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SYNTHESIS AND CHARACTERIZATIONS OF NEW POLYAMIDOXIMES AND THEIR CROSSLINKING BY METAL IONS

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Abstract—Two new polyamidoximes having appropriate functions to bind transition metal ions such as Ni(II) and Pd(II) were prepared. Polymers were obtained by the reactions of (E,E)-dichloroglyoxime with new aromatic primary amines. Polymers and their complexes were characterized by elemental analyses, i.r. and ^{1}H-NMR spectra, DSC, and electrical conductivity measurements. The molecular weights of polymers were determined by light scattering technique.

INTRODUCTION

Recently, there has been growing interest in polymeric materials which are crosslinked by transition metals. Polymer–metal complexes show interesting and important characteristics, especially in areas such as catalysis [1, 2], semiconductors [3], heat resistance materials [4], and gas separators [5]. On the other hand, several liquid crystalline polymers containing metals have been reported and particular attention is paid to their properties [6, 7].

It has been demonstrated that the polymeric amidoximes show high complexing affinity toward metal ions [8]. They have much higher stability constants for UO_2(VI) than for Co(II), Ni(II), Cu(II) and Zn(II) [9]. These results strongly imply that the amidoxime polymer possesses high adsorptivity for uranium in sea-water. Actually there have been many reports for the recovery of uranium from sea-water [10, 11]. Polyamidoximes can be also be used for the determination of trace metals in natural waters [12]. Riveros [13] has reported the extraction of gallium from a real Bayer solution using an amidoxime resin. Recently Lin and coworkers [14] have prepared a kind of chelating nonwoven fabric with the amidoxime group which has a high adsorption capacity for the ions of mercury, copper, platinum, silver, and gold besides uranium.

Crown ethers as a relatively new class of compounds have received much interest, especially in the area of complexation. Moreover considerable work has also been done on polymeric crowns [15]. Kopolow and coworkers [16] are the major contributors for the synthesis of polycrowns and study of their cation binding properties. Crown ether moieties immobilized on polymeric supports are effective catalysts for aqueous-organic two-phase reactions [17]. Polymer supported crown ethers have also been used for separation of some metal cations, anions, and organic compounds in analytical chemistry [18]. Recently some authors have investigated the synthesis of liquid crystalline polymers containing macroheterocyclic ligands [19, 20].

The aim of the present study was to synthesize and characterize new polyamidoximes containing benzimidazoles and crown ether groups and to obtain their Ni(II) and Pd(II) complexes.

EXPERIMENTAL

Schemes 1–3 outline the synthesis of monomers, polymers and crosslinked polymeric complexes.

Techniques

^{1}H-NMR spectra were obtained at ambient temperature on a Bruker AC-200 and Varian T-60 spectrophotometers. Chemical shifts were being quoted with respect to tetramethylsilane as internal standard. i.r. spectra were performed on a Perkin–Elmer 1600 FT–i.r. and Perkin–Elmer 177 spectrophotometers, as KBr pellets. The metal contents of polymers and elemental analysis were determined by a Hilger–Watts A.A.H. 1550 atomic absorption spectrophotometer and a Perkin–Elmer 240C elemental analyser, respectively (Tubitak and Metu, Turkey). The intrinsic viscosities of the polymers were measured in DMSO at 25°C in an Ubbelohde digital viscometer (Table 1). Decomposition temperatures were determined on a Perkin–Elmer [4] DSC-calorimeter at a 10 and 20°C/min rates. Conductivity measurements were carried out by using Keithley 614 Electrometer (4 probes). Molecular weights of the polymers were determined by using Dawn B.–Wyatt Technology Light Scattering Instrument.

Materials and monomer synthesis

cis-4,4′-Diaminodibenzo(18-Crown-6) [21] and 1,4-Bis(5-nitrobenzimidazol)butane (DNBB) [22] were synthesized according to reported procedures as the starting materials. All reagents were reagent grade and purified by conventional procedures [23].

