

# Amide Derivatives of Poly(3,4-Dimethylenepyrrolidine): Synthesis, Characterization, and Complexation Studies

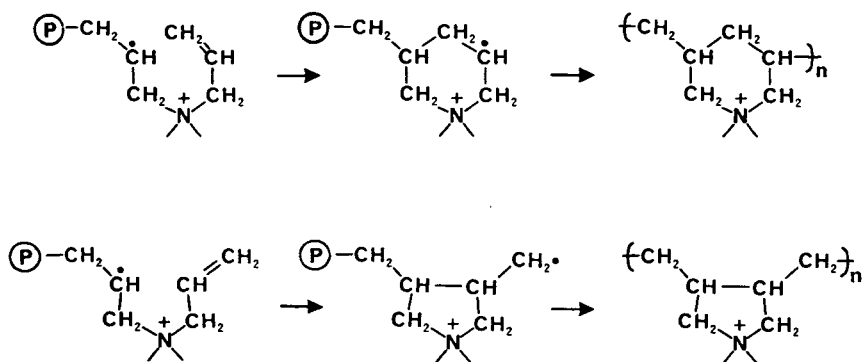
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## Synopsis

Improved synthesis of polydiallylamine provides ready access to an entire family of amide-functionalized polymers. Complete conversion to the acetamide derivative was attained under mild conditions. Formation of the formamide polymer required harsher conditions and did not give complete functionalization. The formamide polymer displayed typical polyelectrolyte behavior caused by residual amine units. Complexation with iodine and transition metal cations was strong as shown by UV, IR, and  $^{13}\text{C}$ -NMR evidence indicating potential of these polymers for trace metal recovery, waste water treatment, and antiseptic formulations.

## INTRODUCTION

In 1949, Professor George Butler and his co-workers at the University of Florida discovered that quaternary diallylammonium salts underwent free radical polymerization to give soluble high polymers.<sup>1</sup> Monomers containing one or three allyl groups reportedly did not polymerize or yielded crosslinked products.<sup>2</sup> Five years later a thermodynamically reasonable mechanism involving alternate inter- and intramolecular radical addition to yield piperidine rings in the polymer backbone was proposed (Scheme 1, upper pathway).<sup>3</sup> Degradation studies of the polymers supported the presence of six-membered cyclic amines as part of the polymer backbone.<sup>4</sup>



Scheme 1. Reaction pathways for cyclopolymerization

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In 1960, Professor Butler discovered that cyclopolymerization of allyl crotonate yielded polymers containing five-membered lactones.<sup>5</sup> Such cyclic units can only be formed if the intramolecular radical attack occurs at the beta carbon to yield the less stable primary radical (as in Scheme 1, lower pathway). Subsequently, a large number of cyclopolymerizations were shown to proceed via the less stable radical intermediate. Recent spectroscopic investigations have shown that cyclopolymers of diallylammonium salts contain five-membered pyrrolidine rings rather than piperidine rings proposed earlier.<sup>6</sup>

Rationalization of this preference for five-membered ring formation has been based on steric and electronic factors.<sup>7</sup> The approach of a secondary radical (from intermolecular addition) to the gamma carbon is hindered by the hydrogen on the  $sp^2$  gamma carbon. No hindrance exists for attack at the beta carbon. Through-space electronic interaction between the initial radical and the double-bond of the other allyl moiety may also direct reaction to the beta carbon. The overall result is that the five-membered ring is the preferred kinetic product, although the six-membered product is thermodynamically more stable.

Since the discovery of cyclopolymerization, a large number of substituted diallylamines have been cyclopolymerized with varying success. Substitution of bulky groups on the beta carbon was shown to increase piperidine ring formation.<sup>8</sup> Numerous *N*-substituents have been incorporated into diallylamine monomers with the intent of synthesizing functionalized polyamines.<sup>9-12</sup> Diallylamines have been copolymerized with sulfur dioxide<sup>13</sup> and acrylic monomers,<sup>12,14</sup> but copolymerizability with vinyl monomers was generally found to be poor. Comonomers used to promote crosslinking have included triallylamine,<sup>15</sup> 1,6-bis(diallylamino)hexane,<sup>16</sup> and other bisdiallylamines.<sup>9,10</sup> Crosslinked polymers may also be synthesized by reacting neutral polyamines with dihaloalkanes after cyclopolymerization.<sup>17</sup>

Initiation of cyclopolymerizations in aqueous acidic media initially involved water-soluble peroxides.<sup>1,2</sup> A redox initiation system consisting of  $TiCl_3/H_2O_2$  was later claimed to yield better results.<sup>18</sup> Recently the use of a water-soluble azo initiator (V-50) has proved to be very effective for polymerization of allyl amines in aqueous media.<sup>19</sup> Solvents such as dimethylsulfoxide (DMSO), dimethylformamide, or methanol have been used as nonaqueous media for cyclopolymerizations initiated with ammonium persulfate, benzoyl peroxide, or AIBN.<sup>13</sup> Diallylamine-hydrochloride has been reported to yield its highest molecular weight cyclopolymer when polymerized in DMSO with ammonium persulfate.<sup>20</sup>

