

Synthesis and Properties of Poly-Schiff Base Containing Bisthiazole Rings

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ABSTRACT: Poly-Schiff base containing bisthiazole rings (TAPDA) has been prepared from terephthalaldehyde and 2,2'-diamino-4,4'-bisthiazole. It was found that the TAPDA polymer film is permeable to H₂, O₂, and N₂ and can be converted into an electrical conductor by pyrolysis at high temperature in nitrogen. TAPDA is a novel chelate polymer. The complex of Cu(II) with TAPDA was readily obtained; and the noble metal ions Au(III), Pt(IV), Pd(II), and Ag(I) can be adsorbed quantitatively by the TAPDA powder. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2309–2315, 1997

INTRODUCTION

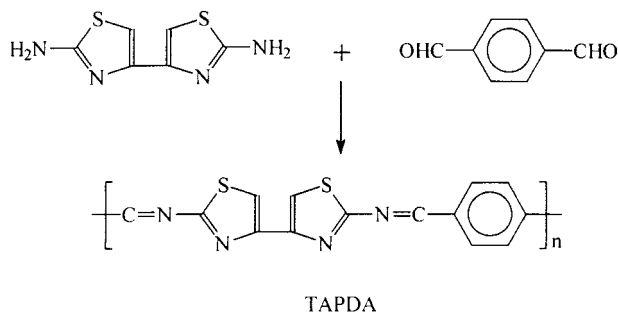
Poly-Schiff bases have been studied for more than 50 years.¹ However, molecular weights of these polymers thus far obtained were too low to make them useful. The product was still a powdery solid and not tough or plastic. Earlier work dealt with heat stability studies on chelates from Schiff bases.^{2–5} Numerous attempts have been made to increase the molecular weights. Now these polymers and their derivatives have been investigated as high-performance polymers for use in ferromagnetic materials,^{6,7} conductors,^{8,9} new composite and photoelectronic materials,¹⁰ potential contrast agents in magnetic resonance imaging,¹¹ and so on.

This article reports the synthesis of a new poly-Schiff base (TAPDA) by solution condensation of terephthalaldehyde with 2,2'-diamino-4,4'-bisthiazole and studies the properties of permeability, conductivity, and metal chelating.

EXPERIMENTAL

Polymer Synthesis

The polymer synthesis is shown in Scheme 1. An equimolar ratio of terephthalaldehyde and 2,2'-



Scheme 1 Polymer synthesis of TAPDA.

diamino-4,4'-bisthiazole at a concentration of 10% solids content in dimethyl sulfoxide (DMSO) was magnetically stirred in a round bottom flask at 80°C. The reaction solution turned homogeneous as the reaction proceeded. After three to four hours, the viscosity of the solution increased. The solution of polymer was filtered and stored in a refrigerator until needed for film casting. Inherent viscosity of 0.23 dL/g for this polymer was measured at a concentration of 0.5 g/dL in DMSO at 30°C.

Film Preparation

The film was prepared by casting the solution of this polymer on a clean and dried glass plate and heated at 80°C for 3 h to evaporate most of the

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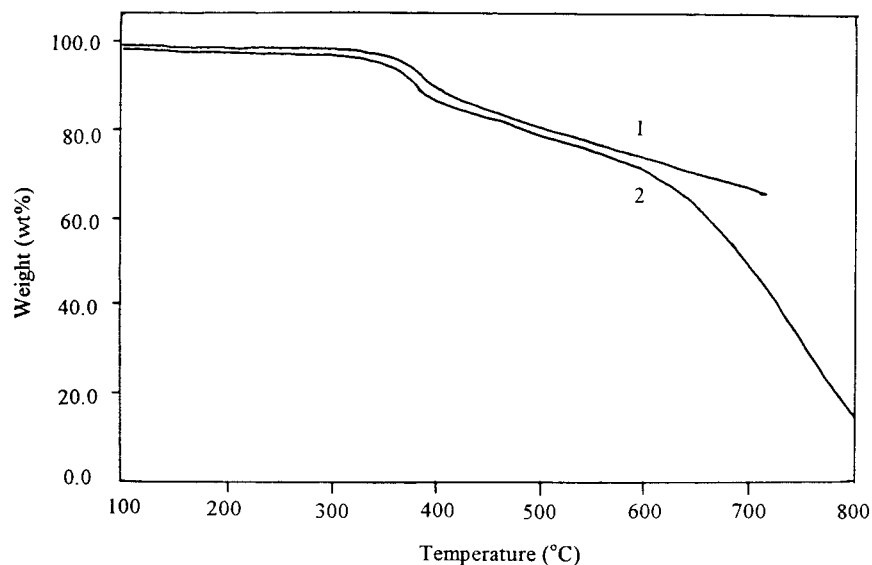


