Synthesis of New Polyamidoximes and Their Crosslinking by Transition Metal Ions

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Synopsis

Three new polyamidoximes (PAO) having appropriate functionalities to bind transition metal ions were prepared. The polymers were obtained by the reaction of dichlorooximino ethane with the corresponding diamine. Characterization and crosslinking of PAOs via coordination with transition metal ions such as Ni(II), Co(II), Cu(II), and UO_2(II) are presented. The crosslinked polymer complexes exhibit good thermal stability. It was also found that both square planar and tetrahedral coordination structures are present in the crosslinked polymers.

INTRODUCTION

Metal ions may be chelated to a polymer in several ways.[1] One is the use of an organic molecule possessing a suitable number of functional groups by which coordination with metal ions causes polymerization. Polymerization and copolymerization of metal containing monomers is another method[2] to synthesize corresponding polymers wherein practically all functional groups are bound to the metal. Alternatively, attachment of suitable ligands to preformed polymer as terminal or pendant units would afford a convenient procedure for chain extension or crosslinking by coordination with metal ions.

In this article we report the synthesis and characterization of new polyamidoximes (PAO) having appropriate functionality for subsequent coordination with transition metals which results in crosslinking.

RESULTS AND DISCUSSION

Generally amidoximes cannot be synthesized by the reaction of an amide and hydroxylamine due to the reduced activity of carbonyl group in the amide. One way[3] to synthesize amidoximes is to treat hydroxamic acid chlorides with primary or secondary amines. In this work, three new PAOs have been obtained by the reaction of dichlorodioxymino ether (DDE) with benzidine, trans-4,4′-diaminodibenzo-18-crown-6 (DADC) and with a mixture

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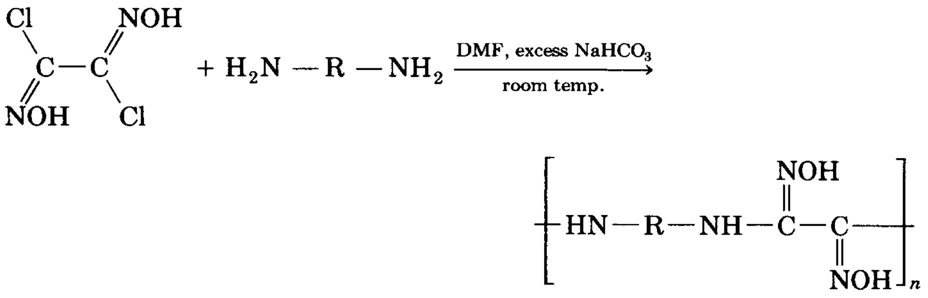
of these amines. The general synthesis reaction may be represented as follows:



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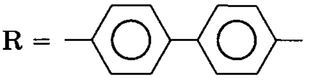
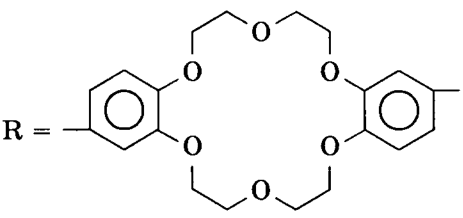
I:(a)



(b)



(c) R = **(a)** and **(b)**

The evolved hydrogen chloride was captured by excess solid $NaHCO_3$ in DMF. $NaHCO_3$ was chosen so as to carry out the reaction under mild conditions. A stronger base such as NaOH would have caused undesired side reactions of DDE. The results of synthesis and characterization data on PAOs are summarized in Table I.

