then quenched, the equilibrium scattering curve is more likely to be measured so that all the data can be used to obtain χ. If the data are obtained at low q, then extrapolation to zero q should result in χ values that relate to the annealing temperature. However, at high q the values of χ will tend toward those associated with temperatures closer to T_g. If measurements are made on unquenched samples, which are equilibrated at the measuring temperature, no ambiguities should arise.

Finally, the evidence from this work that the PS/PM2PO system shows no composition dependence of χ supports that from mutual diffusion measurements.[2]

Acknowledgment. We thank our local contact at the Institut Laue-Langevin, Dr. A. Rennie, for his assistance. J.R.F. thanks the NSF and the SERC for Visiting Fellowships. P.E.T. thanks the SERC for support during the period of this work. We are grateful to Prof. E. Kramer for very helpful discussions and for allowing us to see ref 2 and 23 before publication.

Registry No. PS, 9003-53-6; PM_2PO, 24938-67-8; P_4MS, 24936-41-2; neutron, 12586-31-1.

References and Notes

(1) Maconnachie, A.; Kambour, R. P.; White, D. M.; Rostami, S.; Walsh, D. J. *Macromolecules* **1984**, *17*, 2645.
(2) Composto, R. J.; Kramer, E. J.; White, D. M. *Macromolecules* **1988**, *21*, 2580.
(3) Jelenic, J.; Kirste, R. G.; Oberthür, R. C.; Schmitt-Strecker, S.; Schmitt, B. J. *Makromol. Chem.* **1984**, *185*, 129.
(4) Fried, J. R.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1978**, *11*, 150.
(5) Vukovic, R.; Karasz, F. E.; MacKnight, W. J. *J. Appl. Polym. Sci.* **1983**, *28*, 219.
(6) Vukovic, R.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1983**, *24*, 529.
(7) Maconnachie, A.; Kambour, R. P.; Bopp, R. C. *Polymer* **1984**, *25*, 357.
(8) Fried, J. R.; Lorenz, T.; Ramdas, A. *Polym. Eng. Sci.* **1985**, *25*, 1048.
(9) Dickinson, L. C.; Yang, H.; Chu, C.-W.; Stein, R. S.; Chien, J. C. W. *Macromolecules* **1987**, *28*, 1757.
(10) Maier, B., Ed. *Neutron Research Facilities at the ILL High Flux Reactor*; Institut Laue-Langevin: Grenoble, France, 1983.
(11) Ragnetti, M.; Geiser, D.; Höcker, H.; Oberthür, R. C. *Makromol. Chem.* **1985**, *186*, 1701.
(12) Hayashi, H.; Flory, P. J.; Wignall, G. D. *Macromolecules* **1983**, *16*, 1328.
(13) Rawiso, M.; Duplessix, R.; Picot, C. *Macromolecules* **1987**, *20*, 630.
(14) Gawrisch, W.; Brereton, M. G.; Fischer, E. W. *Polym. Bull.* **1981**, *4*, 687.
(15) Maconnachie, A. *Polymer* **1984**, *25*, 1068.
(16) O'Reilly, J. M.; Teegarden, D. M.; Wignall, G. D. *Macromolecules* **1985**, *18*, 2747.
(17) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, NY, 1979.
(18) Warner, M.; Higgins, J. S.; Carter, A. J. *Macromolecules* **1983**, *16*, 1931.
(19) Reanalysis of the data from ref 1 gives a value of R for PM2PO-d in PM2PO of 88 Å, not 100 Å as originally published.
(20) Tomlins, P. E.; Higgins, J. S. *Macromolecules* **1988**, *21*, 425.
(21) Bates, F. S.; Fetters, L. J.; Wignall, G. D. *Macromolecules* **1988**, *21*, 1086.
(22) Wignall, G. D.; Child, H. R.; Li-Aravena, F. *Polymer* **1980**, *21*, 131.
(23) Kramer, E. J.; Sillescu, H. *Macromolecules* **1989**, *22*, 414.
(24) Murray, C. T.; Gilmer, J. W.; Stein, R. S. *Macromolecules* **1985**, *18*, 996.
(25) Higgins, J. S.; Fruitwala, H.; Tomlins, P. E. *Macromolecules*, in press.
(26) Wellinghoff, S. T.; Koenig, J. L.; Baer, E. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 1913.

Monomer and Polymers Derived from 2,6-Bis((dimethylamino)formyl)-4-(diallylamino)pyridine

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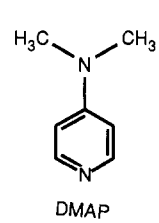
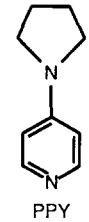
ABSTRACT: A new metal complexing polymer has been synthesized. The corresponding monomer and model compounds are obtained from 4-hydroxypyridine-2,6-dicarboxylic acid (chelidamic acid). The monomer is a diallylamine derivative that can be cyclopolymerized with free radical initiators in aqueous acid. Similar to other diallylamines, it yields a linear and water-soluble polymer. The complexing activity is due to the pyridine nitrogen along with amide functions in positions 2 and 6. These provide not only a chelating effect that strongly enhances the complex stability but also the possibility of different binding geometries as suggested by changes in the solution NMR spectra upon addition of diverse transition-metal salts. This variability is probably responsible for the ability to complex metals that bind to the ligand in different preferred ways.

Introduction

4-(Dialkylamino)pyridines have been used as nucleophilic catalysts for several years. The range of applications has been the object of several reviews.[1-3] The most commonly used derivative is 4-(dimethylamino)pyridine (DMAP, below) due to both high efficiency in a number of reactions and low price. Although 4-pyrrolidinopyridine (PPY, below) has been reported to be in several cases more effective than DMAP,[2] its use has been restricted due to its higher price.



DMAP



PPY

We have been involved for several years in the synthesis and characterization of polymers containing PPY units in the backbone.[4,5] 4-(Diallylamino)pyridine (DAAP) was synthesized and shown to polymerize by a free radical mechanism yielding a non-cross-linked, water-soluble polymeric catalyst (below) whose activity is superior to that

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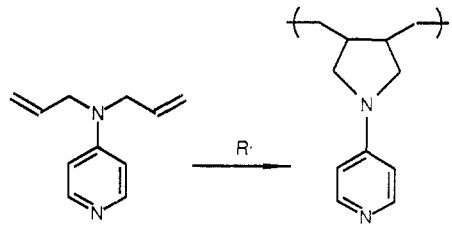
of PPY in the esterolysis of *p*-nitrophenyl esters.[6] The efficiency of the homopolymer in a selected esterification reaction was also high but not superior to that of low molecular weight catalysts.



