

But, these were the early days of mechanistic photochemistry, and naive ideas were still acceptable. Thus, the author and his students looked at hydrogen abstraction from a series of carbinols by use of polymer acetophenone. None of the alcohols gave much oxidation product when irradiated in the presence of the polymer beads, but dicyclopropyl carbinol completely disappeared in a short time and a new product, dicyclopropylcarbiny ether, appeared. Control experiments indicated that 1) the light was unnecessary and 2) the acetyl chloride could be left out of the preparation with no change in the activity of the catalyst. Hence the terms polymer-protected reagent and polymer aluminum chloride were born. Some early examples of the uses of these reagents are given in Table 1.

The chemical structure of polymer aluminum chloride was essentially unknown until recently [14] when Hirai's group restudied the matter thoroughly. We suggested that  $\pi$ -complex formation occurred in the swelling solvent, carbon disulfide. When water was added to hydrolyze the excess aluminum chloride, the lightly crosslinked polymer swollen in the original solvent closed down. This resulted in entrapment of the  $AlCl_3$  complex, essentially as  $AlCl_3$  [15]. Electron microscopy on the bead showed the dispersion of the aluminum and chlorine throughout the bead but did not identify the extent of hydrolysis of the aluminum chloride during the work-up [16].

Because our primary interest was in the preparation of an immobilized benzophenone or acetophenone derivative for study as an energy-transfer donor, we published the concept of the polymer-protected reagent at this stage and returned to the original goal. This culminated in the synthesis of several systems useful as heterogeneous energy transfer donors [17], but none of these was as successful as polymer Rose Bengal. There was substantial industrial interest in the polymer-protected reagent concept, however, and some indica-

TABLE 1. Chemical Dehydration Processes Catalyzed by Polymer Aluminum Chloride

Reagent(s)	Product(s)	Conditions	Yield, %
		60°C, 90 min	90.4
		Reflux, CS <sub>2</sub>	81.4
<i>o</i> -Nitrobenzaldehyde	<i>p</i> -AlCl <sub>3</sub> , acetal, <i>n</i> -BuOH	95°C, 18 h	62

tions that this received attention to protect Ziegler-Natta catalysts of various kinds from environmental degradation.

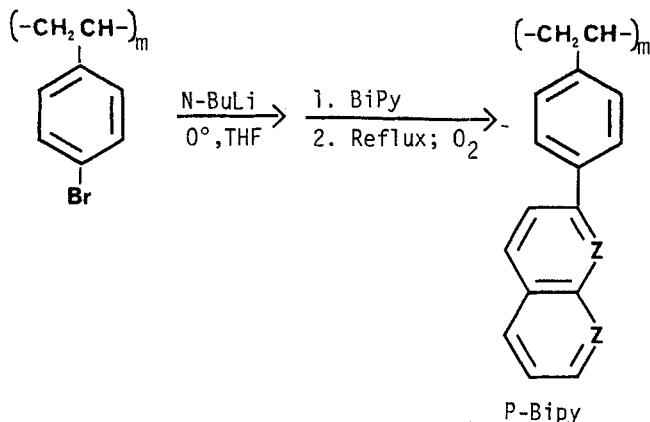
### IMMOBILIZED BIPYRIDINES

Poly-based organo transition-metal catalysts offer several advantages in synthetic and industrial chemistry. Of these, the ease of separation of the catalyst from the desired reaction product(s) and the ease of recovery and reuse of the catalyst are most important. Polystyrene is an excellent support for transition-metal catalysts because one can control the pore size of macroreticular crosslinked polymers with some regularity. This provides some stereoselectivity under appropriate conditions. Such selectivity has been demonstrated in the relative rate of olefin hydrogenation [18] and in the regioselectivity of the hydroformylation process [19] when polymer-supported transition metals are used as catalysts.

At the outset of our work [20], there were a number of examples of ligands immobilized to synthetic polymers from which transition metal catalysts had been made [21]. The problem with all of them was that the complexes were too labile. Leaching of the metal, particularly palladium and rhodium, was far above the acceptable limits for industrial applications. Our

original goal, therefore, was to design a versatile polymer-immobilized chelating agent which would be able to form complexes with a number of metals, but which would also decrease the lability of the metal complex once it was formed. 2,2'-Bipyridine (BiPy) was selected as the chelating ligand most closely fitting these goals.

Bipyridine is attached to the phenyl residues of poly(styrene-*co*-divinylbenzene 2%) by the following series of reactions:



Ring bromination of the polystyrene was controlled such that less than 25% of the aromatic residues were functionalized with bipyridine residues in the resulting polymer which we eventually called P-Bipy.