Figure 1 TGA of TAPDA polymer. 20°C/min in N₂ (1) and air (2).

solvent. Then, the plate was placed in an oven and kept at 180°C for 2 h with a slow flow of argon through the oven. After cooling, the film was removed from the glass plate by soaking in water and dried.

Chelation of the Poly-Schiff Base with Cu²⁺ ion

To a stirred DMSO solution of a concentration of 10% poly-Schiff base in a round bottom flask, CuSO₄ solution was added slowly, and stirring was continued at 80°C for 10 h. An olive green precipitate was formed, filtered with suction, and washed with water, then the precipitated chelate was soaked in methanol for 24 h. The chelate then was isolated by filtration and dried over phosphorus pentoxide in vacuum at 60°C for 12 h.

Polymer Characterization

Fourier transform infrared (FTIR) spectra of poly-Schiff base were obtained with a thin TAPDA film on a Perkin-Elmer 1760 FTIR spectrometer. Thermogravimetric analyses (TGAs) were performed on a Perkin-Elmer TGA7 thermogravimetric analyzer at 20°C/min in air or nitrogen. Wide-angle X-ray diffraction (WAXD) was measured using a MXP 18A-HF X-ray diffractometer with a Cu target ($\lambda = 1.5405 \text{ \AA}$). X-ray photoelectron spectroscopy (XPS) data were obtained on a Kratos model ES-300X photoelectron spectrophotometer, excited by Mg X-rays ($E_x = 1235.6 \text{ eV}$). Elemental analysis was performed and is discussed.

Permeability Measurements

The measurement of gas permeability was performed on a K-315N-01 GTR measurement apparatus (RSK Rikaseiki Kogyo Co. Ltd.). The purity of the gases used in the study was at least 99.5%. Permeability was measured at 30°C under 1 atm.

Conductivity Measurements

The conductivity of doped TAPDA and pyrolyzed TAPDA films was measured by a four-probe method using Keithley 196 SYSTEM DMM Digital Multimeter at room temperature.

RESULTS AND DISCUSSION

Polymer Properties

To prepare TAPDA with a high molecular weight, we applied an equimolar ratio of diamine to dialdehyde and paid careful attention to absolutely drying the solvents. The polymer are found to be insoluble in dimethylformamide (DMF), Dimethylacetamide (DMAc), or N-methylpyrrolidone (NMP), etc., except DMSO. The thermal stability of TAPDA polymer appeared fairly good. TGA curves for TAPDA in air and nitrogen are shown in Figure 1. The decomposition temperatures were 356 and 360°C in nitrogen and air, respectively. Moreover, when the temperature was raised to 700°C, the TAPDA still kept more than 60% of its original weight. The rigidity of the re-