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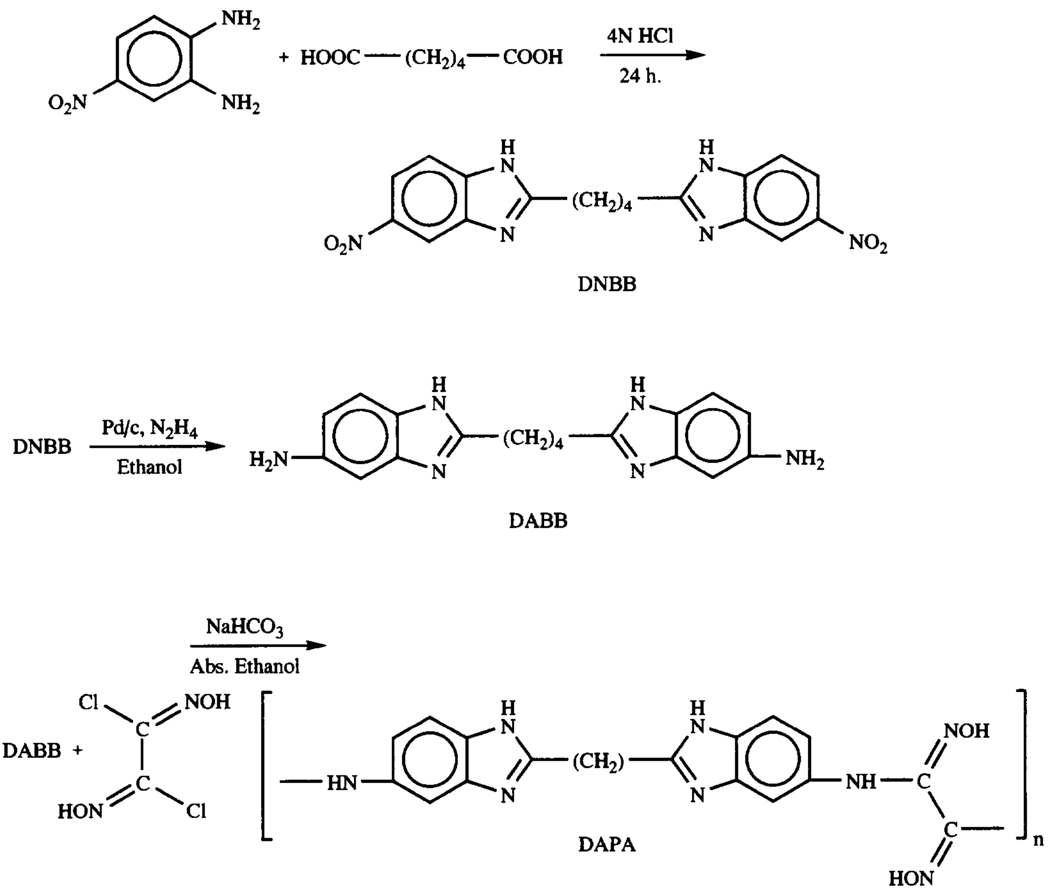


Scheme 1

1,4-Bis(5-aminobenzimidazole)butane (DABB)

A solution of 1,4-bis(5-nitrobenzimidazole)butane (DNBB) (6.2 g, 16.3 mmol) in ethanol (150 ml) was heated under reflux with 10% palladium/activated carbon (0.6 g). Hydrazine hydrate (100%, 25 ml) was added to the above solution in 0.5 ml portions Then, the mixture was refluxed until the solution became colorless. The mixture was cooled, filtered and the insoluble material washed with ethanol. The ethanol solvent was then removed under vacuum. The resulting residue was recrystallized from ethanol: yielding 4.35 g (83.5%) of white crystals; m.p. 213°C. ^{1}H-NM (DMSO-d_6, TMS, δ, ppm): 4.68 (4 protons, NH_2, s), 7.16 (2 protons, NH, s), 2.85 (8 protons, —CH_2—, s), 6.73–6.47 (6 protons, ArH, m). i.r. (KBr pellets, cm^{-1}): 3375(NH_2), 3300(N—H), 3020(Ar—H), 2920(C—H), 1605 (NH_2).