DAAP

Substituted pyridines like DMAP have been shown to display metal complexing activity as well.[7] One application of this property is the extraction of hazardous metals and metal salts from waste water. Polymer-bound DMAP can also be used as a support for metal ion catalysts, especially when there exists a need for catalyst recycling. For instance, a Cu^{2+} complex of a polystyrene-supported DMAP was used successfully as a catalyst for the oxidative polymerization of 2,6-dialkylphenols.[8] Recent reports have also shown that incorporation of the pyridine ring into diester–polyether macrocyclic compounds enhances the metal complex stability.[9,10] Polymerization of polydentate derivatives of DMAP offers a method of obtaining metal complexing reagents with both improved metal selectivity and tighter binding. An additional advantage of such a polymeric reagent is that it should display better stability and resistance to humidity. In the insoluble cross-linked state, a polymeric catalyst is useful for reactions that need to be carried out to a limited yield because they can be easily removed by filtration before product isolation. Even if the polymeric reagent were soluble, operational costs should be reduced because the reagent can be recycled by extraction or precipitation.

This paper deals with the synthesis and characterization of new polymeric metal complexing reagents and a preliminary evaluation of their metal complexing activity. The chelating groups are based on 4-aminopyridine with amide groups in the 2- and 6-positions. We chose this type of compound for several reasons. First, diallylamines and specifically DAAP are known to be polymerizable by a free radical mechanism yielding non-cross-linked water-soluble homo- and copolymers. Second, the starting material for the synthesis (chelidamic acid) was readily available. Finally, monomers of this kind may be used for subsequent synthesis of polymers with macrocyclic monomeric units.

Experimental Section

All reagents were used as purchased or purified as indicated. ^{13}C and ^{1}H NMR spectra were recorded on a Bruker MSL-200 spectrometer. Purity was checked by GC with a Hewlett-Packard 5880A instrument using a flame ionization detector and a J&W Scientific fused silica megabore column with 5% poly(phenylmethylsiloxane).

2,6-Bis(chloroformyl)-4-chloropyridine (3). Chelidamic acid (1, 4-hydroxypyridine-2,6-dicarboxylic acid, 35.15 g, 0.192 mol) was suspended in 300 mL of dry chloroform in a 1-L three-neck flask provided with a Graham condenser, a $CaCl_2$-moisture trap, and a magnetic stirrer. The mixture was cooled to 0 °C in an ice bath; PCl_5 (140 g, 0.67 mol) was added over a 10-min period. Gentle bubbling and HCl evolution through the moisture trap were observed after the addition of all the PCl_5. The light brown suspension was left overnight at 0 °C and was then heated at reflux for 72 h to give a dark brown solution. The reaction flask was cooled to 0 °C, and the contents were slowly poured into 1 L of an ice–water mixture. The addition had to be controlled carefully because local overheating would cause some hydrolysis of the product along with that of PCl_5. Good results were obtained on keeping the temperature under 10 °C. The two-phase mixture was then poured into a separation funnel. The chloroform phase containing **3** was separated and filtered through phase separation filter paper (Whatman PS-1) to remove most of the water. The addition of more chloroform speeds up the separation of both phases that sometimes tend to form emulsions. Formation of some diacid **2** could never be avoided completely. This product separates as a brown precipitate between the two phases rendering their separation more difficult. In cases where too much of this product was formed, we first filtered the entire cooled mixture (normal filter paper) and isolated **2** for further use. While the mixture was always kept cold, the liquid phases were then separated and the organic layer was filtered again, this time with phase separation paper. The organic solution was then treated with anhydrous $CaCl_2$ and filtered and the solvent removed by rotary evaporation. The dark brown product obtained was sublimed in an oil bath at 120 °C under a vacuum of 5 mmHg. The sublimation was repeated at least once to yield **3** as long white needles, mp 98–100 °C. This material must be stored under anhydrous conditions. In order to increase the yield, the isolated byproduct **2** was dried and submitted to the same treatment as described for the synthesis of **3**.

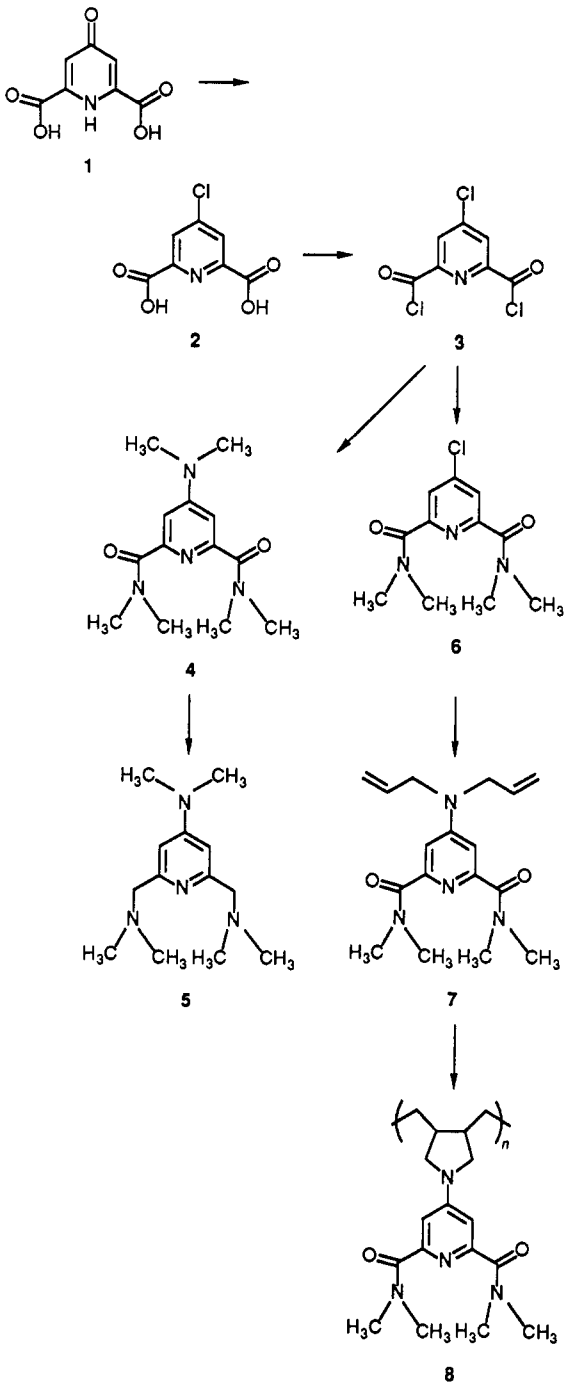
Alternative Synthesis of 3. After the reaction of **1** with PCl_5, complete hydrolysis of the reaction mixture to 4-chloro-2,6-pyridinedicarboxylic acid (**2**) was brought about by allowing the water–chloroform mixture to stir at room temperature. The brown precipitate was filtered and dried under vacuum. To convert **2** into **3**, the precipitate was then refluxed with excess $SOCl_2$ overnight. Thionyl chloride was removed by vacuum distillation, and the crude acid chloride **3** was recrystallized from $CHCl_3$–petroleum ether and then sublimed as described above.