P-Bipy was virtually a metal-ion "sponge." A wide range of transition-metal complexes could be easily prepared, usually from THF as the solvent by using an organic gegenion, such as acetate or benzoate, to improve solubility. Table 2 indicates the amounts of various metal salts that chelate with P-Bipy in THF.

Obvious color changes, both of the solution and on the polymer surface, took place upon the binding of the metal. The color change can be monitored spectrophotometrically and used to determine the amount of metal bound to the polymer surface.

The factors that determined the amount of metal ion bound to the surface are many. The amount of metal ion incorporated decreases as the initial concentration of the metal in solution decreases. Metal ion incorporation is also a function of solvent. The greater the swelling of the polymer matrix in the solvent, the greater the amount of metal ion incorporated into the polymeric chelating resin. Ethyl acetate turned out to be the best solvent for our purposes, and the amount of iron incorporated was greatest from this solvent.

TABLE 2. Amounts of Various Metal Salts Which Bind to P-Bipy from THF

Metal salt	meq/g bound to P-Bipy
Cr(NO <sub>3</sub> ) <sub>3</sub>	0.22
MnI <sub>2</sub>	0.14
FeCl <sub>2</sub>	0.36
FeCl <sub>3</sub>	0.83
CoCl <sub>2</sub>	0.35
Ni(NO <sub>3</sub> ) <sub>2</sub>	0.70
Pd(OAc) <sub>2</sub>	0.69

One of the potential advantages of the use of polymer-bound chelating metals was the expected decrease in complex lability. P-Bipy does, indeed, form impressively stable metal complexes. For example, when the iron(III) chloride complex was stirred for 48 h with a 100-fold excess of KCN, 39% of the metal remained polymer bound. When the palladium complex was similarly treated for 8 h, 64% of the Pd remained bound to the polymer.

The metal complexes can also be oxidized or reduced while remaining bound to the polymer. Reduction with LAH, for example, produces the Pd(0) complex. The reaction is accompanied by a color change from brown to black and by loss of the infrared stretching frequencies due to the anion, which is generally the acetate. The Pd(0) complex can be reoxidized to Pd(II) either with dilute nitric acid or with ceric ammonium nitrate.

The principal uses described to date for polymer-Bipy-Pd(II) acetate are catalytic. The reduced lability of the complex relative to other palladium species turns out to be an asset. Polymer-Bipy-Pd(II) is a selective hydrogenation catalyst for carbon-carbon multiple bonds under conditions where Pd(OAc)<sub>2</sub> cannot be used since it is reduced to palladium metal. Hydrogenation of simple olefins with polymer-Bipy-Pd(II) occurs readily in THF at room temperature with 1 atm of hydrogen. Plots of total hydrogen consumption were linear with time up to approximately 80% olefin consumption. The relative rates of hydrogenation of several simple olefins are given in Table 3.



TABLE 3. The Relative Rates of Olefin Hydrogenation with P-Bipy-Pd(II)<sup>a</sup>

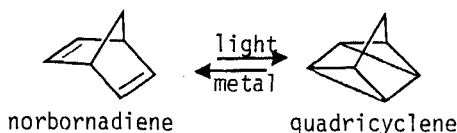
Olefin	Relative rate
2-Methyl-3-buten-2-ol	2.7
1-Octene	2.0
<i>p</i> -1-Propenylanisole	1.3
Cyclohexene	1.0
<i>trans</i> -Stilbene	0.8
Cyclooctene	0.3
Cyclododecene	0.2
Oleic acid	—

<sup>a</sup>100 mg of P-Bipy-Pd(II), 10 mmol olefin, 10 mL dry THF, and 1 atm H<sub>2</sub> at room temperature.

In general, hindered olefins are reduced less readily than less hindered olefins, and very hindered alkenes such as 1-pinene are not reduced at all under the conditions. The rates of reduction are very similar to those reported by Grubbs and Kroll for a polymer-based rhodium catalyst [22]. Olefins with hydrogens on the carbon in the alpha position relative to the double bond undergo a competitive olefin isomerization. Thus the formation of octane from 1-octene was accompanied by the formation of 2-octene. The isomerization reduced the turnover number by almost an order of magnitude. The amount of leaching of metal during the hydrogenation process is dependent on reaction conditions. At room temperature with 1 atm hydrogen, leaching of palladium is in the range of parts per 1000 per hour.

The active catalytic species was shown to be Pd(0) by the following experiment. The isomerization of quadricyclene to norbornadiene is a transition-metal-induced process. Quadricyclene has a high volumetric storage capacity and norbornadiene is relatively inexpensive. Therefore, since quadricyclene can be made from norbornadiene photochemically, this reaction has received some attention in solar-energy storage.