4,4′-Bis(4-nitrobenzylidenimino)dibenzo(18-Crown-6) (DNDC)

To a solution of cis-4,4′-diaminodibenzo(18-Crown-6) (2.6 g, 6.66 mmol) in the mixture of absolute ethanol and DMF (3:2) (50 ml), 4-nitrobenzaldehyde (1.99 g, 13.32 mmol) was added in small portions. The reaction mixture was stirred for 3 hr at ambient temperature and then filtered. The crude product was washed several times with the mixture of the absolute ethanol and DMF (1:1) and recrystallized from methanol/DMF (3:1): yielding 3.7 g (84.8%) of dark yellow crystals; m.p. 205°C. ^{1}H-NMR ($DMSO_{-d6}$, TMS, δ, ppm): 8.87 (2 protons, HC=N—,s), 3.45–3.30 (16 protons, —CH_2—CH_2—O, m), 7.21–6.88 (6 protons, ArH, m), 8.38–8.14 (8 protons, ArH, m). i.r. (KBr pellets, cm^{-1}): 3030(Ar—H), 2920–2830 $(C—H)_{etheral}$, 1660 (C=N), 950 (N—O).

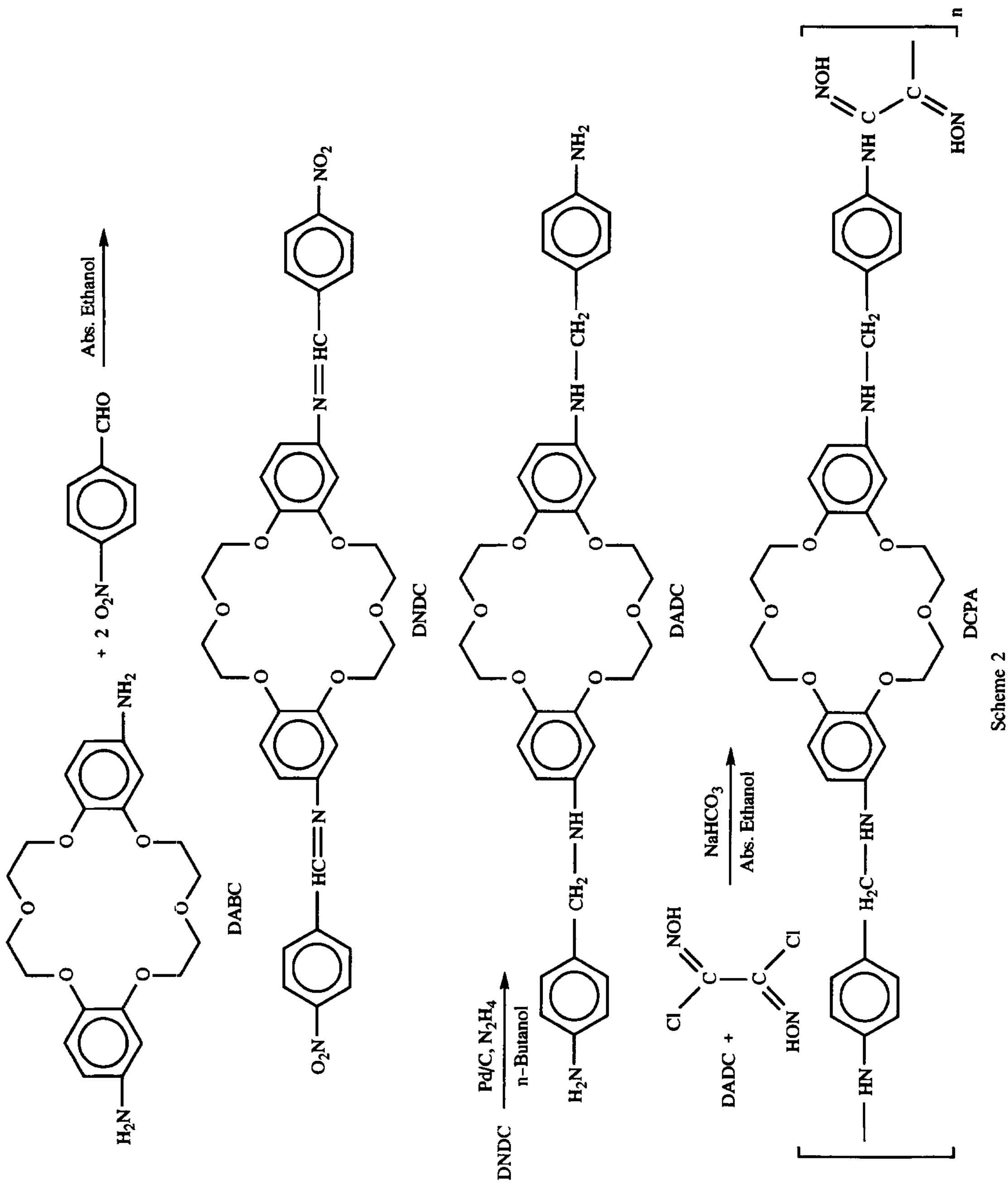
4,4′-Bis(4-aminobenzylamino)dibenzo(18-crown-6) (DADC)

