Macromolecules 1991, 24, 5203-5207

Synthesis and Characterization of Coordination Polymers of Poly(butanethiooxamide) with Co(II), Ni(II), and Cu(II) Salts

Milind Khandwe, Anjali Bajpai, and U. D. N. Bajpai*

Department of Postgraduate Studies and Research in Chemistry, Rani Durgavati University, Jabalpur 482 001, India

Received May 1, 1990; Revised Manuscript Received February 26, 1991

ABSTRACT: Poly(butanethiooxamide) has been synthesized by condensation of dithiooxamide and 1,4-diaminobutane. Its complexes have been prepared with Co(II), Ni(II), and Cu(II) salts. The complexes were characterized by elemental analyses, IR spectra, and thermogravimetric analyses and have been proposed to have an aromatized coordination structure. dc conductivity of the coordination polymers shows them to be electrically conductive, in comparison to the uncoordinated polymer. Thermal stability data of coordination polymers have been discussed. It shows an entirely different behavior from the degradation pattern of the ligand.

Coordination polymers have shown very interesting results in the field of development of semiconductors,[1] catalysts,[2] and heat-resistant materials.[3] Dithiooxamide and its N,N′-disubstituted products form coordination polymers with various metal ions.[4,5] Analytical applications and investigation of semiconducting properties of these materials are also known.[6-8] The molecular weight data are not available due to intractability of these materials. However, in most of the cases of Ni(II) complexes, low molecular weight polymers are formed.[9]

In our laboratory, we are studying the coordination polymers of various ligands containing S and N with transition metal ions,[10,11] with a view to obtain a new material having specific properties like good thermal stability, semiconductivity, or conductivity. Dithiooxamide–Cu(II) multilayer thin films have been used as photosensitizers.[12] This has motivated us to choose dithiooxamide and its derivatives for our present studies. In the present paper, we report the synthesis of the ligand poly(butanethiooxamide), abbreviated as PBTO, by the reaction of dithioxamide and 1,4-diaminobutane. The coordination polymers of this ligand were prepared with acetates and chlorides of Co(II), Ni(II), and Cu(II). Characterization of the new materials was done with the purpose of proposing the structure and determining their specific application as a thermally stable material and/or a conducting material.

Experimental Section

Preparation of Ligand. Poly(butanethiooxamide) was prepared by a known method[13] (eq 1). An ethanolic solution of

$$n\mathrm{H_2NCSCSNH_2} + n\mathrm{H_2N(CH_2)_4NH_2} \rightarrow \mathrm{NH_2\{(CH_2)_4NHCSCSNH\}H} + n\mathrm{NH_3} \quad (1)$$

dithiooxamide and diaminobutane in a 1:1 molar ratio was constantly stirred for 3 h at 50 °C. The original orange of the mixture slowly turned to tan with stirring. A pale yellow polymer precipitated, which was filtered and washed with ethanol. The resulting polymer was soluble in pyridine; therefore, it was purified by dissolving it in pyridine and then reprecipitating it by the addition of ethanol. A calculated amount of ethanol was added to recover only the high molecular weight fractions. By this procedure, only 80% of the dissolved polymer was recovered and the low molecular weight species remained in the solution. The molecular weight of the resulting polymer was on the order of 10^3.

Preparation of Coordination Polymers. Coordination polymers were prepared by using equimolar amounts of the ligand (PBTO) and metal salts, viz., acetates and chlorides of Co(II), Ni(II), and Cu(II). The weight of the repeat unit was considered to be the moles of ligand. The ligand solution in pyridine and the solution of metal salts in a minimum quantity of water were mixed and refluxed at 60 °C with constant stirring. The precipitated coordination polymers were washed several times with water to remove occluded metal salt, if any. Further, the polymers were stirred in 0.1 N $\mathrm{HNO_3}$ and HCl for $^1/_2$ h, and the filtrate was tested for the presence of metal ions. A negative result ensured that the metal salt is not occluded with the coordination polymers. Finally, the polymers were washed with water, pyridine, and acetone and were dried at 70 °C in an oven for 8 h.