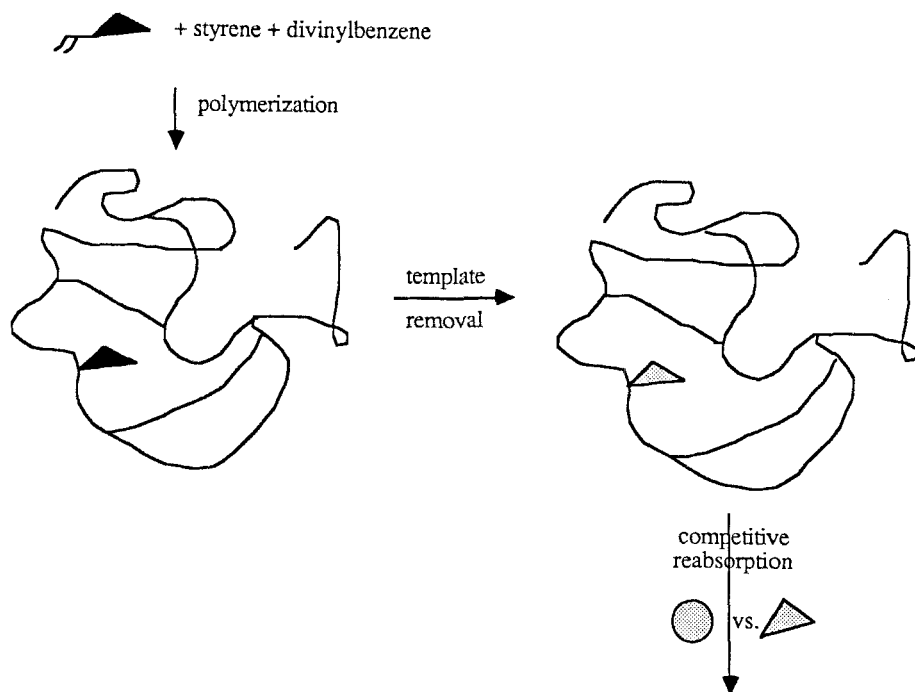
One of the designs most frequently discussed for using these processes in solar-energy conversion requires the development of heterogeneous catalysts



to sensitize the photochemical conversion of norbornadiene to quadricyclene as well as the reverse process, which liberates heat. Though other polymer-bound catalysts are more effective [23], P-Bipy-Pd(II), reduced with LAH to P-Bipy-Pd(0) can also be used to cause this isomerization. The details of this work have been published elsewhere [24] and are summarized as follows: Though the reaction does not follow simple first-order kinetics, we concluded that 1) the rate of isomerization of quadricyclene increases with palladium loading on the polymer; 2) the rate of isomerization depends on the amount of catalyst added; 3) the activity of the catalyst greatly decreases upon reuse; 4) norbornadiene itself poisons the catalyst; and 5) the catalyst cannot be reactivated after several uses with LAH. This means that the catalyst is not being deactivated in an oxidation process. Upon several reuses, however, the catalyst still remains more active than an equal weight of palladium metal supported on charcoal. Perhaps the most important observation pertained to the nature of the catalyst upon treatment with hydrogen at room temperature. P-Bipy-Pd(II) was not active prior to being reduced either with molecular hydrogen or with LAH. Therefore, the active catalyst formed from P-Bipy-Pd(II) must be P-Bipy-Pd(0).

Other uses of polymer-based metal catalysts have also been explored. One of the areas of our work, which has received the most attention, is our use of a polymer matrix to direct the outcome of a subsequent chemical process. Termed by Wulff [25] and by Shea [26] a "template effect" when applied to vinyl polymers, styrene-divinylbenzene copolymers are constructed in such a way so as to make them rigid enough to hold the memory of a small molecule or metal ion after its removal.

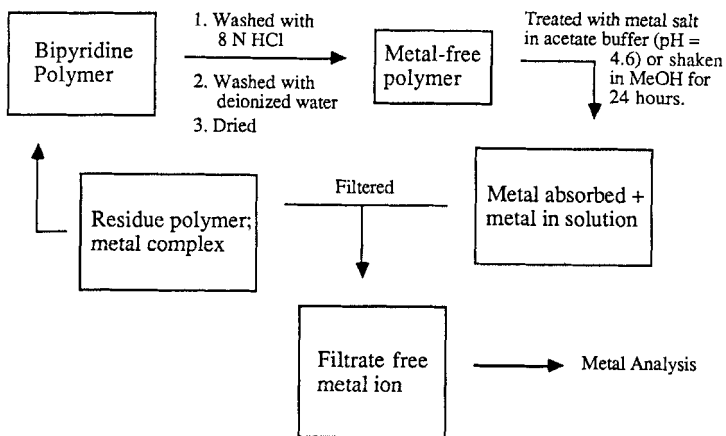
Our first results were published in conjunction with Damen [27-29] and established the principle that a chemical reaction between two template small molecules produced a more significant template effect than did simple reabsorption of the template molecule. As a continuation of this work we synthesized chelating polymers from metal-ion complex templates [30]. It was reasoned that simplicity would facilitate the effect of a template polymer and that the template effect would maximize in the equilibrium process. The idea was to prepare a polymer from a metal-chelated monomer, to remove the metal ion, and to then measure the selectivity of the prepared polymer for the metal ion of the template. Introductory work somewhat along these lines had