4,4′-Bis(4-nitrobenzylidenimino)dibenzo(18-Crown-6) (DNDC) (1.97 g, 3 mmol) was dissolved in n-butanol (200 ml) and heated to 120°C 0.70 g of Pd/C (10%) was then added to this solution at the same temperature and 20 ml of hydrazine hydrate (100%) was added dropwise; the mixture was stirred and refluxed for 50 min. After having been cooled to room temperature, the mixture was filtered and then evaporated until no n-butanol could be detected. The yellow product was extracted with chloroform. The extract was reduced under vacuum and cooled in a refrigerator at −15°C. The pale yellow crystals were filtered off, washed with cold diethyl ether: yielding 1.42 g (78.8%), m.p. 166°C. ^{1}H-NMR ($DMSO_{-d6}$, TMS, δ ppm): 4.05 (4 protons, NH_2, s), 7.45 (2 protons, —NH, s), 3.55–3.20 (16 protons, —CH_2—CH_2—O, m), 6.75–6.60 (8 protons, ArH, m), 6.35–6.14 (6 protons, ArH, m), 3.80 (4 protons, —CH_2—, s). i r. (KBr pellets, cm^{-1}): 3380 (NH_2), 3310 (N—H), 3025 (Ar—H), 2910–2830 $(C—H)_{etheral}$, 1610 (NH_2).

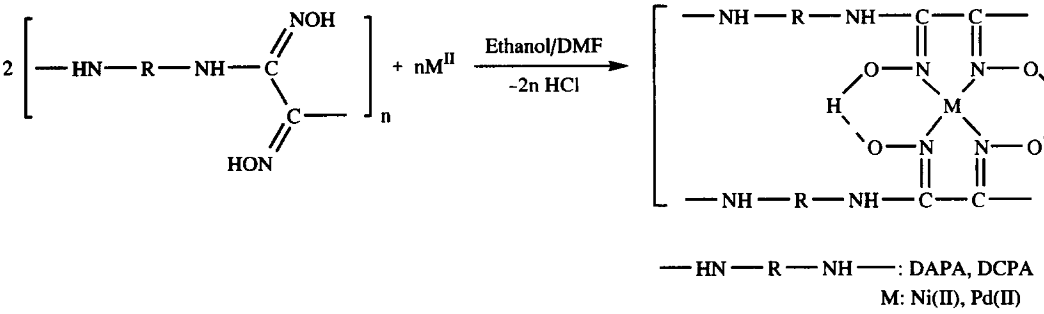
Synthesis of polyamidoximes (DAPA and DCPA)

To a solution of DABB (0.64 g, 2 mmol) or DADC (1.20 g, 2 mmol) in absolute ethanol (75 ml) containing anhydrous sodium bicarbonate (0.425 g, 5 mmol), a solution of (E, E)-dichloroglyoxime (0.314 g, 2 mmol) in absolute ethanol (20 ml) was added dropwise over 30 min. After stirring vigorously for about 3 hr, the white precipitates are formed as in Schemes 1 and 2. Polymers were then removed by filtration. The crude products were washed successively with water, ethanol and diethyl ether. The polyamidoximes were dried at 70°C *in vacuo*.

The yield of DAPA 0.68 g (84.15%), m.p. 232°C. ^{1}H-NMR ($DMSO_{-d6}$, TMS, δ, ppm): 10.2 (2 protons, OH, s),


DABC
+ 2 O2N–C6H4–CHO
Abs. Ethanol
DNDC
DNDC
Pd/C, N2H4
n-Butanol
DADC
DADC +
NaHCO3
Abs. Ethanol
DCPA
n

Scheme 2



Scheme 3

7.68 (2 protons, NH, s), 7.22 (2 protons, NH, s), 2.80 (8 protons, —CH_2—, s), 7.07–6.65 (6 protons, ArH, m). i.r. (KBr pellets, cm^{-1}): 3200 (O—H), 3340 (N—H), 3300 (NH), 3025 (Ar—H), 2925 (C—H), 1635 (C=N), 935 (N—O).