Measurements. C, H, and N analyses were carried out with a Carlo-Erba elemental analyzer. The metal contents were determined by decomposing the metal complexes with concentrated $\mathrm{HNO_3}$ and titrating against EDTA.[14] The IR spectra were recorded in the 4000–200-$\mathrm{cm^{-1}}$ range on a Perkin-Elmer spectrophotometer using CsI pellets. Electronic spectra were recorded in the 200–1500-nm range on a Varian–Cary 2390 spectrophotometer. Thermogravimetric analyses were carried out on a Perkin-Elmer thermal analyzer in air at a heating rate of 15 °C/min.

The measurement of conductivity was made under dust-free and nonhumid atmosphere. For measuring the conductivity, the samples were powdered and filled in the die and were kept under high vacuum. Then the die was pressed using a Carver laboratory press, applying 8 tons of pressure for 2 min. The room temperature (22 ± 2 °C) conductivity was obtained by pressing the pellets in silver-coated copper plates and applying a constant disk potential for 3 V across the sample. The time of electrification was about 40–50 s. (No change in current was observed when the voltage was applied continuously for 20 min.) Current measurements were made indirectly on a biopotentiostat (electrochemical processor) supplied by Applied Photo Physics, U.K.

Results and Discussion

PBTO, obtained by the procedure mentioned above, was a pale yellow solid, insoluble in common organic solvents and soluble in pyridine. All the coordination polymers were intense colored solid materials, which decompose before melting. Co(II) complexes are dark brown, Ni(II) complexes are dark red, and Cu(II) complexes are dark green solid materials. All the coordination polymers are insoluble in common organic solvents. The determination of molecular weight and molecular weight distribution is not possible due to the insoluble and nonfusable nature of the coordination polymers.

Elemental Analyses. Results of elemental analysis (Table I) show correspondence between observed and calculated values for a 1:1 metal-to-ligand mole ratio. Slight

0024-9297/91/2224-5203$02.50/0

Table I
Elemental Analysis[a]

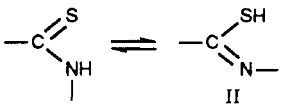
	elem anal.: found (calcd), %			
	C	H	N	M
PBTO(L)	41.24 (41.27)	5.98 (5.74)	16.99 (16.09)	
LCo(A)	29.15 (31.12)	4.02 (3.46)	13.05 (12.14)	23.74 (25.41)
LCo(B)	29.26 (31.12)	4.05 (3.46)	12.67 (12.14)	23.93 (25.41)
LNi(A)	31.24 (31.18)	4.14 (3.44)	13.78 (12.12)	26.16 (25.50)
LNi(B)	31.33 (31.18)	4.15 (3.44)	13.96 (12.12)	25.34 (25.50)
LCu(A)	29.50 (30.52)	3.70 (3.39)	13.01 (11.88)	24.79 (26.96)
LCu(B)	29.65 (30.52)	3.71 (3.39)	12.74 (11.88)	26.36 (26.96)

[a] M = Co, Ni, and Cu. (A) and (B) are used to denote complexes prepared with the acetate and chloride salts of the metal, respectively.

deviation may be due to the polymeric nature of the complexes, as the values of end groups are not taken into account for theoretical calculations. Further, the exact amount of coordinated/lattice water molecules could not be determined,[9] and the possibility of some unreacted repeat units exists as the reactivity of the segment toward coordination may decrease after precipitation. The complexes were found to be nonelectrolytic in nature; hence, for estimation of chlorine, Steponov's method[15] was followed. The complexes prepared with metal chlorides were treated with sodium metal and ethanol to extract chlorine as soluble sodium chloride, but the qualitative tests indicate absence of chlorine in the complexes. Further the analytical data are also in agreement with the composition, having no chlorine and acetate in the complexes prepared with metal chlorides and acetates, respectively.