All the polymers were insoluble in water, whereas they dissolved in dilute alkali hydroxide solutions due to the weak acidic character of the oxime groups. They were also soluble in organic solvents such as DMF and DMSO. The DSC thermogram of **Ia** and **Ib** are shown in Figure 1. DSC curves show that these polymers begin to fuse at about 250°C with a sharp exotherm which may be due to decomposition. The polymers were characterized by infrared spectra on KBr discs. As shown in Figure 2 the main absorptions appear at 3110–3400 cm^{-1} (NH and NOH stretching), 1640 cm^{-1} (CN stretching), 1600 cm^{-1} (NH bending), 1500 cm^{-1} (benzene ring), and 930 cm^{-1} (NO stretching). The spectrum of **Ia** exhibits characteristic absorptions due to the *p*-disubstituted benzene ring at 1270 cm^{-1}. **Ib** shows additional absorptions at 2850–2910 cm^{-1} (CH aliphatic stretching) and 1120 and 1230 cm^{-1} (CO stretching), which indicate the presence of crown ether units. The spectrum of **Ic** exhibits the characteristic bands which also appear in the spectra of **Ia** and **Ib**. The ^1H-NMR data are in agreement with the expected structures. The spectrum of **Ia** (Fig. 3) displays three resonances CH δ 6.5–7.7, 8.1, and 10.2 ppm attributable to the benzene, NH, and NOH protons, respectively. **Ib** has the same pattern but different chemical shifts (Fig. 4). The corresponding

TABLE I
Synthesis and Characterization of Polyamidoxime

		Polymer									
						Elementary analysis[c]					
DDE	Diamine/DADC		Yield	η_{inh}[a]	mp[b]	C (%)		H (%)		N (%)	
(mol)	(mol/mol)	Code	(%)	(dL/g)	(°C)	Calcd	Found	Calcd	Found	Calcd	Found
2×10^{-2}	$2 \times 10^{-2}/0$	**Ia**	93	0.088	250	62.68	63.01	4.47	4.53	20.89	19.19
2×10^{-2}	$0/2 \times 10^{-2}$	**Ib**	82	0.070	243	55.60	54.00	5.48	6.04	11.81	11.01
2×10^{-2}	$10^{-2}/10^{-2}$	**Ic**	85	—	230	58.22	—	5.12	—	15.09	—

[a] Measured at a concentration of 0.5 g/dL in DMF at 30°C.
[b] Decomposition temperature.
[c] End groups are neglected.

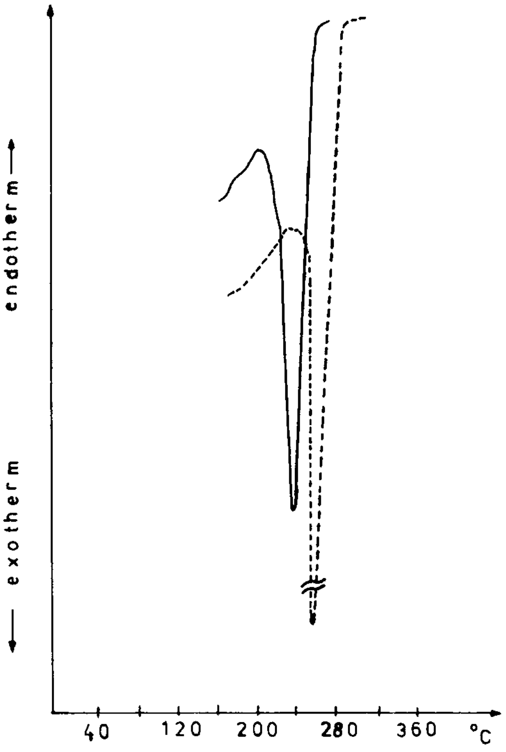


Fig. 1. DSC curves for **Ia** (- - - -) and **Ib** (——) heated at 10°C/min in nitrogen.