2,6-Bis((*N*,*N*-dimethylamino)formyl)-4-chloropyridine (6). 2,6-Bis(chloroformyl)-4-chloropyridine (**3**) (23.5 g, 0.1 mol) was dissolved in dry dimethylformamide (72 g) in a three-neck (500 mL) flask provided with a thermometer, a magnetic stirrer, and an addition funnel with pressure compensation. The mixture was cooled to 0 °C, and a solution of dimethylamine (27 g, 0.6 mol) in dry dimethylformamide (75 g) was added through the addition funnel. After complete addition, the funnel was replaced by a Liebig condenser and the mixture heated 2 h at 80 °C. A vacuum distillation head was attached and most of the dimethylformamide distilled. Aqueous KOH was added to the remaining product to raise the pH to 11. This was then extracted with $CHCl_3$, which was filtered with phase separation paper and rotary evaporated to give white crystals that were 99% pure by GC: mp 138–140 °C; yield 40%.

2,6-Bis((*N*,*N*-dimethylamino)formyl)-4-(diallylamino)-pyridine (7). 2,6-Bis((*N*,*N*-dimethylamino)formyl)-4-chloropyridine (**6**) (8.7 g, 0.039 mol) was refluxed at 110 °C with freshly distilled diallylamine (30 mL) in a 100-mL three-neck flask provided with a Liebig condenser, a N_2 inlet, a thermometer, and a magnetic stirbar. After 72 h, 98% conversion was achieved as indicated by GC. The cooled reaction mixture was shaken with excess 10% NaOH and extracted with $CHCl_3$. The organic phase was then filtered through phase separation filter paper and rotary evaporated to give a brown oil. Distillation under vacuum yielded a product still contaminated with diallylamine. Pure product (97%) was obtained by recrystallization from ethyl acetate–cyclohexane (50/50). In order to obtain monomer grade product, the monomer was purified by column chromatography on neutral silica gel. Unreacted **6** eluted first with ethyl acetate, and pure monomer **7** eluted with methanol in 99% purity by GC.

Polymerization of 2,6-Bis((*N*,*N*-dimethylamino)-formyl)-4-(diallylamino)pyridine (7). 2,6-Bis((*N*,*N*-dimethylamino)formyl)-4-(diallylamino)pyridine (**7**) (1.72 g, 5.5×10^{-3} mol), 5 mL of H_2O, 0.7 mL of concentrated HCl, and 2,2′-azobis(2-amidinopropane) hydrochloride (V50, Wako Chemicals USA) (0.015 g, 5.5×10^{-5} mol) were charged to a 50-mL Schlenk flask. The solution was submitted to three freeze–thaw cycles and immersed in a water bath at 60 °C. Additional V-50 (0.024 g, 8.8×10^{-5}) was added after 30 h. Precipitation of a pale yellow solid was observed after 2 days. Polymerization was stopped after 5 days, and the yellow supernatant liquid dialyzed 3 days against water with dialysis bags of MW cutoff 3000–6000. The bag

Scheme I



contents were then freeze-dried. The polymer was obtained as a yellow-orange powder that was very soluble in water and methanol but insoluble in THF or $CHCl_3$. The yield was approximately 10%.

2,6-Bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)pyridine (4). 2,6-Bis(chloroformyl)-4-chloropyridine (3) (5 g, 0.06 mol) was dissolved in dry dimethylformamide (60 mL) in a three-neck flask (500 mL) provided with a thermometer, a stirbar, and an addition funnel. A solution of dimethylamine (29 g, 0.61 mol) in dry dimethylformamide (72 g) was added slowly through the addition funnel while the reaction mixture was stirred. The flask was kept at room temperature for 6 h and then heated 6 h at 80 °C. Stirring at room temperature was continued overnight. Dimethylformamide was then distilled off under vacuum. The yellow product remaining in the flask was dissolved in 200 mL of 10% NaOH and extracted with four portions of $CHCl_3$ (50 mL each). After filtration through phase separation filter paper, the organic solvent was rotary evaporated to give a pale yellow solid. Recrystallization from $CHCl_3$–cyclohexane yielded white crystals, mp 175–178 °C.

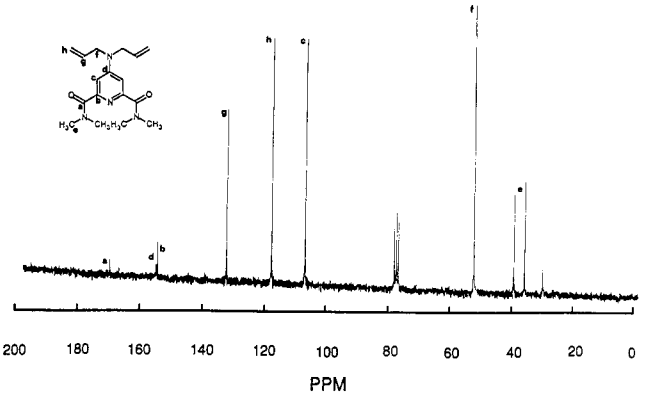


Figure 1. ^{13}C NMR spectrum of 2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(diallylamino)pyridine (7) in $CDCl_3$ (16 227 scans).

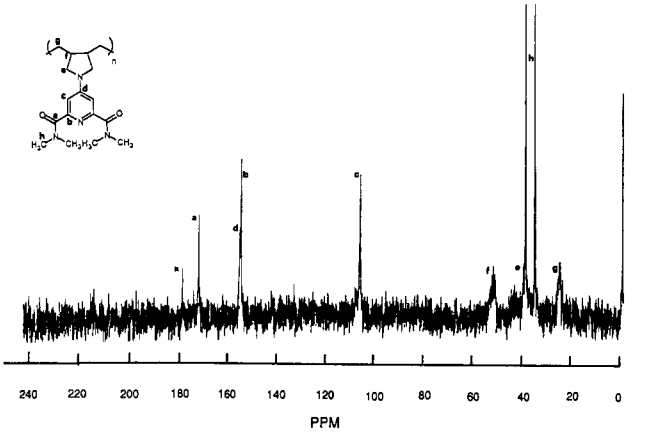


Figure 2. ^{13}C NMR spectrum of poly(2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(diallylamino)pyridine (8) in D_2O (2254 scans).