Infrared Spectra. Important IR bands and their assignments based on typical bands generally observed for the trans thioamide group[16,17] are given in Table II. The spectrum of the ligand is compared with the spectra of the coordination polymer to elucidate the nature of the coordination. The two bands observed at 1380 and 1350 cm^{-1} in the spectrum of the ligand attributed to ν_{CN} of the thioamide group merge into one intense band at 1360 cm^{-1} on complexation. The bands observed at 1530, 1460, and 1440 cm^{-1} in the spectrum of the ligand have a mixed contribution from δ_{NH} and ν_{CN} of the thioamide groups. In the spectra of the coordination polymers intensity as well as the position of these bands is greatly altered. These observations clearly indicate coordination through the N atom of the ligand. The strong absorption due to ν_{NH} at 3190 cm^{-1} becomes very broad on coordination and it observed at 3400 cm^{-1}. The broadening of this band and shifting toward higher frequency by more than 200 cm^{-1} also support the coordination through N.

The thioamide group exists in tautomeric equilibrium (eq 2). The very strong absorption due to ν_{CS}, at 870 cm^{-1}



I II (2)

in the spectrum of the ligand, is observed between 870 and 890 cm^{-1} as a week absorption band in the spectra of the complexes, which indicates a decreased double-bond character of the C–S bond and an increased contribution of structure II in the coordination polymers. On the basis of this observation, a salt linkage with sulfur is suggested in the complexes under study and an S,N-chelated structure has been proposed (Figure 1). The appearance of a weak absorption band between 500 and 350 cm^{-1}, characteristic of the chelate ring deformation vibration,[9] supports a five-membered chelate ring, as has been proposed in Figure 1. The stretching vibrations due to metal–chloride and metal–oxygen bonds appear in the far-IR spectra of inorganic and coordination compounds.[18,19] ν_{CuCl} gives rise to two absorption bands in the 260–290-cm^{-1} region. Absorption due to ν_{NiCl} appears around 290 cm^{-1}, and that due to ν_{CoCl} appears as two bands around 290–301 cm^{-1}. The bands[18] due to ν_{MCl} are not observed in the far-IR spectra of the complexes under present investigation. An acetate group shows absorption due to a carbonyl group as well as metal–oxygen[19] bonds, when coordinated to a metal atom, which are not observed in the coordination polymers. Further, the IR spectra of coordination polymers prepared with different salts of a metal are similar. These observations suggest that anions are not present in the coordination polymers.

On comparison with the ligand spectrum, the IR bands of the coordination polymers are quite broad and a new band of weak intensity due to C=C is also observed near 1000 cm^{-1}. This is indicative of considerable electron delocalization within the five-membered chelate ring.

Electronic Spectra. Since the coordination polymers are insoluble in common organic solvents, the electronic spectra were recorded in the solid state. The electronic spectra show very broad bands. In polymeric complexes of dithiooxamide, the electronic spectra do not give any clear idea about the geometry of ligand molecules around metal ions. Hofmans, Desseyn, and Herman[9] have made an attempt to explain electronic transitions, assuming a planar and octahedral configuration about the nickel atom in its dithiooxamide complexes. Menabue, Pellacani, and Peyronel[5] have explained Ni(II) complexes of dithiooxamide and its N,N′-disubstituted derivatives to contain square-planar and octahedral symmetry, but no clear-cut conclusion was given, as the characteristic band at 1000 nm was not observed. However, the Co(II) complexes were reported to have an octahedral coordination.[5]

The electronic spectra for coordination polymers prepared with cobalt and nickel acetates are shown in Figure 2. The bands observed between 260 and 370 nm in all the coordination polymers are very peculiar. Hofmans, Desseyn, and Herman[9] suggested that $\pi \rightarrow \pi^*$ bands observed in the 300–330-nm region indicate the high conjugation over the carbon–carbon bonds. On the basis of IR and electronic spectral studies, we have proposed a five-membered chelate ring structure (Figure 3) for the coordination polymers and suggested considerable electron delocalization within the ring. The $\pi \rightarrow \pi^*$ transition observed in electronic spectra further supports our conclusion. It is further suggested that this type of delocalization enhances the covalent character of metal–sulfur and metal–nitrogen bonds, and the five-membered ring acquires aromatic character. Because of this increased covalent character and aromatized structure, the geometry around the metal ion becomes difficult to predict. This is in accordance with the observed facts.