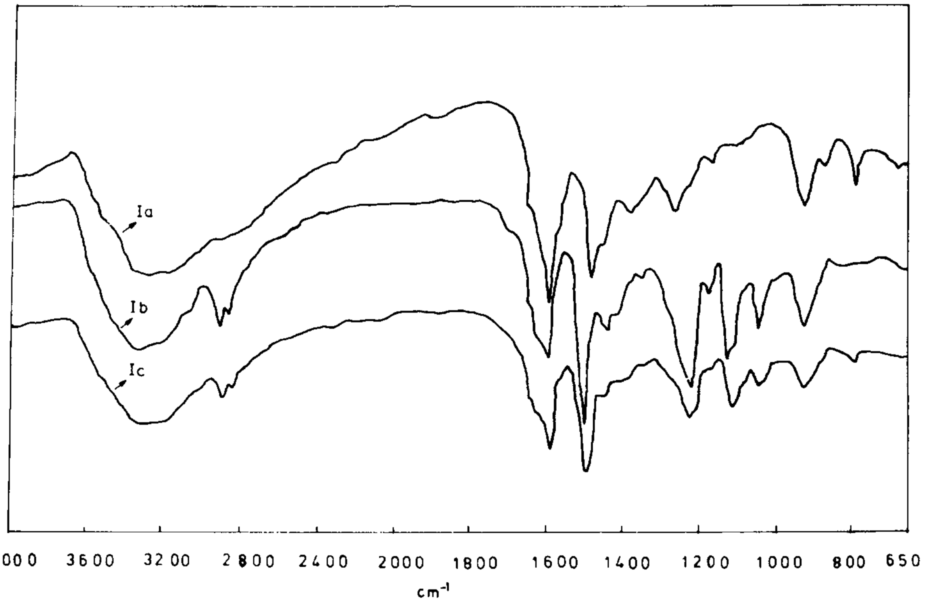


Fig. 2. Infrared spectra of **Ia**, **Ib**, and **Ic** on KBr disc.

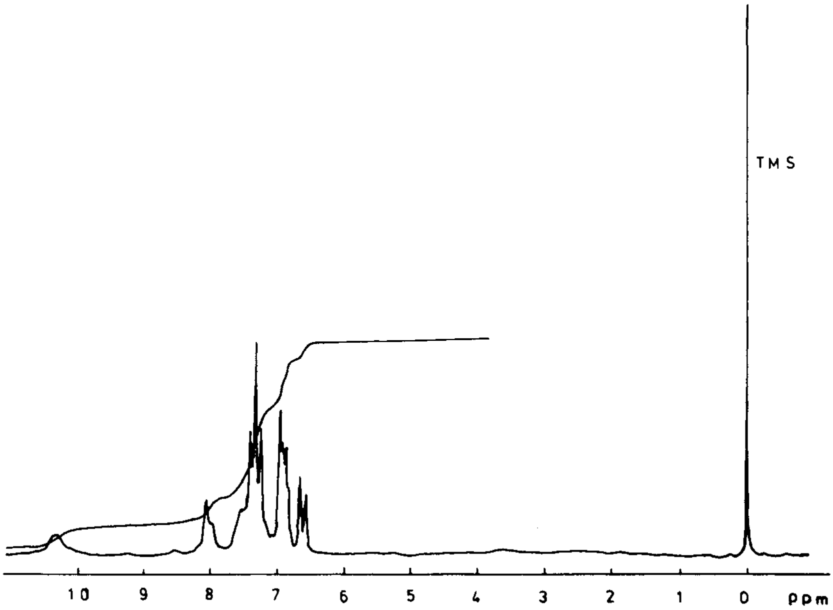


Fig. 3. ^{1}H-NMR spectra of **Ia** obtained in DMSO-d_6 at 60°C.

three resonances appear at δ 6.0–7.0, 7.8, and 11.0 ppm, respectively, in addition to the peak at δ 3.7 ppm due to aliphatic CH protons. The ratio of the integrated intensity of the peaks at δ 3.8 and 7.7 ppm (Fig. 5) indicate the mol ratio of crown ether/benzidine units to be approximately 1/1.1 in the polymer (**Ic**).