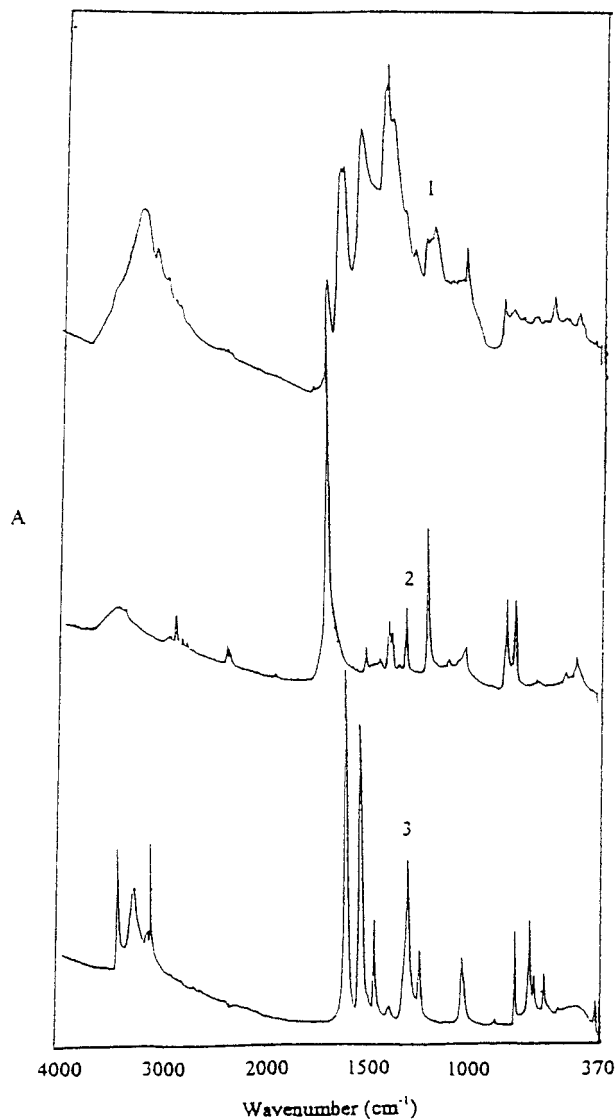


Figure 2 IR spectra of TAPDA polymer (1), terephthalaldehyde (2), and 2,2'-diamino-4,4'-bisthiazole (3).

sulting polymer chains resulted in a very high glass transition temperature (T_g), which is 346°C.

Polymer Characterization

TAPDA film appeared bright red with good light transmittance. An elemental analysis for TAPDA was done. The analysis data for $C_{14}H_6N_4S_2$ are as follows: calcd S, 21.77%; found S, 21.92%. Figure 2 shows the IR spectra of TAPDA polymer, terephthalaldehyde, and 2,2'-diamino-4,4'-bisthiazole. The IR absorption at 1630 cm^{-1} , attributed to the stretching mode of the $-CH=N-$

Table I Permeability and Permselectivity of TAPDA

P_{H_2}	P_{O_2}	P_{N_2}	α_{H_2/N_2}	α_{O_2/N_2}
1.6	0.0631	0.00741	216	8.5

Unit: 1 barrer = $10^{-10} cm^3 (STP) cm/cm^2 s cm Hg$.

group, appeared; a weak band at 1697 cm^{-1} showed aldehyde end groups. These results indicated formation of the TAPDA.

Permeation Property

Gases permeate through a nonporous polymer membrane by a solution diffusion process. The permeability P can be written as the product of solubility S , and the diffusivity of the penetrant in the polymer matrix D , as shown in eq. (1), as follows:^{12,13}

$$P = DS \quad (1)$$

The ideal separation factor α , which is an index of the overall selectivity of a polymer, can be expressed in terms of eq. (2), as follows:

$$\alpha = P(A)/P(B) \quad (2)$$

where $P(A)$ and $P(B)$ are the permeability for gases A and B.

The permeability, diffusivity, and solubility data of TAPDA measured at 30°C under 1 atm for H_2 , O_2 , and N_2 are shown in Tables I–III.

The data revealed that the permeability of the membrane for H_2 , O_2 and N_2 studied here decreased in the following order:

$$P_{H_2} > P_{O_2} > P_{N_2}$$

Though the gas permeability P_{H_2} of the membrane was only 1.6 barres, it is worth noting that

Table II Diffusivity and Diffusivity Selectivity of TAPDA

D_{H_2}	D_{O_2}	D_{N_2}	D_{H_2}/D_{N_2}	D_{O_2}/D_{N_2}
1870	12.7	3.78	497	3.28

Unit: $10^{-10} cm^2/s$.