In the nickel complexes a very broad band is observed between 400 and 640 nm with λ_{max} at 500 nm. The broadness of this band indicates superimposition of different bands. It may be assigned to the charge-transfer transition or superimposition of the band at 500 nm due to a $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition and at 610 nm due to a $^3A_{2g} \rightarrow {}^3T_{1g}$ (F)

Table II
IR Spectra[a]

PBTO(L)	LCo(A)	LCo(B)	LNi(A)	LNi(B)	LCu(A)	LCU(B)	assignments
3190 vs	3400 vb	3400 vb	3400 vb	3400 vb	3400 vb	3400 vb	ν_{NH} or ν_{OH}
2940 m	2940 m	2940 m	2940 m	2940 m	2940 m	2940 m	ν_{CH}
2880 m	2880 m	2880 m	2880 m	2880 m	2880 m	2880 m	
1630 w	1630 m	1630 m	1630 m	1630 m	1630 m	1630 m	δ_{NH} or δ_{OH}
1530 vs	1520 b	1520 b	1530 b	1530 b	1520 b	1510 b	ν_{CN}
1460 m	1440 m	1440 m	1440 m	1450 m	1440 m	1440 m	NCS group vibration
1440 m							
1100 m	1130 m	1120 m	1120 m	1130 m	1120 m	1120 m	NCS group vibration
870 m	880 w	890 w	880 w	880 w	870 w	870 w	$\nu_{C=S}$
	450 w	450 w	460 w	400 w	500 w	340 w	chelate ring vibrations
	390 w	390 w			340 w		

[a] (A) and (B) are used to denote complexes with the acetate and chloride salts of the metal, respectively.

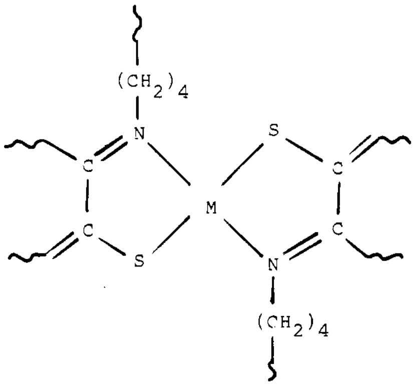


Figure 1. Proposed coordination structure where M = Co, Ni, and Cu.

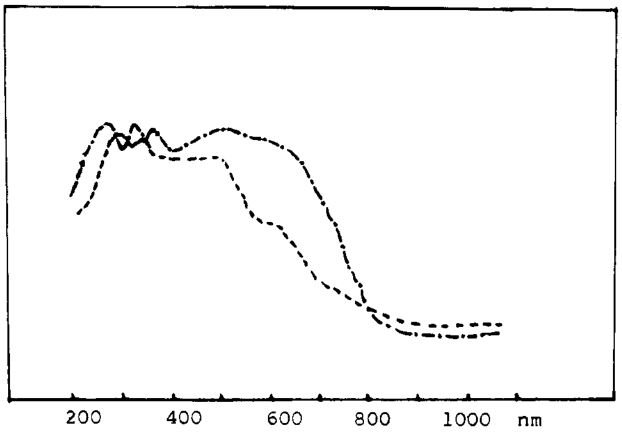


Figure 2. Electronic spectra of coordination polymers prepared with (- - -) copper acetate and (– • –) nickel acetate.

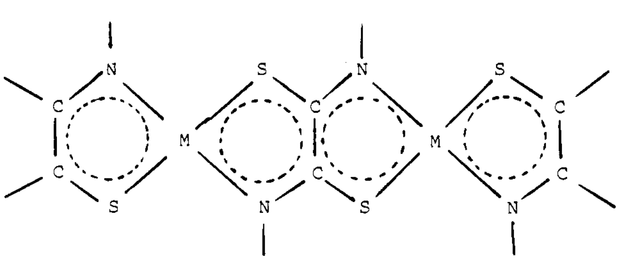


Figure 3. Aromatized structure of the metal cross-link.

transition of the octahedral field. However, the very characteristic band of an octahedral geometry around 1000 nm due to $^3A_{2g} \rightarrow {}^1T_{2g}$ transition is not present.