been reported by Nishide and Tsuchida [31, 32]. These workers reported that when poly(vinyl pyridine) was chelated to a metal and the polymer was crosslinked, it induced recognition in the derived copolymer.

We chose a bipyridine as a chelating ligand principally because 1) it forms strong complexes with many different metals and 2) some of the chelated complexes have interesting photochemical properties. Our entire analytical scheme is outlined in Scheme 1. This analytical scheme has the advantage of analyzing both for metal absorbed by the polymer and for metal remaining free in solution. Thus a metal-ion balance can be obtained.

As the data in Fig. 1 show in the case of the simple homopolymer, the absorption of copper is greater than the absorption of nickel. This is to be expected because of the higher stability constant for  $\text{Cu}^{2+}/\text{Bipy}$ . In the case of the template polymer, however, nickel ion is more highly absorbed by the polymer than is copper. This demonstrates that there is a degree of specificity to the template effect. Even though the  $\text{Bipy}/\text{Cu}^{2+}$  stability constant is greater than is the  $\text{Bipy}/\text{Ni}^{2+}$  stability constant, templated copolymers absorb more nickel ion. Data for cobalt have been published by Gupta and Neckers [30].



SCHEME 1.

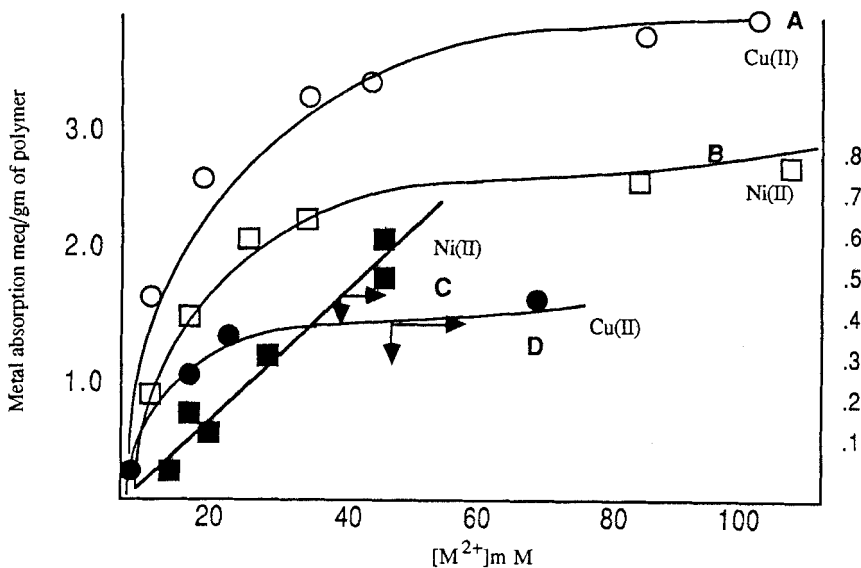


FIG. 1. Absorption of  $Ni^{2+}$  and  $Cu^{2+}$  by  $Ni^{2+}$  template polymers (C, D) (13.9% bipyridine) compared with nontemplate polymer (A, B) [poly(vinyl-bipyridine)]. Acetate buffer, pH 4.6.