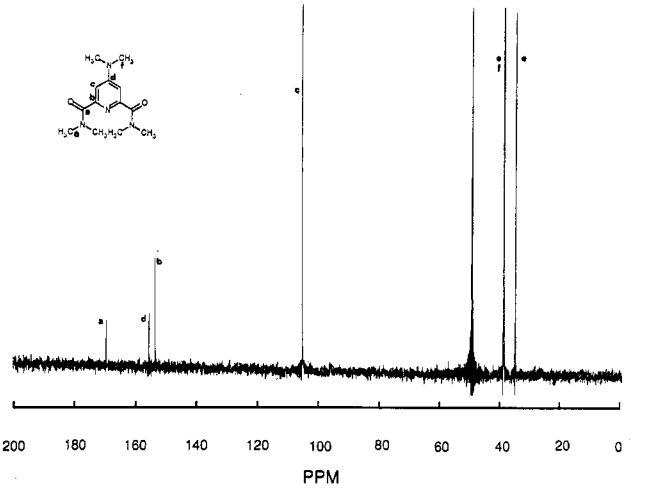


Figure 3. ^{13}C NMR spectrum of 2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)pyridine (4) in MeOD (2031 scans).

2,6-Bis((*N*,*N*-dimethylamino)methyl)-4-(dimethylamino)pyridine (5). A three-neck 500-mL flask provided with a dropping funnel, a reflux condenser, and a magnetic stirbar was dried at 100 °C and allowed to cool to room temperature in a dry N_2 atmosphere. 2,6-Bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)pyridine (4) (5 g, 0.019 mol) was suspended in dry THF (20 mL) and the solution cooled to 0 °C. BH_3·THF solution (120 g, 0.08 mol of BH_3) was transferred by means of a hypodermic syringe into the dropping funnel. This solution was then added over a 20-min period under stirring and cooling. After 2 h, the white suspension was brought to reflux and held there for 48 h

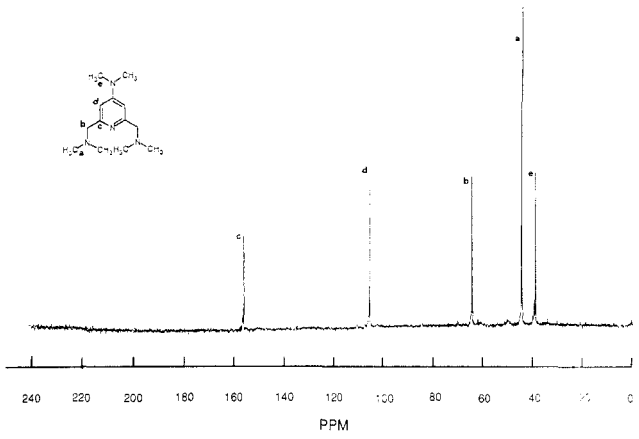


Figure 4. ^{13}C NMR spectrum of 2,6-bis((*N*,*N*-dimethylamino)methyl)-4-(dimethylamino)pyridine (**5**) in D_2O (2171 scans).

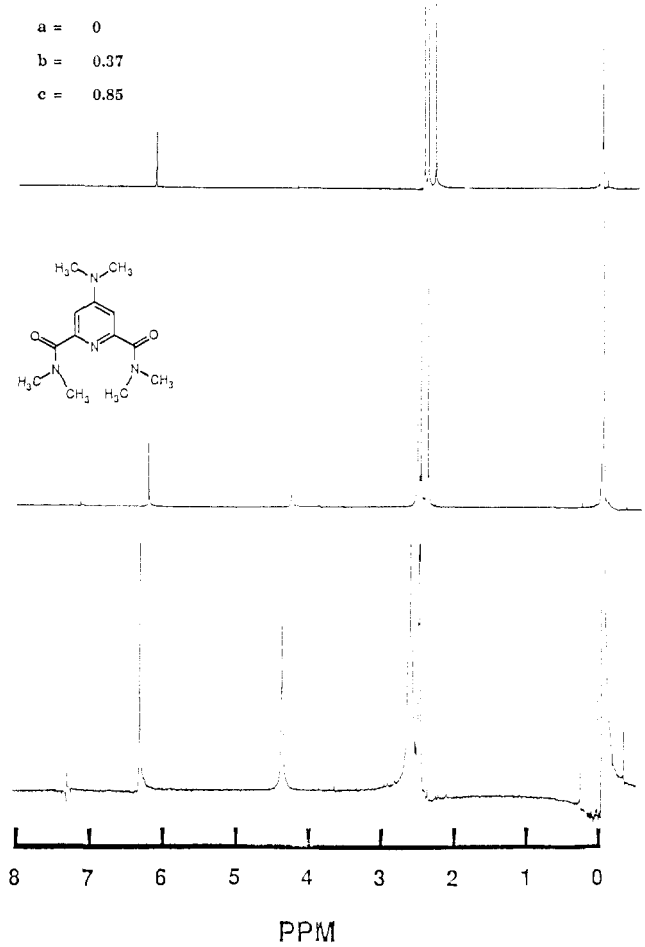


Figure 5. Effect of Ni^{2+} salt on the ^1H-NMR spectrum of 2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)pyridine (**4**) (32 scans each): top, no metal salt; center, metal/ligand ratio 0.37; bottom, metal/ligand ratio 0.85.

during which it turned into a pale green solution. (200 mL, 6 M, HCl) was then added carefully at 0 °C under stirring whereby H_2 gas evolved. THF was then distilled away at atmospheric pressure; further H_2 evolution indicated the decomposition of the amine–borane complex. After setting overnight at room temperature, NaOH pellets were slowly added under cooling and stirring until pH 11 was reached. The solution was transferred to a separation funnel, some H_2O was added to redissolve NaCl, and the mixture was extracted with CH_2Cl_2. The organic phase was filtered through phase separation filter paper and rotary evaporated. Final solvent removal in high vacuum yielded 2.2