The brown of the cobalt coordination polymers is suggestive of the octahedral geometry, which is further confirmed by the appearance of bands at 480 and 610 nm assigned for $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1T_{2g}$ transitions,[5] respectively. The spectra of copper complexes contain $\pi \rightarrow \pi^*$ transitions, and no band is observed in the visible region. The behavior of copper complexes can be explained on the basis of Cu–Cu interaction as proposed by Kanda et al.[8] The complexes were found to be diamagnetic, and the geometry was considered as square planar.

Electrical Conductivity. The conductance of the material is measured in terms of its conductivity. When the electrical conductivity (dc) is measured for polymeric materials, in pellatized form, two possible factors give error in the results. The first factor may be due to contact resistance. Because of the possible air gap between the electrode and the material, the pressure applied to press the pellet between the electrodes may not be the same.[20] The second factor involves material packing, which may differ due to a difference in particle size and crystal structure. These errors are significant for the measurement of electronic conductivity of a single material, and results may differ, if different measurement setups are used. In the present study we have taken extreme precautions to avoid the possible errors in measurements. The conductivity data were obtained under exactly identical conditions, using the same setup and same procedure.

The conductivity of a Co(II) coordination polymer was found to be $1.13 \times 10^{-12}\ \Omega^{-1}\ cm^{-1}$, that of the Ni(II) complex was found to be $8.84 \times 10^{-12}\ \Omega^{-1}\ cm^{-1}$, and that of the Cu(II) complex was found to be $9.04 \times 10^{-12}\ \Omega^{-1}\ cm^{-1}$. Although, the values are low, but still significant, when compared to that of the ligand, which is an insulating material. An N,N′-disubstituted dithiooxamidocopper(II) polymer[21] also showed conductivity (electronic and protonic) in this range. The complexes were prepared by using different salts of the metal (chloride and acetate); the electrical conductivities of a coordination polymer prepared with different metal salts were found to be similar. Further, it has been observed that the structure of the ligand has no specific features, such as conjugated double bonds, necessary for conduction. The conductivities of the coordination polymers further support the delocalization of electrons over a macromolecule. It has been observed[22] that π electron delocalization profoundly influences the electrical conductivity; the electron–electron interactions are important for long-range electron delocalization and thus for the electrical conductivity in polymers. If we compare our observation with the electrical conductivity of polyacetylene,[23] we find that the polyacetylene is not a conducting material still possessing a conjugated structure, but after doping with iodine or other dopant, it behaves as a metallic conductor. The reason given for the nonconducting (intrinsic) nature of polyacetylene is that it has a delocalization path[22] of 100 Å due to structural defects. Structural defects are possible in the coordination polymers, but in the present studies

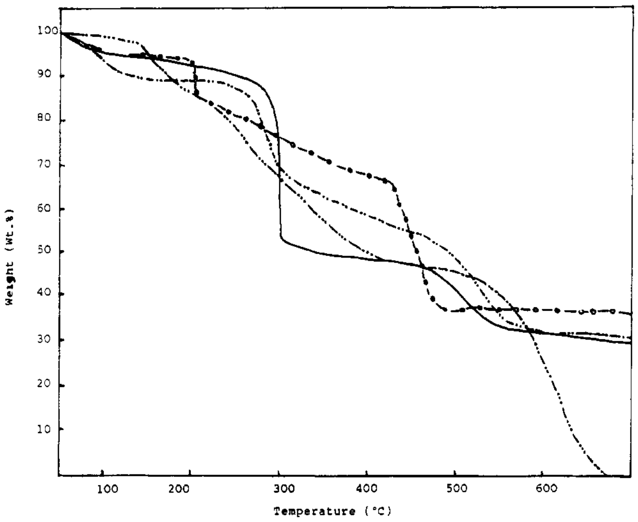


Figure 4. Thermogravimetric analysis curves: (–···–) Co complex; (—) Ni complex; (–o–) Cu complex; (–····–) ligand.

it shows that the intrinsic conductivity therefore supports the structure shown in Figure 3. The observed conductivity can be explained on the basis of the aromatized structure (Figure 3).