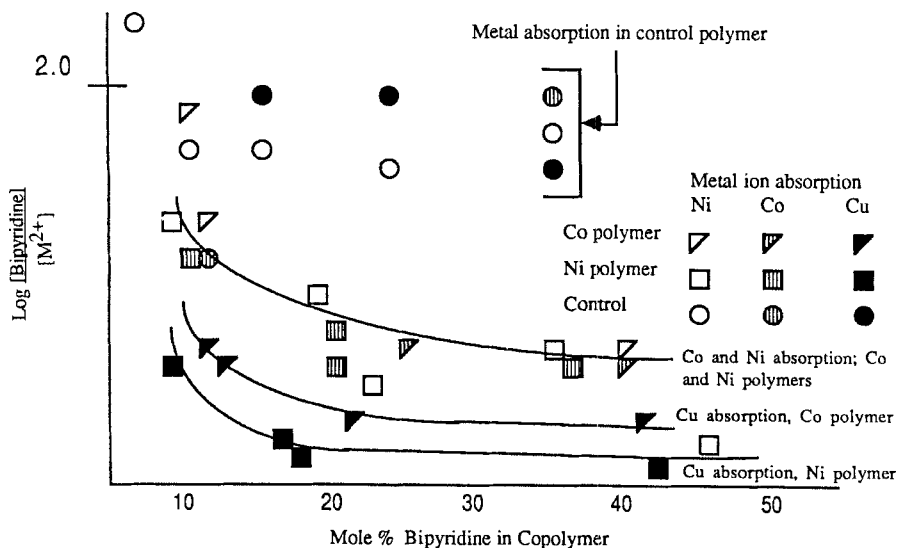


FIG. 2. Absorption capacity of different metal ions in different polymers (solvent: methanol).

Since the wettability of the polymers in water decreases with the divinylbenzene content in the copolymer, the absorption of metal ions from a solvent containing 50% methanol was also measured. As shown in Fig. 2, the absorption of copper, nickel, and cobalt is substantially higher with the templated polymers than with the polymers used as controls, but there is no observed specificity with respect to reabsorption of the template metal ion. Thus, although the overall extent of metal-ion absorption increased in the template polymer over the control (possibly due to enhanced mobility of the polymer chains), the template specificity observed when the metal ion was absorbed from water solution was lost. Thus, it appears that a compromise between wettability and rigidity is required in order to maximize the template effect (Fig. 2).

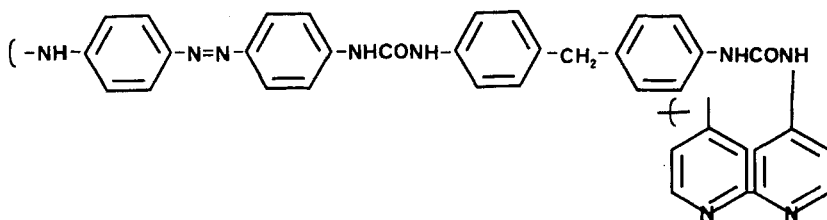
Although a noticeable template effect was observed with 4-methyl-4'vinylbipyridine copolymers in the present context, the effect was not sufficient to be of practical application, at least for  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$ . Perhaps this results from the fact that 4-methyl-4'vinylbipyridine forms all three possible metal complexes,  $\text{ML}$ ,  $\text{ML}_2$ , and  $\text{ML}_3$ , though there is even some doubt about the importance of this in the case of the solid polymer.

### CHELATING COPOLYMERS CONTAINING PHOTSENSITIVE FUNCTIONS

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. The well-studied *cis-trans* photoisomerization of an azobenzene has also been studied with it incorporated in a macromolecule. In particular, several groups have investigated the conformational changes induced by the absorption of a light quantum and the subsequent isomerization process [34-36].

Our work [37] was initiated in an attempt to design an all-or-nothing photoisomerizable metal-ion switch. Our objectives were 1) to prepare various macromolecular ligands by the incorporation of photochromic azobenzene functionalities in the polymeric backbone, in the crosslinks, or as pendant groups; 2) to investigate the binding ability of different ligands in the presence of the 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 the metal ions on the isomerization process.

The polymers chosen for study were diaminobipyridine-based azoaromatic polyureas. Polymerizations were stopped at low molecular weight in order to obtain soluble polymers. The details have been previously published [37]. One example, polyurea terpolymer, called PU-IV, is shown; it combines the chelating agent bipyridine and the azoaromatic moiety in a random array.



PU-IV

The photoisomerization of the polymers could be followed readily by using the absorption maximum of the *trans* compound at 395 nm. The isomerization is reversible, but the thermal reaction is much slower in the normal case than is the photochemical reaction. The steady state after irradiation substantially favors the *trans* compound. In general, the reverse thermal reaction is more conveniently followed by absorption techniques.

As others have observed previously [38], the thermal isomerization of a polymeric azobenzene requires an activation energy ( $E_a$ ) of about 20 kcal/mol in the normal case. The  $E_a$  for polymeric azoaromatics does not vary much from low molecular weight models, even when the azobenzene unit is part of the polymeric backbone. In the polyureas that we studied, all of which differed from PU-IV in the diamine monomer only, the  $E_a$  for the thermal reversion was  $19.0 \pm 0.05$  kcal/mol in every case. However,  $E_a$  for thermal reversion was somewhat higher, being 19.8 kcal/mol the  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  complexes of PU-IV. The invariance of the absorption spectrum in the 400-nm region for the complexes and for the uncomplexed PU-IV indicates that the  $E_a$  increase cannot be the result of changes in the ground-state configuration of the azobenzene function. The increase is instead attributed to the formation of temporary crosslinks via complex formation which alter chain mobility and interchain interactions.