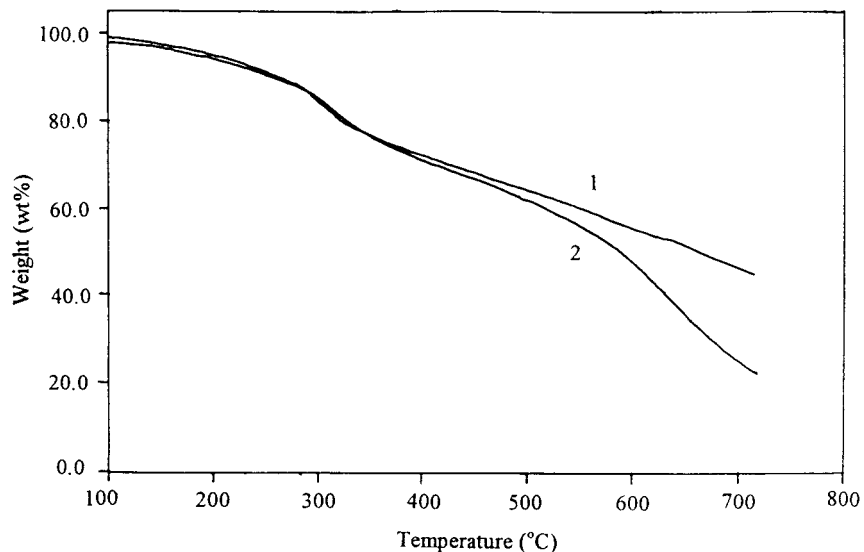


Figure 3 TGA of the complex of Cu(II) with TAPDA. 20°C/min in N₂ (1) and air (2).

its permselectivity $\alpha_{\text{H}_2/\text{N}_2}$ was high and equaled to 216.

Conductivity

The TAPDA polymer is an outstanding insulator with high thermal stability. When TAPDA film was doped by I₂ vapor at room temperature, it

exhibited a color change from bright red to purplish black, and the conductivity increased to 7×10^{-7} s/cm. It has been shown to be a transformation from insulator to semiconductor. Moreover, TAPDA film could be converted into electrical conductor by pyrolysis at high temperature in nitrogen atmosphere. For the pyrolysis method, it has been demonstrated that the transformation