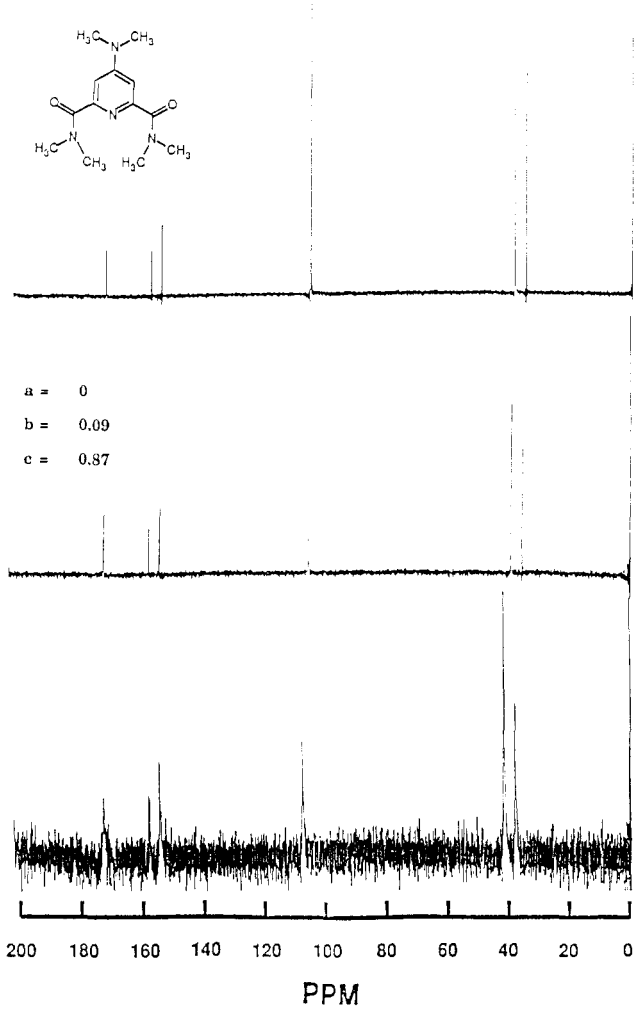


Figure 6. Effect of Ni^{2+} salt on the ^{13}C NMR spectrum of 2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)pyridine (**4**): top: 4254 scans, no metal; center, 2,641 scans, M/L ratio 0.09; bottom, 2300 scans, M/L ratio 0.87.

g of a greenish white, slightly fishy smelling syrup that solidified in the refrigerator to give a product that was 99% pure by GC.

Results and Discussion

The synthetic steps yielding 2,6-bis((dimethylamino)-formyl)-4-(diallylamino)pyridine (**7**) and related compounds are shown in Scheme I.

Reasonable to good yields for the synthesis of these compounds were obtained. Polymerization of **7** was slow and required relatively large amounts of initiator. Similar behavior had been observed before for DAAP homo- and copolymerization. We were happy to see any homopolymerization of **7**, however, because of the large steric inhibition to monomer addition to the growing chain that can be imagined for the bulky pendant group.

^{13}C NMR analysis of the monomer (Figure 1) was made by comparison with previously synthesized compounds. Figure 2 shows the spectrum of the homopolymer and the corresponding peak assignments. The ×-labeled peak (178 ppm) could not be assigned to any carbon of the monomer unit. It is probably due to the carboxylic acid carbon that may form by partial hydrolysis of the amide groups of the polymer or monomer under strong acid conditions necessary to ensure polymerizability. The poor resolution of the peaks corresponding to the backbone and pyrrolidinic carbons is probably the result of tacticity and/or cis–trans isomerism. This has been observed also in the homo-

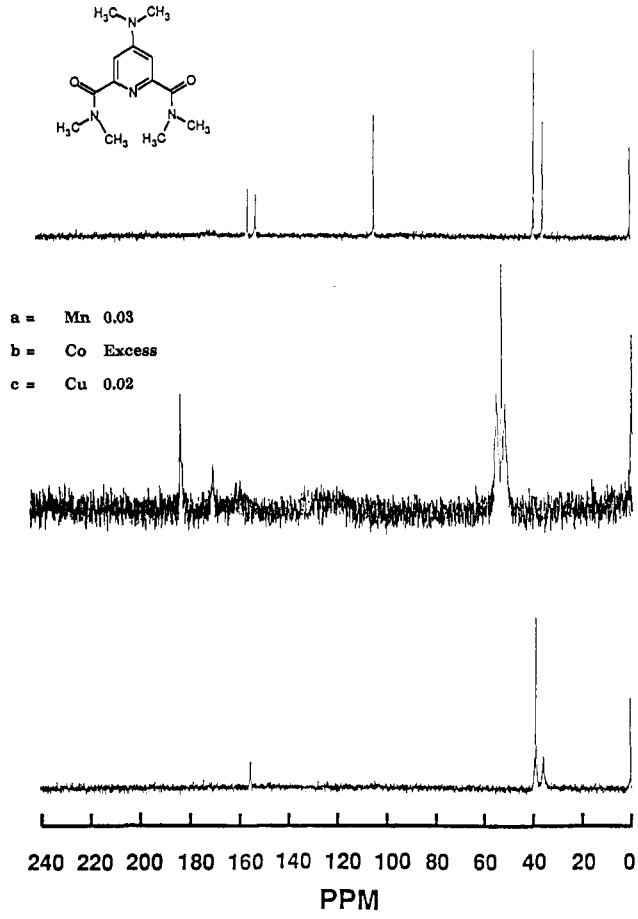


Figure 7. ^{13}C NMR spectra of some metal complexes of 2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)pyridine (**4**): top, 1536 scans, Mn^{2+}/L ratio 0.03; center, 7,894 scans, Co^{2+} excess; bottom, 2087 scans, Cu^{2+}/L ratio 0.02.

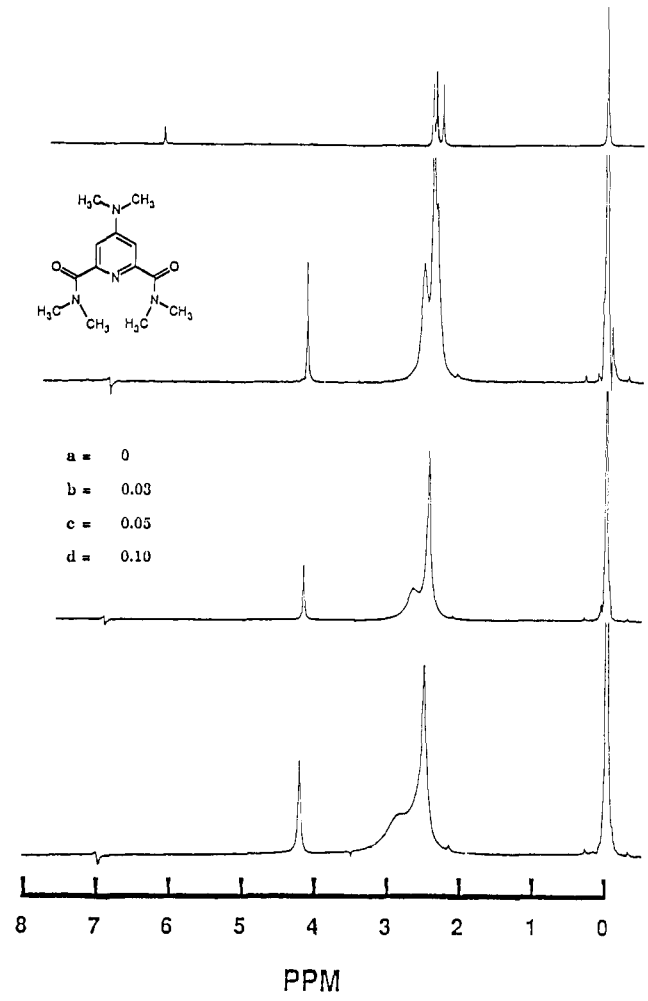


Figure 8. Effect of Cu^{2+} salt on the ^1H NMR spectrum of 2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)pyridine (**4**) (16 scans each): top, M/L ratio 0; second, M/L ratio 0.03; third, M/L ratio 0.05; bottom, M/L ratio 0.10.