The macromolecules designated as rubiconjugated very probably contain limited interrupted conjugation. Rubiconjugated polymers[24] generally show conductivity on the order of 10^{-15}–10^{-10} Ω^{-1} cm^{-1}. The macromolecules designated as ekaconjugated, however, are known to contain extended planar nets of aromatized residues. The proposed coordination structure resembles that of ekaconjugated polymers[24] but does not show conductivity in the expected range of 10^{-9}–10^{-4} cm^{-1}. The above observation can be explained on the basis of the fact that molecular structure may not be as pure as the probability of structural defects due to partly reacted segments; intermolecular or intramolecular coordination still persists.[2] Further, in the present case hydrocarbon chains were introduced in the macromolecules to impart flexibility; however, due to the network structure, flexibility is limited. Since the hydrocarbon chains are not conjugated, the macromolecule is ekaconjugated only in the direction of metal cross-links and only this part of network is responsible for conduction.

Although the difference in conductivities of Cu(II), Ni(II), and Co(II) may not be significant, but in such a low conductivity range, these small differences also become quite significant. The order of the conductivity was found to be Cu > Ni > Co.

Thermal Analysis. The TGA of the ligand and its coordination polymers are shown in Figure 4. Since the degradation patterns for the coordination polymers prepared with different anions are almost similar, we have shown the TG curves for the coordination polymers prepared with metal acetates in Figure 4. Degradation of the ligand is observed in two steps while the coordination polymers degrade in more than three steps. All the coordination polymers show an initial weight loss between 50 and 100 °C. Co(II)-coordinated polymers show about 9% and Ni(II)- and Cu(II)-coordinated polymers about 4% weight loss in this temperature range. The results presented in elemental analysis and TG analysis suggest that it is inappropriate to regard a water molecule as the third component of the coordination polymers besides a metal ion and a ligand unit. The weight loss in this temperature range can be attributed to the loss of adsorbed gases or moisture and not due to the degradation of the coordination polymers.[17] However, cobalt polymer may contain two water molecules per unit. The IR spectra show the presence of the coordinated or lattice water in these polymers. It may possibly be due to different geometries of the repeat units in the macromolecule, and water may be present in the units with octahedral geometry. Hofmans et al.[9] were unsuccessful to determine the number of water molecules present in a polymeric dithiooxamidonickel(II) complex by thermal analysis, as the complexes started to decompose, releasing CO_2 by the reaction of the ligand with water molecules at about 120 °C. The Co(II) and Ni(II) coordination polymers show a high rate of weight loss at about 270 °C, whereas in Cu(II)-coordinated polymers the high rate of weight loss is observed between 200 and 400 °C. This steep change in weight can be considered for the release of CO_2 and other gaseous products, leading to the structural changes and decomposition of the polymers. The dithiooxamidonickel(II) polymer was found to have linear chains,[9] whereas in the present study we have proposed a network structure (Figures 1 and 3) for the coordination polymers. In comparison to polymeric dithiooxamidonickel(II), the PBTO complexes of Ni(II) start degrading at higher temperature. This observation indicates that, due to network structure, the thermal stability of the coordination polymers under study has been increased. Further, the aromatized ring structure may also be responsible for the increased thermal stability. The order of stability for the different coordination polymers was found to be as Ni > Co > Cu, which is in accordance with spectrochemical series.