The viscosity of polymer solutions in DMSO also turns out to be a function of the stereochemistry of the azobenzene unit in the polymer backbone. The intrinsic viscosity of PU-IV in DMSO at different concentrations after irradiation is about 40% lower than the corresponding sample kept in the dark. A similar result is observed for the  $\text{Co}^{2+}$  complex. Since the *cis* isomer amounts to about 70% at the photoequilibrium or the photostationary state, the decrease in viscosity upon irradiation in both cases derives from changes in conformation.

Another series of experiments was carried out to follow the change in viscosity of PU-IV solutions upon complexation and the subsequent change after irradiation.

Figure 3 shows that the intrinsic viscosity of PU-IV solution (the polymer had been held entirely in the dark) increases as complexation with either cobalt or nickel ion takes place. If the PU-IV solution is irradiated until the stationary state is formed prior to the addition of the metal salt, there is a much greater viscosity change upon addition of the metal ion.

If PU-IV's are prepared which contain larger quantities of the bipyridine chelating agent and smaller quantities of the azobenzene function, the photo-viscosity effect is even larger, as shown in Fig. 4.

PU-II was synthesized from 5 mmol aminobipyridine, 5 mmol *p*-aminobenzene, and 10 mmol 4,4'-methylenebis(phenylisocyanate). PU-III was prepared from 7.5 mmol aminobipyridine, 2.5 mmol *p*-aminoazobenzene, and 10 mmol 4,4'-methylenebis(phenyl isocyanate).

What this suggests is 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

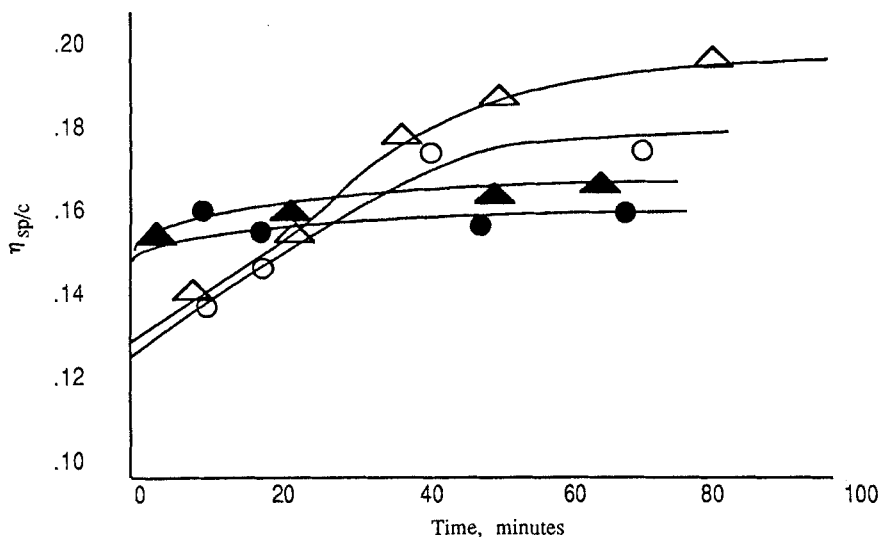


FIG. 3. Change in reduced viscosity of Pu-IV on complexation with  $\text{Co}(\text{OAc})_2$  (0.0001 M) ( $\Delta$ ) and with  $\text{NiOAc}_2$  (0.0001 M) ( $\circ$ ) in the dark ( $\bullet$ ,  $\blacktriangle$ ) and under preirradiation conditions ( $\circ$ ,  $\Delta$ ). Temperature  $30^\circ\text{C}$ .