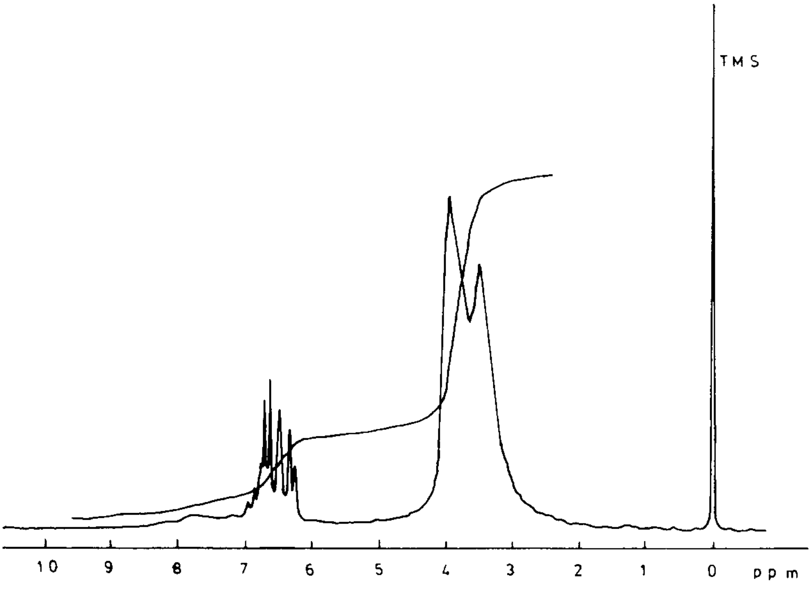


Fig. 4. ^{1}H-NMR spectra of **Ib** obtained in DMSO-d_6 at 60°C.

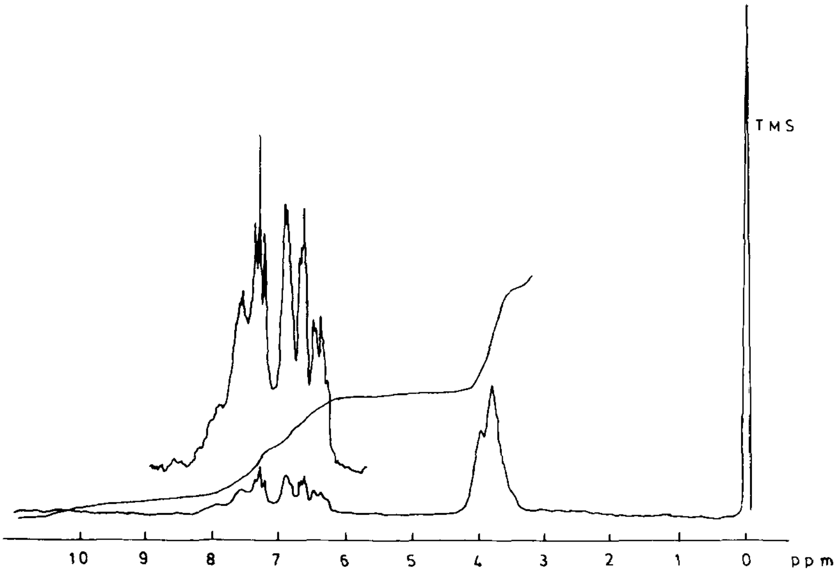
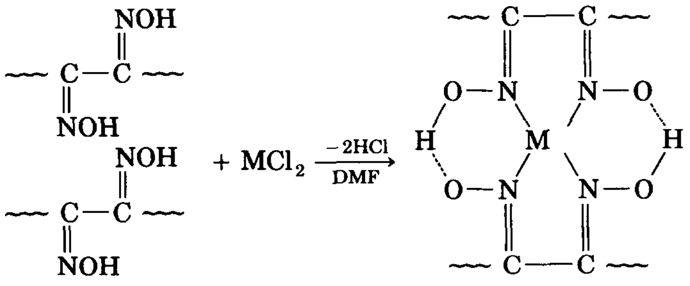


Fig. 5. ^{1}H-NMR spectra of Ic obtained in DMSO-d_6 at 60°C.