The yield of DCPA 1.15 g (80.1%), m.p. 248°C. ^{1}H-NMR (DMSO-$_{d6}$, TMS, δ, ppm): 10.2 (2 protons, OH, s), 7.75 (2 protons, NH, s), 7.25 (2 protons, NH, s), 3.45–3.12, (16 protons, —CH_2—CH_2—O, m), 6.65–6.42 (8 protons, ArH, m), 6.31–6.11 (6 protons, ArH, m), 3.85 (4 protons, —CH_2—, s). i.r. (KBr pellets, cm^{-1}): 3220 (O—H), 3360 (N—H), 3020 (Ar—H), 2928–2860 (C—H)$_{\text{etheral}}$, 1640 (C=N), 940 (N—O).

The synthesis of crosslinked polymeric complexes

Complexation of DAPA with Pd(II) ion. A mixture of $PdCl_2$ (17.6 mg, 0.1 mmol) and NaCl (11.7 mg, 0.2 mmol) in ethanol (40 ml) was heated and stirred at 70°C until $PdCl_2$ dissolved completely. A solution of DAPA (0.808 g, 2 mmol) in the mixture of ethanol/DMF (1/3) (75 ml) at 40°C was added to the solution of Na_2PdCl_4 with continuous stirring. A KOH solution (0.1 M in ethanol) was used to adjust pH = 4.60 whereupon precipitation started. After heating for 3 hr, the brown Pd(II) complex precipitated completely. It was removed by filtration and washed successively with water, DMF, ethanol and diethyl ether. The complex was dried at 120°C *in vacuo*. Yielding 0.69 g (75.8%) pale brown solid; m.p. > 400°C. ^{1}H-NMR (TFA, TMS, δ, ppm): 16.45 (2 protons, O—H··O, s), 7.62 (4 protons, NH, s), 7.45 (4 protons, NH, s), 2.80 (16 protons, —CH_2—, s), 7.00–6.70 (12 aromatic protons, m). i.r. (KBr pellets, cm^{-1}): 3350(N—H), 3290(N—H), 3025(Ar—H), 2920(C—H), 1690(O—H·O), 1630(C=N), 930(N—O).

Complexation of DCPA with Ni(II) ion. A solution of $NiCl_2 \cdot 6 H_2O$ (0.119 g, 0.5 mmol) in ethanol (15 ml) was added to a solution of DCPA (0.684 g, 1 mmol) in the mixture of ethanol:DMF (2:3) (60 ml) at 70°C. After the addition of metal, the acidity of the solution dropped pH = 1.85 and the acidity was adjusted with 0.1 N KOH in ethanol *ca* 4.60 at which the precipitation of the complex started. This mixture was heated at 75°C for a further 3 hr, and during this period precipitation was completed. The dark red complex was removed by filtration, washed with water, DMF, ethanol and diethyl ether. The complex dried at 120°C *in vacuo*. Yielding 0.63 g (88.7%) dark red solid, m.p. > 400°C. ^{1}H-NMR (TFA, TMS, δ, ppm): 16.20 (2 protons, O—H··O, s), 7.55 7.37 (8 protons, NH, m), 3.30–3.02 (32 protons, —CH_2—CH_2—O, m), 6.70–6.38 (16 protons, ArH, m), 6.25–6.02 (12 protons, ArH, m), 3.80 (8 protons, —CH_2—, s). i.r. (KBr pellets, cm^{-1}): 3360 (N—H), 1705 (O—H··O), 1635 (C=N), 3020 (Ar—H), 2920–2870 (C—H)$_{\text{etheral}}$, 935 (N—O).

RESULTS AND DISCUSSION

The route for the synthesis of two novel polyamidoximes (DAPA and DCPA) are given in Schemes 1 and 2.