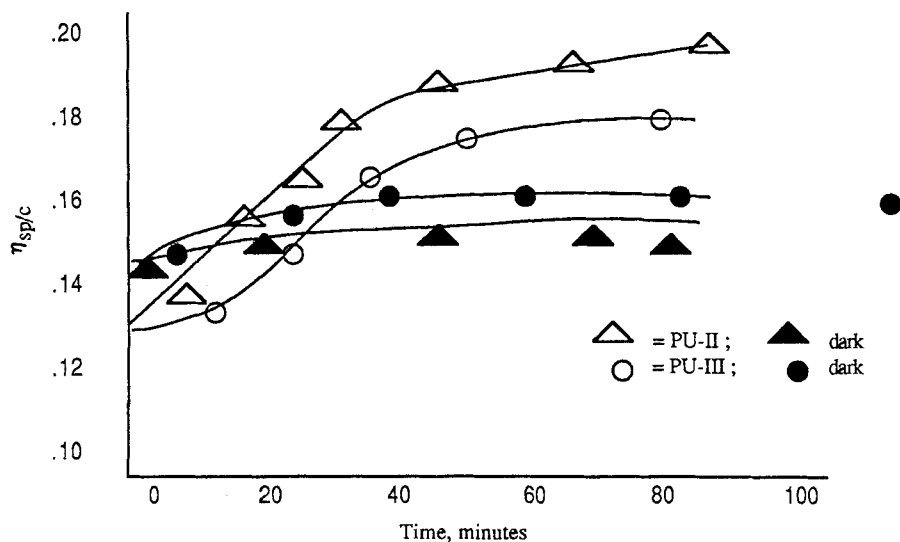


FIG. 4. Progressive change in reduced viscosity of PU-II and PU-III; complexation with cobalt acetate in the dark ( $\blacktriangle$ ,  $\bullet$ ) and under preirradiated conditions ( $\Delta$ ,  $\circ$ ). Solvent: DMSO. Temperature  $30^\circ\text{C}$ .



photostationary state of the azobenzene provides the spatial structure required by the electronic configuration of the metal ion, at least in the majority of conformation sites. The bipyridines of two different polymer chains thus are likely to coordinate to the same metal ion in this new conformation, and this serves to increase the intrinsic viscosity. The higher energies of activation of the metal complexes, the increase in viscosity upon complexation, and enhancement of the viscosity in the preirradiated samples points to the presence of temporary crosslinking by the metal ion.

### OTHER POLYMERS ON WHICH TO SUPPORT METAL IONS

During the last several years, we have reported several other polymers containing bipyridine which can be successfully used as chelating agents and catalysts [39-43]. These polymers are generally soluble condensation polymers based on 4,4'-diaminobipyridine and a diisocyanate. Their synthesis was made possible based on an improved preparative method for 4,4'-diaminobipyridine worked out by K. Zhang [39].

Both hydrogenation systems and condensation reactions requiring metal catalysts were studied with these polymers and some crosslinked analogs. Y. P. Wang has studied these polymeric catalysts by electron microscopy, and this extensive work will be published later [44].

### CONCLUSION

Polymeric reagents involving metal ions and macromolecules have many potential applications and possibilities. Our group has investigated several of these: polymer-protected reagents; immobilized-metal chelates as catalysts; template effects leading to enhanced metal-ion absorption on polymeric surfaces; and photoinduced complexation and decomplexation.

### ACKNOWLEDGMENTS

This paper was presented at the first China-USA-Japan Trilateral Seminar on Macromolecule-Metal Complexes held in Beijing October 20-23, 1985. The author gratefully acknowledges the extensive efforts of the organizing committee, Ying-Yang Jang (Beijing), Eishun Tsuchida (Tokyo), and Yoshi Okamoto (Brooklyn). The support of the National Science Foundation in the form of travel funds is also acknowledged.

This work was supported by the National Science Foundation, Division of Materials Research. The author is grateful for their support. The work would have been impossible without the significant experimental skills and creative input of the following coworkers: Roger Card, S. N. Gupta, Bertus Thijs, Julien Damen, N. Asai, Erich Blosssey, G. W. Green, Dale A. Kooistra, L. M. Turner, G. Sudesh Kumar, Keda Zhang, Yu-Pei Wang, and Patti DePra. The author acknowledges both their skills and recognizes their friendship in dedicating this review to them.