Our interest in diallylamine polymerizations involved use of the known preference for five-membered ring formation to achieve two goals simultaneously: polymer formation plus generation of *N*-substituted pyrrolidine repeat units that were stable to various reaction conditions. This approach has led to the first synthesis of a highly active homopolymer containing supernucleophilic 4-pyrrolidinopyridine units.<sup>21</sup> As part of this project, clean synthetic approaches to various homo- and copolymers of amide derivatives of the basic poly(3,4-dimethylenepyrrolidine) were needed. This paper describes the best methods we have found for synthesis and derivatization of the parent polymer, characterization of the amide polymers by spectroscopy and viscom-

etry, and qualitative evaluation of the ability of the amide derivatives to function like poly(*N*-vinylpyrrolidone) in the complexation of iodine and metal salts.

## EXPERIMENTAL

### Materials

All reagents and chemicals were used as received from commercial sources or purified as indicated. Reagent grade solvents and deionized water were utilized for all synthetic procedures. Spectrophotometric grade absolute methanol was used for the spectroscopic analysis.

### Diallylamine Hydrochloride

The pale yellow diallylamine obtained commercially was only 97% pure. Distillation at a vacuum of 15 in. mercury, with a pot temperature of 75°C and a vapor temperature of 62°C, gave a clear, colorless liquid that was > 99% pure by GC.

Freshly distilled diallylamine (200 mL) was diluted with anhydrous ether (500 mL) and the solution cooled to 0°C. Technical grade HCl gas (Matheson) was bubbled through the solution for 10 min to form the hydrochloride salt which precipitated as white crystals. The precipitate was filtered and washed with cold anhydrous ether. The diallylamine hydrochloride was recrystallized from acetone to give product with a melting point of 165°C. This salt must be stored under dry, inert conditions.

### Polymerization of Diallylamine Hydrochloride

Diallylamine hydrochloride (20 g) was dissolved in deionized water (20 g) and the solution placed in a capped polymerization tube. The contents were degassed by bubbling nitrogen through the solution. *t*-Butylhydroperoxide (400 μL, Lucidol, 90% aqueous solution) was injected into the tube which was then immersed in a bath maintained at 65°C. Polymerization was carried out at this temperature for 96 h with a constant flow of nitrogen through the headspace. The resulting polymer solution had a light brown color and was highly viscous. The fact that the polymer was completely soluble indicated absence of crosslinking.

The "as-polymerized" aqueous solution of poly(diallylamine hydrochloride) was diluted with deionized water to reduce the viscosity to a manageable level. The diluted solution was cooled to 2–3°C and an excess of 6*N* sodium hydroxide was added slowly. The polymer precipitated, and was filtered and washed with deionized water.

Alternative initiation involved the use of a TiCl<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> redox system. A 14% by weight solution of TiCl<sub>3</sub> in deionized water was made inside a dry glove bag (caution: The solution gets very hot as the salt dissolves). A 15% by weight solution of H<sub>2</sub>O<sub>2</sub> in water was used as purchased. Initiation involved alternative addition of one drop of each solution till the polymerization mixture became very viscous. The polymerization temperature was held at 0°C. Post-polymerization work-up was the same as before. The polymer made by this procedure was much darker in color than the peroxide product.

### Alternative Polymerization of Diallylamine

Freshly-distilled diallylamine (5 g, 0.0515 mol) was added to concentrated aqueous HCl (5.3 mL, 10% molar excess) held at 0 °C. The solution was purged with nitrogen for 15 min, and V-50<sup>19</sup> (2,2'-azobisamidinopropane hydrochloride, 0.14 g, 1 mol%) was added. The reactor was sealed and kept under nitrogen. The contents were heated at 60 °C for 36 h. The resulting viscous solution was cooled in an ice bath and excess 6N NaOH was added slowly. The precipitated polymer was filtered, washed with deionized water, and dried *in vacuo*.

### Synthesis of Poly(diallyl Acetamide) (PDAA)

Poly(diallylamine) (2.15 g) was dissolved in chloroform (30 mL). The polymer took 4–5 h to give a cloudy solution which appeared to be on the brink of phase separation. Acetic anhydride (3 eq) was added, and the mixture stirred for 18 h at room temperature. The resulting clear solution indicated that the product polymer was soluble in chloroform. The polymer was precipitated by adding the reaction mixture to dry ether (300 mL). The gelatinous precipitate was separated by decanting and then washed with more dry ether. The precipitate was dried *in vacuo* for 24 h to remove solvent. The intrinsic viscosity of the polymer in chloroform at 25 °C was determined to be 0.50 ± 0.01 dL/g.

### Synthesis of Poly(diallyl Formamide) (PDAF)

Polydiallylamine (5 g) was weighed into a round bottom flask and 100 mL of 88% formic acid was added. The inhomogeneous reaction mixture was heated to reflux and maintained at that temperature for 24 h during which complete dissolution of the polymer took place. Most of the formic acid was distilled from the reaction mixture. The resulting mixture was dissolved in water and precipitated by adding excess cold aqueous 6N NaOH. The precipitated polymer was redissolved in a small amount of water and freeze-dried to obtain clean, dry product.