polymer of the parent monomer DAAP (**3**). ^{13}C NMR of the model compounds (Figures 3 and 4) and off-resonance spectra confirmed the expected structures.

Complexing Activity of the Model Compounds 4 and 5 and the Homopolymer 8

The metal binding capacity of pyridines and similar N-containing compounds is well-known.[7,11] The products under investigation should also display ligand character, especially with transition-metal cations. The effect of complexation was observed macroscopically by mixing aqueous solutions of Cu^{2+} salt and homopolymer **8**. Immediate separation was observed of a green precipitate that could be redissolved slowly by the addition of more ligand. For low molecular weight compounds, precipitation of the complex did not occur, although color changes were evident when mixtures were prepared of ligand **5** and Cu^{2+} salt in water.

NMR spectroscopy gives better insight into the nature and strength of the binding between metal and ligand due to the interaction between the nucleus attached to the metal and the unpaired electron spin density.[12-14] Even if binding does not involve H or C directly, the chemical shifts are expected to vary due to changes in electron densities on the atoms complexing the metal. Changes in the peak width are also possible as the result of changes in the relaxation times of the nuclei close to the paramagnetic centers. We decided to investigate the binding ability for different metals in a qualitative way using both ^1H and ^{13}C NMR spectroscopy by observing changes in chemical shift and/or peak shape upon addition of increasing amounts of metal salt solution. All spectra were recorded at room temperature with TMS (tetramethylsilane) as chemical shift standard.

First we investigated the effect of Ni^{2+} on the ^1H NMR spectrum of **4**. Figure 5 shows the spectrum in D_2O after the addition of Ni^{2+} salt to metal-to-ligand ratios of 0.37 and 0.85. The peak at 6.08 ppm corresponds to the aryl protons, the doublet centered at 2.42 ppm to the nonequivalent amide N-methyl protons, and the singlet at 2.38 ppm to the 4-*N*-methyl protons. The peak at 4.15 ppm is DHO, and its intensity increases with increasing amount of salt that contains water of crystallization. Addition of $NiCl_2$ solution at a 0.37 metal/ligand ratio resulted in a shift of the pyridine proton absorption to 6.2, while those of the amide methyl protons shift 0.1 ppm downfield. The distortion observed at a 0.85 ratio is due to a too strong TMS signal which could not be phased properly. The other protons were present at too low a concentration to be observed after successive dilutions with the salt solution.

Figure 6 shows the ^{13}C NMR spectrum of **4** in D_2O. Additions of Ni^{2+} salt produce no substantial changes in the chemical shifts or in the bandwidths. The poor signal to noise ratio is most probably due to the increasing dilution of the ligand with increasing salt concentration. The effect of other metal ions (Cu^{2+}, Co^{2+}, and Mn^{2+}) on the NMR spectra of this ligand was also studied. Figure 7 shows that all three metal cations cause considerable

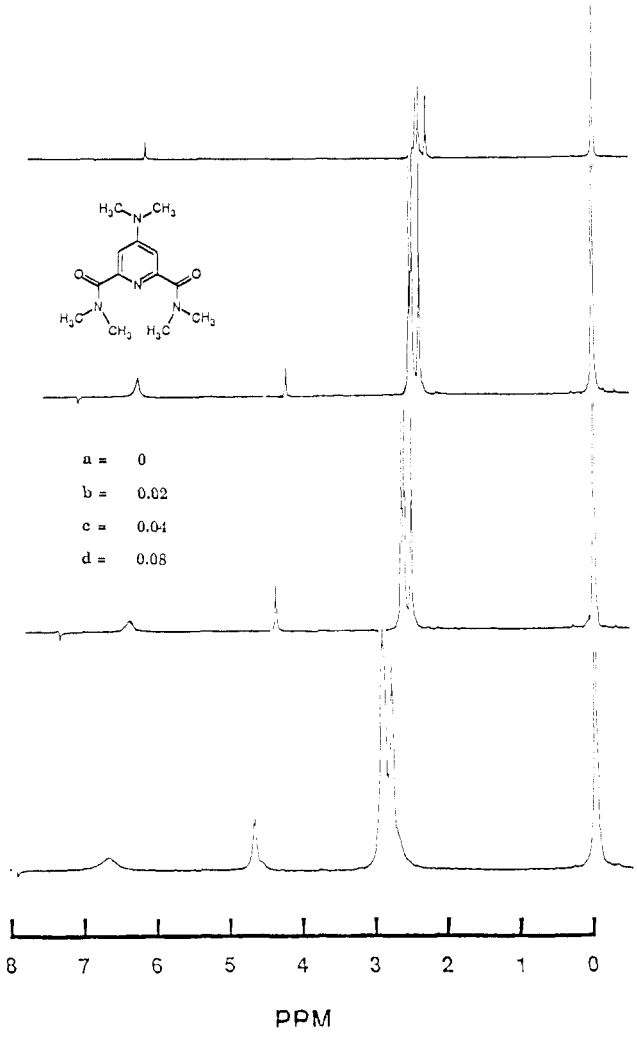


Figure 9. Effect of Co^{2+} salt on the ^1H NMR spectrum of 2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)pyridine (**4**) (16 scans each): top, M/L ratio 0; second, M/L ratio 0.02; third, M/L ratio 0.04; bottom, M/L ratio 0.08.