## REFERENCES

- [1] R. B. Merrifield, *Science*, **150**, 178 (1965).
- [2] R. B. Merrifield, *Chem. Eng. News*, pp. 22-26 (August 2, 1971).
- [3] R. B. Merrifield, *J. Am. Chem. Soc.*, **85**, 2149 (1963).
- [4] This synthesis is reported in Ref. 3. The extent to which it was successful is illustrated by the synthesis of Ribonuclease A. See, e.g., B. Gutte and R. B. Merrifield, *J. Biol. Chem.*, **246**, 1922 (1971).
- [5] D. C. Neckers, *Nouv. J. Chim.*, **6**, 645 (1982).
- [6] D. C. Neckers, *Reactive Polym.*, **3**, 277 (1985); J. J. M. Lamberts and D. C. Neckers, *Zeit. f. Naturforsch.*, **39b**, 474 (1984).
- [7] D. C. Neckers, D. A. Kooistra, and G. W. Green, *J. Am. Chem. Soc.*, **94**, 9284 (1972).
- [8] A. I. Vogel, *A Textbook of Practical Organic Chemistry*, Longmans, New York, 1948.
- [9] G. S. Hammond, W. P. Baker, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2795 (1961).
- [10] D. C. Neckers, *Mechanistic Organic Photochemistry*, Reinhold, New York, 1967.
- [11] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowen, R. C. Counsell, V. Vogt, and J. C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).
- [12] G. Ciamician and P. Silber, *Ber.*, **33**, 2911 (1900).
- [13] See, e.g., D. C. Neckers, *Chemtech*, **8**, 108 (1978).
- [14] H. Hirai has published extensively in the area of polymer-protected reagents. See, e.g., H. Hirai, H. Wakabayashi, and M. Komiyama, *Chem. Lett.*, p. 1047 (1983).
- [15] Subsequent papers in the series: D. C. Neckers, E. C. Blosssey, and L. M. Turner, *Tetrahedron Lett.*, p. 1823 (1973); E. C. Blosssey, L. M. Turner, and D. C. Neckers, *J. Org. Chem.*, **40**, 959 (1975).
- [16] D. C. Neckers, E. Su, and T. Su, Unpublished.

- [17] L. Thijs, S. N. Gupta, and D. C. Neckers, *Macromolecules*, **13**, 1037 (1980); N. Asai and D. C. Neckers, *J. Org. Chem.*, **45**, 2903 (1980).
- [18] E. S. Chandrasekaran, R. H. Grubbs, and C. H. Brubaker Jr., *J. Organomet. Chem.*, **120**, 49 (1976) and references cited therein.
- [19] C. U. Pittman and R. M. Hanes, *J. Am. Chem. Soc.*, **98**, 5402 (1976).
- [20] R. J. Card and D. C. Neckers, *Ibid.*, **99**, 7733 (1977); R. J. Card and D. C. Neckers, *Inorg. Chem.*, **17**, 2349 (1978).
- [21] A. J. Moffat, *J. Catal.*, **18**, 193 (1970).
- [22] R. H. Grubbs and L. C. Kroll, *J. Am. Chem. Soc.*, **93**, 3062 (1971).
- [23] R. B. King, E. M. Sweet, and R. M. Hanes, 174th National Meeting of the American Chemical Society, Abstract 41.
- [24] R. J. Card and D. C. Neckers, *J. Org. Chem.*, **43**, 2958 (1978).
- [25] G. Wulff, A. Sarhan, and K. Zabrocki, *Tetrahedron Lett.*, p. 4329 (1970).
- [26] K. J. Shea, *J. Org. Chem.*, **43**, 4253 (1978).
- [27] J. Damen and D. C. Neckers, *J. Am. Chem. Soc.*, **102**, 3265 (1980).
- [28] J. Damen and D. C. Neckers, *J. Org. Chem.*, **45**, 1382 (1980).
- [29] J. Damen and D. C. Neckers, *Tetrahedron Lett.*, p. 1913 (1980).
- [30] S. N. Gupta and D. C. Neckers, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 1609 (1982).
- [31] H. Nishide and E. Tsuchida, *Makromol. Chem.*, **177**, 2295 (1976).
- [32] H. Nishide, J. Deguchi, and E. Tsuchida, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 3023 (1977).
- [33] D. Tabak and H. Morawetz, *Macromolecules*, **3**, 403 (1970).
- [34] H. S. Blair, H. I. Pague, and J. E. Riordan, *Polymer*, **21**, 1195 (1980).
- [35] M. Irie and W. Schanabel, *Macromolecules*, **14**, 1246 (1981).
- [36] M. Irie and W. Hayashi, *J. Macromol. Sci.-Chem.*, **A13**, 511 (1979).
- [37] G. S. Kumar, P. DePra, K. Zhang, and D. C. Neckers, *Macromolecules*, **17**, 2463 (1984).
- [38] C. Paik and H. Morawetz, *Ibid.*, **5**, 171 (1972).
- [39] K. Zhang and D. C. Neckers, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 3115 (1983).
- [40] K. Zhang, G. S. Kumar, and D. C. Neckers, *Ibid.*, **23**, 1293 (1985).
- [41] K. Zhang, G. S. Kumar, and D. C. Neckers, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1213 (1985).
- [42] Y. P. Yang and D. C. Neckers, *Reactive Polym.*, **3**, 181 (1985).
- [43] Y. P. Yang and D. C. Neckers, *Ibid.*, **3**, 191 (1985).
- [44] Y. P. Yang, C. Heckman, and D. C. Neckers, Unpublished Results.