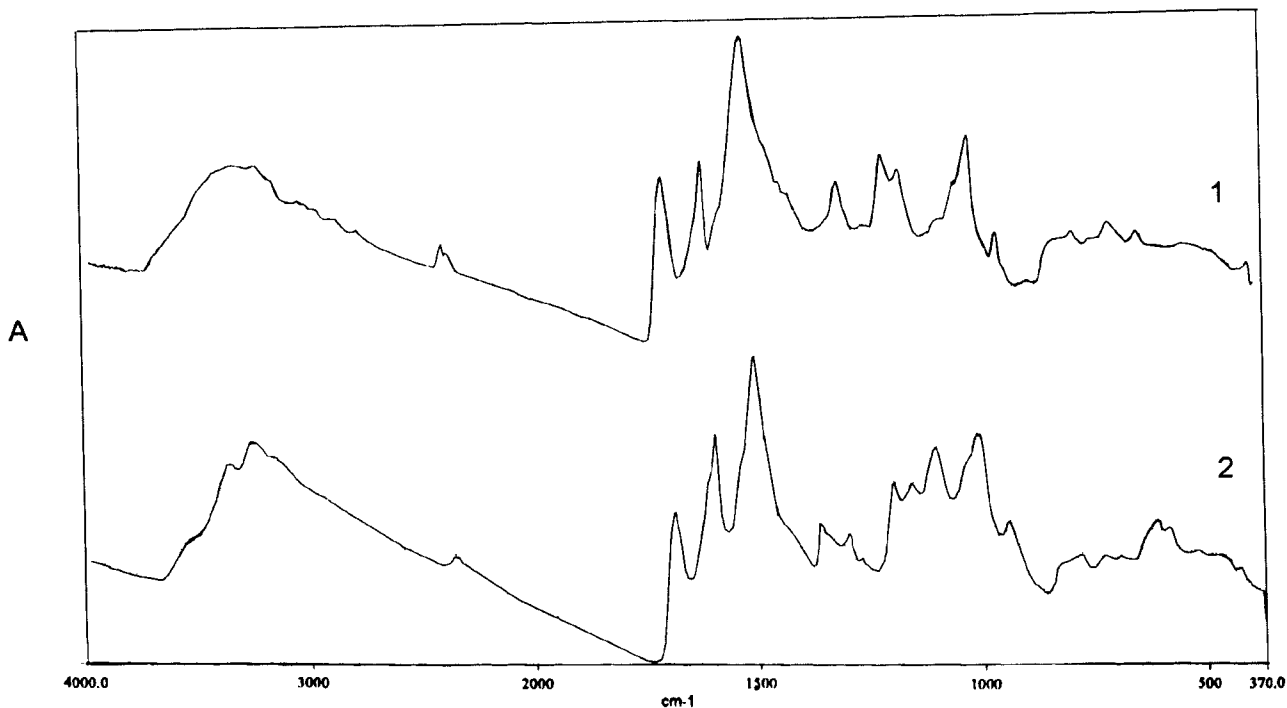


Figure 4 IR spectra of TAPDA (1) and the complex of Cu(II) with TAPDA (2).

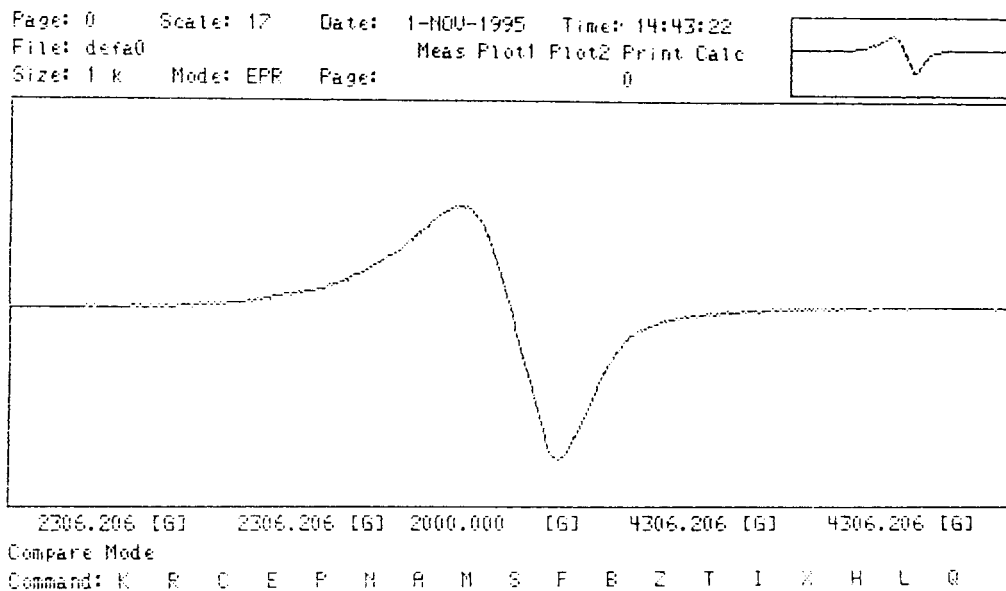


Figure 5 ESR spectrum of the complex of Cu(II) with TAPDA.

from insulator to conductor was due to a structure change; i.e., a graphite-like structure was formed after pyrolysis.¹⁴ Pyrolysis was performed in a tube type electrical oven controlled by a temperature controller. TAPDA film sandwiched between two quartz plates was heat-treated in an oven in nitrogen for 10 min at 1200°C. After pyrolysis, the color of TAPDA film changed to lustrous black. Our experimental results showed that the pyrolysis method is effective in converting insulating TAPDA polymer into a conductor. The room temperature conductivity was as high as 100 s/cm and was very stable in air.