In the ^{1}H-NMR spectrum of DABB, the NH_2 and NH proton resonances appear as the singlets at δ = 4.68 and 7.16 ppm, respectively. The multiplet at δ = 6.73–6.47 and the singlet at δ = 2.85 ppm correspond to the aromatic and aliphatic protons, respectively. The NH chemical shifts which belong to benzimidazole groups were shifted down field due to the amine groups. In the i.r. spectra of DABB, the stretching vibrations at 960 cm^{-1} for N—O group of DNBB disappear after the reduction reaction. The new stretching and bending vibrations, respectively, at 3375 and 1605 cm^{-1} indicate the NH_2 group of DABB. The aromatic and the aliphatic (C—H)

Table 1. Analytical and physical data for compounds

Compounds	Yield (%)	η[a] (dl/g)	m.p.[b] (C)	Conductivity Ω^{-1}	Elemental C (%)	Analysis[c] H (%)	Calculated N (%)	Found M (%)
DABB	83.5		213		67 5	6.25	26.15	
					(67 25)	(6.05)	(26.1)	
DNDC	84.8		205		62 2	4 9	8 5	
					(62.55)	(4.8)	(8 6)	
DADC	78.8		166		68.00	6.7	9.3	
					(67.75)	(6.5)	(9.1)	
DAPA	84.15	0.076	232	$2\ 68\ 10^{-4}$	59.4	4.95	27 7	
					(59.15)	(4.7)	(27.55)	
DCPA	80.1	0.082	248	$2.28\ 10^{-2}$	63.15	5.8	12 3	
					(62 95)	(5.6)	(12.05)	
Pd(II) Comp.	75.8		>400	$2.46\ 10^{4}$	52.6	4.2	24.6	11.6
DAPA					(52.4)	(3.95)	(24.45)	(11.4)
Ni(II) Comp.	88.7		>400	$2\ 07\ 10^{2}$	60.6	5.5	11.8	4.1
DCPA					(60.4)	(5.35)	(11.6)	(3.9)

[a] Measured in DMSO at 25 C.
[b] Decomposition temperature.
[c] End groups are neglected.

stretching vibrations are very close for both DABB and DNBB.

In the ^{1}H-NMR spectrum of DABC, there is a singlet at $\delta = 3.25$ ppm for aromatic primary amine protons. After the condensation reaction these singlets disappear and new resonances at $\delta = 8.87$ ppm appear which can be assigned to the azomethine protons [24]. The chemical shifts for DNDC display three resonances at $\delta = 8.38$–8.14, 7.21–6.88 and 3.45–3.30 ppm attributable to the aromatic and etheral groups, respectively.

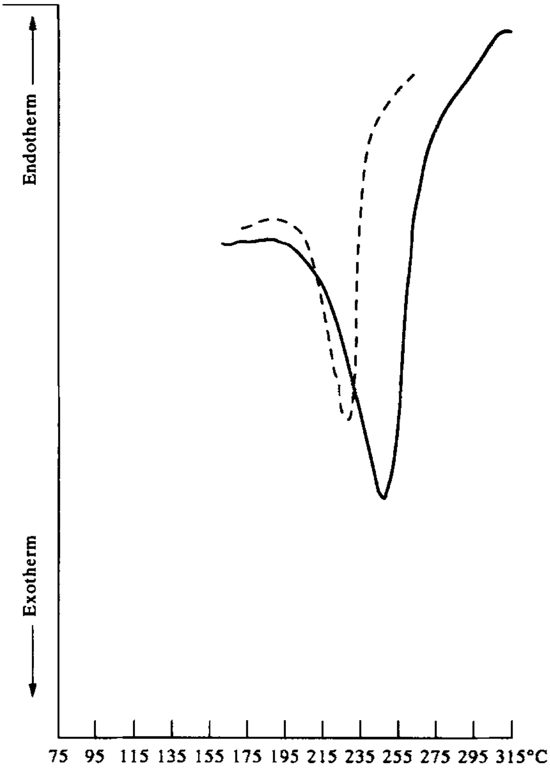
The ^{1}H-NMR spectrum of DADC which shows that two resonances belong to NH_2 and NH protons is in agreement with the expected structure (Scheme 2). These resonances appear as singlets at $\delta = 4.05$ and 7.45 ppm, respectively. The multiplets at $\delta = 6.75$–6.60 and 6.35–6.14 ppm corresponding to different benzene groups have considerable shifts. The i.r. spectrum of DNDC exhibits ν (C=N) a sharp pike at 1660 cm^{-1}. After the formation of DNDC, the stretching and bending vibrations of NH_2 groups, which belong to DABC, disappear. A broad vibration at 950 cm^{-1} can be assigned to the stretching vibration of N—O group and this occurrence interprets the formation of DNDC. In the i.r. spectrum of DADC, the NH_2 and NH stretching vibrations are observed at 3380 and 3310 cm^{-1} as sharp bands which are assigned to the formation of primary and secondary aromatic amine groups [25, 26]. After the reduction reaction of DNDC (Scheme 2) the stretching vibrations of C=N group disappear.