Crosslinking of PAOs by Coordination

The PAOs were used to complex with transition metal ions. In these experiments, polymers were complexed with chloride salts of Ni(II), Co(II), Cu(II), and the acetate salt of UO_2(II) by adding equimolar quantities in DMF at room temperature. Within a few seconds, the mixture turned to a clear solution due to the complete precipitation of deep colored polymer which indicates quantitative complexation.

The reaction probably proceeds according to the scheme:



Ia, b, c **IIa, b, c**

M: Ni(II), Co(II), Cu(II), $UO_2(oAc)_2$

The resultant polymers were insoluble in all solvents. This behavior was explained on the basis of intermolecular coordination of oxime groups to the transition metal ions. The **IIb** and **IIc** polymers are expected to exhibit the characteristics of both transition metal and crown ether. Recently, Neckers et al.[4] have prepared transition metal complexes of crown ether containing

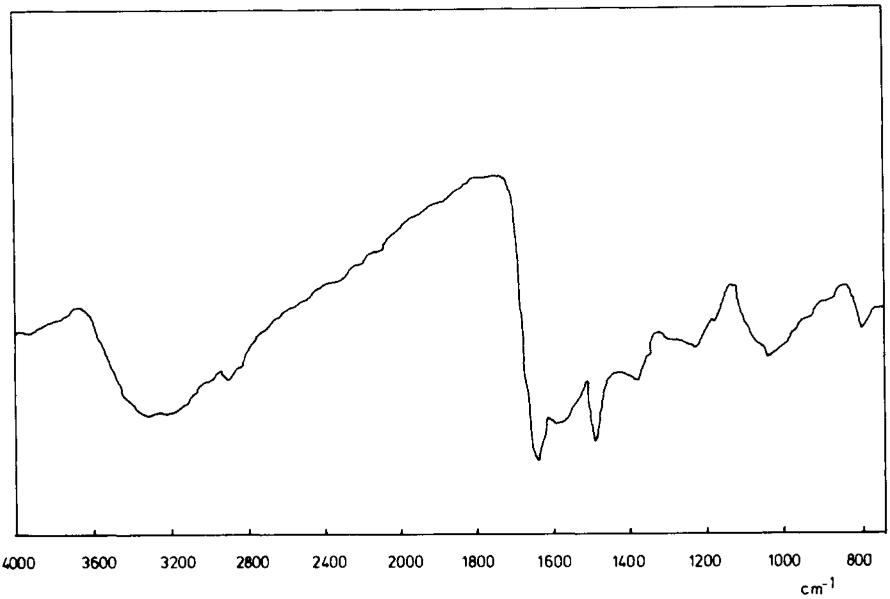


Fig. 6. Infrared spectra of Ni-complexed **IIa** on KBr disc.

polymers and showed their catalytic activity for aldol condensation. We have observed that precomplexing of the crown ether moiety with KI did not affect the subsequent coordination of the polymers with transition metal ions.

Crosslinked polymeric complexes (**IIa, b, c**) showed much better thermal stability than their PAO counterpart (**Ia, b, c**). They did not decompose or melt up to 400°C. The IR spectra of the crosslinked polymers are similar. As a typical example, in the IR spectrum of **IIa** (Fig. 6) the NO stretching band at 930 cm^{-1} is shifted to 1040 cm^{-1} and is broadened due to metal coordination. Similarly, the NH plane deformation vibration at 1600 cm^{-1} is shifted to 1640 cm^{-1}. The absorption band at 800 cm^{-1} assigned to the *p*-disubstituted benzene ring, is unaffected.

Another interesting observation is the yellowish-brown color of **IIa**(M: Ni). This light color did not darken, even after the pH was increased to 9, indicating amphi configuration[5] of oxime groups in the crosslinked polymeric complex.