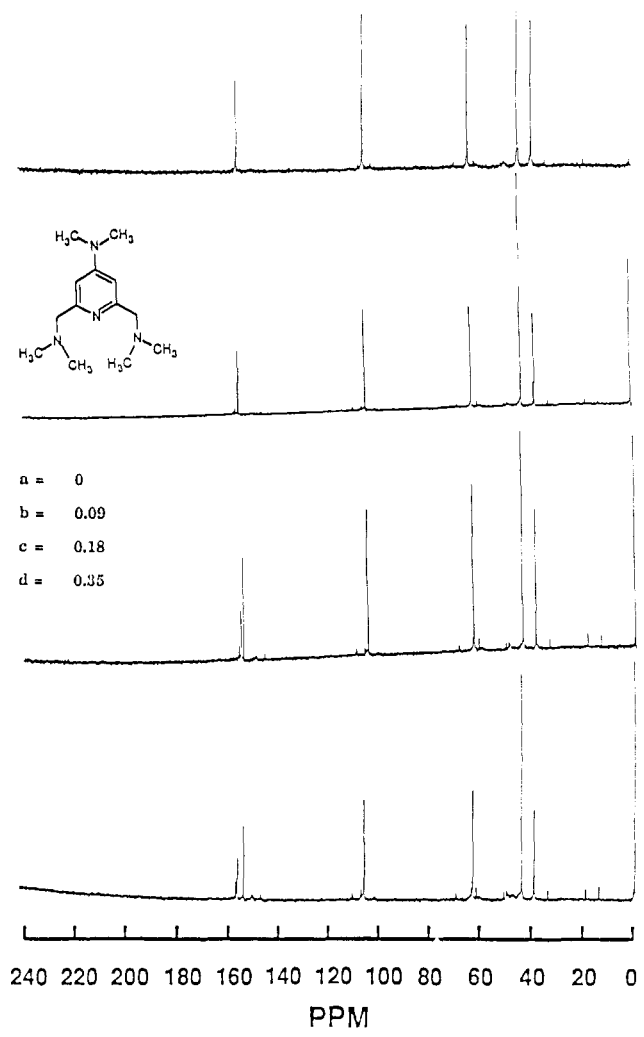


Figure 10. Effect of Cu^{2+} salt on the ^{13}C NMR spectrum of 2,6-bis((*N*,*N*-dimethylamino)methyl)-4-(dimethylamino)pyridine (**5**): top, 2171 scans, M/L ratio 0; second, 14400 scans, M/L ratio 0.09; third, 6134 scans, M/L ratio 0.18; bottom, 17264 scans, M/L ratio 0.35.

changes in the ^{13}C NMR spectrum of **4**. The upper spectrum corresponds to the addition of Mn^{2+} salt at a metal-to-ligand ratio of 0.03. It is evident by comparison with Figure 5, upper spectrum, that the peak corresponding to the carbonyl carbons (173 ppm) completely disappears. The pyridine carbon peaks and the amide carbon peaks suffer only minor chemical shift changes. The middle spectrum in Figure 7 was obtained after addition of more than a stoichiometric amount of Co^{2+} salt to a soltuion of **4**. The modification of both chemical shift and peak widths of all peaks is evident. The fact that not only the carbonyl peak was affected points to a different kind of complexing interaction or medium effect. A 0.02 molar ratio of Cu^{2+} to **4** gave the lower spectrum of Figure 7. Both the carbonyl and two of the three pyridine carbon peaks disappear, showing again a different type of metal–ligand interaction. The ^1H NMR specturm of **4** (Figure 8) confirms this. Disappearance of the pyridine proton peak at 6.5 ppm along with peak broadening of the other peaks upon addition of Cu^{2+} is evident. (The peak at 4.2 ppm corresponds to DHO.)

Figure 9 shows the corresponding changes in the ^1H NMR spectrum upon addition of Co^{2+} salt. In this case, no peaks disappear, although general broadening is observed as in the ^{13}C NMR spectrum (Figure 7, middle). We conclude that the difference in the spectra of the complexed ligand **4** is due to different binding geometries or bonding. For instance, the exclusive disappearance of the carbonyl peak with Mn^{2+} as cation points to a preferential binding of the metal to the oxygen atoms (directly attached to the carbon atoms whose peak is missing) and not to the corresponding nitrogen atoms. In the latter case we would expect a comparatively larger effect on the methyl carbon than on the carbonyl carbon. This is the case when Co^{2+} and Cu^{2+} are used. Several peaks undergo modifications that may be the result of different binding modes. The ligand has also an amine function (as the amide) whose strong affinity for metal cations like Cu^{2+} and Co^{2+} is known. This may be the reason for the changes observed in the pyridine H and C peaks in Figures 7 and 8. With Co^{2+}, the general broadening suggests that both binding geometries are present (Figures 7 and 9).

The chelating ability of **5** was investigated in the same way. Figure 10 shows the ^{13}C NMR spectrum of **5** with increasing amounts on Cu^{2+}. Two of the pyridine peaks (that in the noncomplexed material appear at 156 ppm) are differently affected by complexation. The remaining peaks are not affected by complexation.

Finally, we investigated the effect of Cu^{2+} and Mn^{2+} salts on the ^{13}C NMR spectrum of poly(2,6-bis((dimethylamino)formyl)-4-(diallylamino)pyridine) (**8**) (Figures 11 and 12). In both cases line broadening is evident along with the disappearance of the carbonyl carbon peaks.