Elemental analysis data for pyrolyzed TAPDA film are done as follows: found C, 89.42%; H, <0.3%; N, 2.15%; and S, 3.87%. It can be seen from the results of WAXD that the position of the peak changes from 4.56 to 4.30 Å. Meanwhile, the shape of the peak shows that the pyrolyzed TAPDA film is still amorphous, which indicates that the three-dimensional structure of pyrolyzed TAPDA film is disordered. Considering both the

results of elemental analysis and WAXD, the pyrolyzed TADPA film possesses aromatic heterocyclic rings, implying that a two-dimensional graphite-like structure was formed.¹⁵

Metal Chelation

The complex of Cu(II) with TAPDA was readily obtained. The thermal stability of the complex was examined using TGA. Figure 3 shows TGA curves for the complex in air and nitrogen. The decomposition temperature was 251 and 243°C in air and nitrogen, respectively; and less than 50% of weight was lost at 550°C. The IR spectra of TAPDA and the complex of Cu(II) with TAPDA are shown in Figure 4. The formation of the complex was also identified by the XPS data in that the $\text{Cu}_{2\text{P}_{3/2}}$ binding energy of this complex decreased from 935.5 to 934.1 eV, while the $\text{N}_{1\text{S}}$ binding energy increased, and the $\text{S}_{2\text{P}}$ binding energy remained unchanged. Figure 5 shows the

Table III Solubility and Solubility Selectivity of TAPDA

S_{H_2}	S_{O_2}	S_{N_2}	$S_{\text{H}_2}/S_{\text{N}_2}$	$S_{\text{O}_2}/S_{\text{N}_2}$
0.882	4.97	1.96	0.45	2.53

Unit: $10^{-3} \text{ cm}^3 \text{ (STP)/cm}^3 \text{ cm Hg}$.

Table IV XPS Data of HAuCl_4 , H_2PtCl_6 , and PdCl_2

XPS (eV)	$\text{Au}_{4\text{f}_{7/2}}$	$\text{Pt}_{4\text{f}_{7/2}}$	$\text{Pd}_{3\text{d}_{5/2}}$
HAuCl_4	87.6	—	—
H_2PtCl_6	—	75.6	—
PdCl_2	—	—	338.3

Table V XPS Data of Protonated TAPDA When AuCl_4^- , PtCl_6^{2-} , or PdCl_3^- Was Adsorbed

XPS (eV)	N_{1s}	S_{2p}	$\text{Au}_{4f_{7/2}}$	$\text{Pt}_{4f_{7/2}}$	$\text{Pd}_{3d_{5/2}}$
Protonated TAPDA	400.15, 398.84	164.78	—	—	—
Au(III) adsorbed	400.07, 399.48	164.61	86.59 85.04	—	—
Pt(IV) adsorbed	400.04, 399.73	164.84	—	72.92	—
Pd(II) adsorbed	400.09, 398.62	166.38	—	—	338.49
	—	164.91	—	—	337.57
	—	163.31	—	—	—

electron spin resonance (ESR) spectrum of the complex. It is confirmed that the complex was formed by Cu^{2+} with the TAPDA Schiff base.

Chelating Resin

The TAPDA Schiff base may become a novel chelating resin because of the sulfur and nitrogen atoms contained in the polymer chain. Experimental results showed that noble metal ions Au(III), Pt(IV), Pd(II), and Ag(I) could be adsorbed quantitatively by the TAPDA Schiff Base powder over a specific acidity range. The maximum adsorption capacity of TAPDA powder for Au(III), Pt(IV), and Pd(II) was 454, 468, and 527 mg/g-resin in 2 mol/L HCl solution, respectively, and 2.85 mmol/g-resin in 1 mol/L HNO_3 solution for Ag(I). Ag(I), Au(III), and Pt(IV) adsorbed on the resin could be easily and quantitatively eluted by 15% ammonia aqueous solution and 2–5% thiourea aqueous solution, respectively.