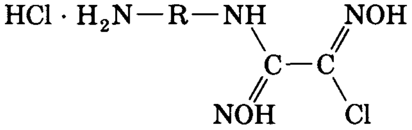
Since the transition metal complexes of glyoximes exhibit square planar structure, the PAOs are expected to coordinate in the same way. Experimentally, all Ni(II) complexes were shown to be paramagnetic and magnetic susceptibility measurements gave 1.04–1.38 unpaired electrons. The value lower than 2 suggests that both tetrahedral and planar structures are present in the coordinated polymers. However, static hindrance of bulky crown ether units (**IIb, c**) coordination may tend to turn to the tetrahedral structure.

EXPERIMENTAL

Benzidine (Merck), transition metal salts ($NiCl_2 \cdot 6\ H_2O$, $CoCl_2 \cdot 6\ H_2O$, $CuCl_2 \cdot 5\ H_2O$, and $UO_2(CH_3COO)_2 \cdot 6\ H_2O$) (Merck) and solvents were reagent grade and purified when necessary by conventional procedures. *Trans*-4,4′-diaminodibenzo-18 crown-6 (DADC) was synthesized according to the method of Pedersen.[6] Dichlorodioximine ethane (DDE) was prepared by the method previously utilized.[7]

General Procedures for Preparation of PAOs

Desired diamine (0.02 mol) was dissolved in 50 mL DMF. DDE (0.02 mol) in 50 mL DMF was added to the above solution at room temperature. After stirring vigorously for about 1 h, a white precipitate is formed with the following structure:



Anhydrous sodium bicarbonate (0.05 mol) was then added to the reaction mixture. Stirring was continued for another 6 h. Evolution of CO_2 caused foam formation during the reaction. At the end of this period excess $NaHCO_3$ and NaCl formed are removed by filtration. The filtrate was poured into 400 mL of distilled water. The polymer was filtered and washed successively with dilute HCl solution, methanol and diethyl ether. After drying at 70°C for 24 h, the polymers were characterized and subjected to further investigation.

Complexation of Polymers with Ions

Solution of a metal salt (0.05 mol) in 50 mL DMF was added to the solution of a PAO (containing 0.1 mol vic-dioxyme) in 50 mL DMF at room temperature. A deep colored precipitate formed immediately, and the PH of the medium was adjusted to 9 by adding a few drops of ammonia solution. The complexed polymer was filtered off, washed with methanol and diethyl ether, and dried.

Characterization of Polymers

^{1}H-NMR spectra were recorded on a JNM-FX-100 Fourier Transform NMR spectrophotometer at 60°C in DMSO-d_6 with tetramethylsilane as internal standard. The IR spectra were taken by a Shimadzu IR-400 spectrophotometer. Decomposition temperatures were determined on a Perkin–Elmer DSC-1B calorimeter under nitrogen at a 16°C/min heating rate. Magnetic susceptibility measurements were carried out by using Gay-Balance technique on a Magnetic Power Supply Type D-104 Newport Instruments. The viscosity measurements were carried out in Cannon–Fenske viscometer at 30°C in DMF.

References

1. M. E. B. Jones, D. A. Thorton, and R. F. Webb, *Makromol. Chem.*, **49**, 69 (1961).

2. A. D. Pomogailo and V. S. Savostyanov, *J. Macromol. Sci Rev. Macromol. Chem. Phys.*, **25**, 375 (1985).

3. C. Grundman, V. Mini, J. M. Dean, and H. D. Frommeld, *Annal. Chem.*, **687**, 191 (1965).

4. K. Zhang, G. S. Kumar, and D. C. Neckers, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 1293 (1985).

5. S. Serin and O. Bekaroglu, *Z. Anorg. Allg. Chem.*, **496**, 192 (1983).

6. C. J. Pedersen, *J. Am. Chem. Soc.*, **89**, 7017 (1967).

7. A. Hantzch, *Chem. Ber.*, **25**, 708 (1892).

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