In the ^{1}H-NMR spectra of DABB and DADC, there are singlets at $\delta = 4.68$ and 4.05 ppm for primary aromatic amine protons. After the polymerization reaction, these singlets disappear and new resonances are formed at $\delta = 7.68$ and 7.75 ppm which indicate the presence of NH protons in these compounds. A sharp resonance at $\delta = 10.20$ ppm can be assigned to hydroxy protons [27, 28], which belong to oxime groups. The OH and NH can be identified easily and disappear upon D_2O exchange. The ratio of these deuterium exchangeable protons (NOH : NH) is 1 : 2. The presence of only one chemical shift for exchangeable oxime protons indicates that the oxime configuration is in the s-trans position [29]. The chemical shifts of the aromatic, aliphatic and etheral protons of polyamidoximes are in accordance with those of the DABB and DADC.

In the i.r. spectrum of DAPA and DCPA, (O—H) and (N—H) stretching vibrations are observed at 3220–3200 and 3340–3360 cm^{-1} as broad absorptions bands. (N—O) and (C=N) stretching vibrations are at 940–935 and 1640–1635 cm^{-1}, respectively. In the i.r. spectrum of polyamidoximes, the stretching and bending vibrations at 3375–3380 and 1610–1605 cm^{-1} for primary amine groups of monomers (DABB and DADC) disappear after the polymerization reactions.

Molecular weights of the polymers were determined using light scattering technique as 2.6 10^3 for DAPA and 2.4 10^3 for DCPA. DSC curves show that these polymers begin to fuse at about 235°C (for DAPA) and 250°C (for DCPA) with a sharp exotherm which corresponds to decomposition (Figs 1 and 2).

Crosslinking of polyamidoximes via coordination with the transition metal ions such as Ni(II) and Pd(II) were performed. Since a distinct increase of acidity in the solution was observed during the complex formation, deprotonation of the vic-dioxime with subsequent N,N′-chelation with the vic-dioxime groups, probably occurs. The crosslinked polymeric complexes were insoluble in all common solvents except DMSO. This behavior can be explained on the basis of intermolecular coordination of oxime groups to the transition metal ions and hydrogen bonding [30] (Scheme 3).



DSC curves for DAPA (——) and DCPA (– – –)

Fig. 1.

The ^{1}H-NMR spectra of crosslinked polymeric complexes indicate N,N-chelation. While the chemical shifts of deuterium exchangeable NH protons are observed at $\delta = 7.62$, 7.45 and 7.55–7.37 ppm, the intramolecular hydrogen bridging O—H··O protons have been shifted to lower field (16.45–16.20 ppm) [31, 32]. As expected for d^8 metal ions in square-planar geometry, the Pd(II) and Ni(II) complexes of polyamidoximes are diamagnetic according to the NMR spectra.

In the i.r. spectra of Pd(II) and Ni(II) complexes of polyamidoximes ν (C=N) peaks appear at 1635–1630 cm^{-1}. These values are slightly lower compared to those of free polyamidoximes as observed in most of the N,N′-chelated vic-dioximes Ni(II) and Pd(II) complexes [33, 34]. The usual intramolecular hydrogen bridges of the square-planar vic-dioxime complexes were characterized by the weak deformation band at *ca* 1705–1690 cm^{-1} as in our cases [35, 36]. The N—O stretching vibrations which belong to the oxime groups are shifted to 935–930 cm^{-1} and are broadened due to the metal coordination.

Crosslinked polymer complexes show much better thermal stability than polyamidoximes. They did not decompose or melt up to 400°C. The electrical conductances of the polymers and their metal complexes were measured by using Four-Point Probe analyses [37]. Calculated conductance values are given in Table 1. These results indicate that the polymers and polychelates are not poor electrical conductors.

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