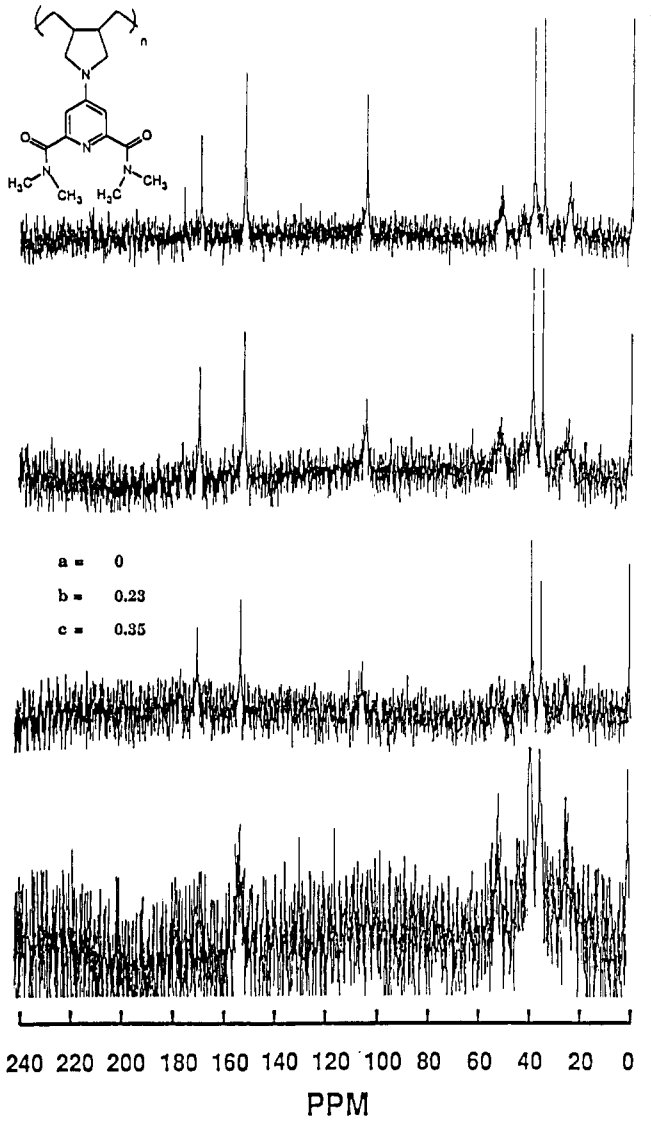


Figure 11. Effect of Cu^{2+} salt on the ^{13}C NMR spectrum of poly(2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)-pyridine) (**8**): top, 2254 scans, M/L ratio 0; second, 4271 scans, M/L ratio 0.23; third, 1,271 scans, M/L ratio 0.35; bottom, 7,980 scans, M/L ratio 0.50.

Comparison with the model compound **4** suggests that this effect is more remarkable with Mn^{2+} (Figure 12) than with Cu^{2+}. On the contrary, the pyridine carbon peak at 109 ppm seems to be more affected than the rest by complexation with Cu^{2+} than with Mn^{2+}, for which peak broadening is less localized. In summary we can conclude that complexation with Mn^{2+} seems to involve the carbonyl oxygens to a higher degree than the amide nitrogens as shown by the disappearance of the corresponding peak. A more stable complex appears to be formed as indicated by the line broadening observed even at low metal:ligand ratios. With Cu^{2+} salts, the line broadening that leads to peak disappearance is not as localized, and chemical shift changes do not take place.

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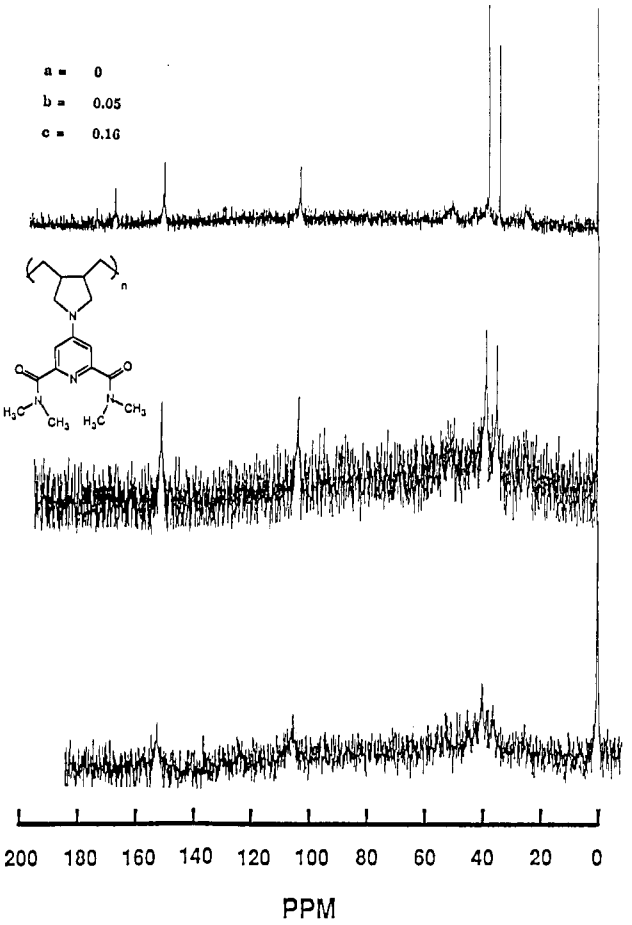

Figure 12. Effect of Mn^{2+} salt on the ^{13}C NMR spectrum of poly(2,6-bis((*N*,*N*-dimethylamino)formyl)-4-(dimethylamino)-pyridine) (**8**): top, 4,470 scans, M/L ratio 0; center, 19,789 scans, M/L ratio 0.05; bottom, 19914 scans, M/L ratio 0.16.

Registry No. **1**, 138-60-3; **2**, 4722-94-5; **3**, 71022-75-8; **4**, 123597-05-7; **5**, 123597-06-8; **6**, 123597-07-9; **7**, 123597-08-0; **8**, 123597-10-4; Cu, 7440-50-8; Ni, 7440-02-0; Mn, 7439-96-5; Co, 7440-48-4; dimethylamine, 124-40-3; diallylamine, 124-02-7.

References and Notes

(1) Hofle, G.; Steglich, W.; Vorbruggin, H. *Angew. Chem., Intl. Ed. Engl.* **1978**, *17*, 569.
(2) Hassner, A.; Krepski, L. R.; Alexanian, V. *Tetrahedron* **1978**, *34*, 2069.
(3) Scriven, E. F. V. *Chem. Soc. Rev.* **1983**, *12*, 129.
(4) Mathias, L. J.; Vaidya, R. A.; Bloodworth, R. H. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 289.
(5) Mathias, L. J.; Cei, G. *Macromolecules* **1987**, *20*, 2645.
(6) Mathias, L. J.; Vaidya, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 5514.
(7) Frechet, J. M. J.; Meftahi, M. V. *Br. Polym. J.* **1984**, *16*, 193.
(8) Koning, C. E.; Eshuis, J. W.; Viersen, F. J.; Challa, G. *React. Polym. Ion Exch., Sorbents* **1986**, *4*, 293.
(9) Bradshaw, J. S.; Asay, R. E.; Maas, G. E.; Izatt, R. M.; Christiansen, J. J. *J. Heterocycl. Chem.* **1978**, *15*, 825.
(10) Pallavicini, P. S.; Perotti, A.; Poggi, A.; Seghi, B.; Fabrizzi, L. *J. Am. Chem. Soc.* **1987**, *109*, 5139.
(11) Nishikawa, H.; Tsuchida, E. *J. Phys. Chem.* **1975**, *79*, 2072.
(12) Milner, R. S.; Pratt, L. *Discuss. Faraday Soc.* **1962**, *34*, 88.
(13) Bradshaw, J. S.; Maas, G. E.; Lamb, J. D., Izatt, R. M.; Christiansen, J. J. *J. Am. Chem. Soc.* **1980**, *102*, 467.
(14) Mathias, L. J.; Vaidya, R. A.; Halley, R. J. *J. Appl. Polym. Sci.* **1987**, *33*, 1157.