Conclusion

Polymeric dithiooxamide ligands have been employed for the first time to synthesize coordination polymers. The molecular weight of the coordination polymer could not be determined due to their insoluble nature. The ligand coordinates through both with sulfur and nitrogen, and a five-membered chelate ring structure is formed. An aromatized ring structure is concluded by IR and UV–vis spectral studies. This aromatized ring structure is further supported by the electrical conductivity exhibited by the coordination polymers. The greater thermal stability of the PBTO–Ni(II) coordination polymers than the dithiooxamidonickel(II) polymer[9] further confirms that the coordination polymers in the present study have a network structure with the presence of a metal in an aromatized ring. Polymeric dithiooxamide ligands may be used to scavenge metal ions from the industrial effluents.

Acknowledgment. We are thankful to the Indian Space Research Organisation, Department of Space, Government of India, for financial assistance under the RESPOND Programme.

References and Notes

(1) Balto, B. A. *Organic Semiconducting Polymers*; Katon, J. E. *Ed.*; Marcel Dekker Inc.: New York, 1968; p 199.
(2) Kaneko, M.; Tsuchida, E. *J. Polym. Sci., Macromol. Rev.* **1981**, *16*, 397.
(3) Bajpai, A. S.; Mishra, D. D.; Bajpai, U. D. N. *J. Macromol. Sci. Chem.* **1983**, *A19* (6), 813.
(4) Pellacani, G. C.; Fabretti, A. C.; Peyronel, G. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 897.
(5) Menabue, L.; Pellacani, G. C.; Peyronel, G. *Inorg. Nucl. Chem. Lett.* **1974**, *10* (2), 187.
(6) Albota, L. A.; Serdyuk, L. S.; Zaverach, M. M. *Zh. Anal. Khim.* **1974**, *29* (3), 590.
(7) Bhowal, S. K. *Anal. Chim. Acta* **1974**, *69* (2), 465.
(8) Kanda, S.; Ito, K.; Nagaito, T. *J. Polym. Sci.* **1967**, *17* (C), 151.

(9) Hofmans, H.; Desseyn, H. O.; Herman, M. A. *Spectrochim. Acta* **1982**, *38A* (II), 1213.
(10) Khandwe, M.; Bajpai, A.; Bajpai, U. D. N. *Polym. Bull.* **1990**, *23*, 51.
(11) Bajpai, A.; Mishra, D. D.; Bajpai, U. D. N. *J. Macromol. Sci. Chem.* **1986**, *A23* (5), 605.
(12) Kanda, S.; Kanezaki, E. *Kenkyu Hokoku–Asahi Garasu Kogyo Gijustu Shoreikai* **1981**, *39*, 27.
(13) Gruber, W. *Makromol. Chem.* **1966**, *92* (2), 87.
(14) Vogel, A. I. *Quantitative Inorganic Analysis*, 3rd ed.; The English Language Book Society and Longmans, Green Co., Ltd.: London, 1961.
(15) Steponov, A. *Ber. Dtsch. Chem. Ges.* **1906**, *31*, 4056.
(16) Desseyn, H. O.; Aarts, A. J.; Herman, M. A. *Spectrochim. Acta* **1980**, *36A*, 59.
(17) Kanda, S.; Suzuki, A.; Ohkawa, K. *Ind. Eng. Chem. Prod. Res. Dev.* **1973**, *12* (9), 88.
(18) Clark, R. J. H.; Dunn, T. M. *J. Chem. Soc.* **1963**, 1198.
(19) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978.
(20) Block, H. *Adv. Polym. Sci.* **1979**, *33*, 93.
(21) Kanda, S.; Yamashita, K.; Ohkawa, K. *Bull. Chem. Soc. Jpn.* **1979**, *52* (II), 3296.
(22) Ulrich, D. R. *Nonlinear Optical and Electroactive Polymers*; Ulrich, D. R., Prasad, P. N., Eds.; Plenum Press: New York, 1988; p 1.
(23) Garnier, F. *World Sci.* **1988**, *26*, 20.
(24) Pohl, H. A. *Organic Semiconducting Polymers*; Katon, J. E., Ed.; Marcel Dekker Inc.: New York, 1968; p 51.

Registry No. PBTO (copolymer), 134847-47-5.