The adsorption mechanism of Au(III), Pt(IV), or Pd(II) adsorbed on the resin was studied by XPS. XPS data of HAuCl_4 , H_2PtCl_6 , PdCl_2 , and protonated TAPDA with AuCl_4^- , PtCl_6^{2-} , or PdCl_3^- are given in Tables IV and V, respectively.

It was found that the binding energy of $\text{Au}_{4f_{7/2}}$ decreased to 86.59 and 85.04, whereas the binding energy of N_{1s} increased, and the binding energy of S_{2p} was unchanged. This suggested that Au(III) was adsorbed on the nitrogen of the bisthiazole rings and in a chelation reaction. In the same way, the adsorption mechanism of Pt(IV) is the same as that of Au(III). On the other hand, Pd(II) was adsorbed on the sulfur of the bisthiazole rings.

CONCLUSIONS

Poly-Schiff base containing bisthiazole rings (TAPDA) with a high molecular weight was prepared. It was found that TAPDA polymer film has permeability for three gases. Though the gas permeability P_{H_2} of the membrane was only 1.6 barres, it is worth noting that its permselectivity $\alpha_{\text{H}_2/\text{N}_2}$ was high.

TAPDA film could be converted into an electrical conductor by pyrolysis at 1200°C in nitrogen atmosphere. Room temperature conductivity was as high as 100 s/cm. TAPDA, containing bisthiazole rings in the polymer chain, was a novel chelate polymer. The complex of Cu(II) with TAPDA was readily obtained; and the noble metal ions Au(III), Pt(IV), Pd(II), and Ag(I) could be adsorbed quantitatively by the TAPDA Schiff base powder.

REFERENCES

1. M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).
2. C. S. Marvel and N. Tarkoy, *J. Am. Chem. Soc.*, **76**, 6000 (1957).
3. C. S. Marvel and N. Tarkoy, *J. Am. Chem. Soc.*, **80**, 832 (1958).
4. C. S. Marvel and N. Tarkoy, *J. Am. Chem. Soc.*, **81**, 2668 (1959).
5. H. A. Coodwin and J. C. Bailar Jr., *J. Am. Chem. Soc.*, **83**, 2467 (1961).
6. N. Nishide, N. Yoshioka, and E. Tsuchida, *J. Polym. Sci. A, Polym. Chem.*, **27**, 479 (1989).
7. Osaka Gass Co. Ltd., Jpn. Pat. Kokai Tokkyo Koho JP 01/118515, 1989.
8. N. Herbert, G. Rudolf, and M. Thomas, Ger. Offen. DE Pat. 4,218,766, 1992.

9. I. M. Brown, D. J. Leopold, S. Mohite, and T. C. Sandreczki, *Synth. Met.*, **72**, 269 (1995).
10. N. Ogata, *Pure Appl. Chem.*, **63**, 951 (1991).
11. O. Kocian, K. W. Chiu, R. Demeure, B. Gallez, C. J. Jones, and J. R. Thornback, *J. Chem. Soc., Perkin Trans. I*, **5**, 527 (1994).
12. R. T. Chern, W. J. Koros, H. B. Hopfenberg, and V. T. Stannett, Material Selection for Membrane Based Gas Separation, in D. R. Lloyd (Ed). *Material Science Of Synthetic Polymeric Membranes ACS Symposium Ser. 269*, American Chemical Society, Washington, D.C., 1985, Chap. 2, p. 25.
13. W. J. Koros, G. K. Fleming, S. M. Jordan, T. H. Kim, and H. H. Hoehn, *Prog. Polym. Sci.*, **13**, 339 (1988).
14. S. D. Bruck, *Polymer*, **6**, 319 (1965).
15. M. Murakami, K. Watanabe, and S. Yoshimura, *Appl. Phys. Lett.*, **48**, 1594 (1986).