### Synthesis of Diallyl Formamide

Distilled diallylamine (50 mL, 0.4 mol), 88% formic acid (30 mL, 0.7 mol), and dimethylformamide (200 mL) were mixed in a round bottom flask and heated to reflux (145 °C) for 24 h. The initial and final reaction mixtures were analyzed by GC, and only small amounts of unreacted diallylamine were found to be present at the end of 24 h. The reaction mixture was distilled under a vacuum of 25 in. of mercury. Fractions boiling at vapor temperatures of 80–128 °C were discarded. The remaining fraction was redistilled to obtain a pure middle fraction boiling at 135 °C. The product was characterized by FTIR, GC, and <sup>13</sup>C-NMR.

### Attempted Polymerization of Diallylformamide

Diallylformamide (3.11 g) was mixed with an equal weight of deionized water. The solution was purged with nitrogen and V-50 (0.67 g, 1 mol %) was

added to the mixture. The polymerization was carried out at 60 °C for 36 h. No increase in viscosity was observed, and the polymerization mixture was found to contain only unreacted monomer. Attempts were also made to polymerize the monomer in aqueous acid and in the presence of a slight excess of  $\text{CaCl}_2$  or  $\text{CuCl}_2$ . All attempts failed to yield polymer.

### Analytical Methods

All viscosities were run on the same #75 Cannon-Ubbelohde semimicro viscometer in a constant temperature bath held at  $25 \pm 0.01^\circ\text{C}$ . Solutions were made immediately prior to the viscosity runs.

All IR spectra were obtained on a Nicolet 5DX FTIR. A CIRcle cell (Spectra-Physics) was used to analyze aqueous solutions of PDAF. Incremental additions of a concentrated solution of  $\text{CuCl}_2$  were made to the solution of polymer in the CIRcle cell, and an IR spectrum was made after each addition. The concentration of the copper solution was high enough so that only a minute change in polymer concentration occurred. The same number of scans were used for all the solutions. IR spectra were also made of films drawn on a polypropylene plate, dried in a vacuum oven, and placed on a salt plate.

All UV spectra were obtained on a Perkin-Elmer 320 UV spectrometer with methanol as the solvent. Comparison was made between spectra of iodine, the polymer, and mixtures of the two.

NMR examination of metal ion complexation involved adding small increments of  $\text{CuCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{MnCl}_2$ , or  $\text{CoSO}_4$  to 50% aqueous solutions of the polymer. Carbon-13 spectra were obtained for each solution with a JEOL FX90Q NMR spectrometer, including one spectrum for each sample with no ions added.  $^{15}\text{N}$ -NMR spectra were obtained on a Bruker 200 MSL using  $^1\text{H}$ - $^{15}\text{N}$  crosspolarization.

## RESULTS AND DISCUSSION

### Polymer Syntheses

There are two basic approaches to the synthesis of functionalized polymers. The one most commonly used involves formation of the polymer backbone followed by incorporation of the desired functionality in one or more steps. This approach requires high-yield reactions so that complete conversion and controllable product formation occur. Usually, however, side products and residual starting functionality are present in the final polymer that can interfere with the intended application.

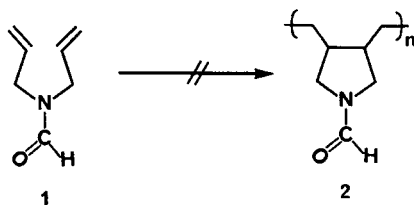
The most efficient approach involves synthesis of a monomer or monomers with needed functionality already present in its active form or in an easily liberated nascent form. Homopolymerization and copolymerization then result in polymers with well-defined, uncontaminated functionality distributed along the backbone. This approach is not always successful, however, because the desired functionalized monomer may not polymerize.

### Attempted Polymerization of *N,N*-Diallylformamide

The goal of this project was formation of homopolymers and especially copolymers containing amide derivatives of backbone pyrrolidine units. The

polymerization process required for copolymer formation involved cyclopolymerization of diallylamine derivatives. The ideal monomer would be the diallylformamide if cyclopolymerization would occur cleanly as is found for diallyl ammonium salts.

*N,N*-diallylformamide (1) was synthesized readily by condensation of diallylamine and excess formic acid. Distillation gave material of spectroscopic and GC purity. Unfortunately, this material, under a variety of conditions used for radical polymerization, failed to give homopolymer (2) even in the presence of HCl and complexing agents added to polarize the amide bond and increase positive charge on the nitrogen:



Scheme 2

During the course of these investigations we developed a  $^{13}\text{C}$ -NMR method for predicting free radical polymerizability of allyl monomers.<sup>22</sup> This technique utilizes the chemical shifts of the alkene carbons of the allyl group. It was found empirically that the closer these two peaks are in the spectrum, the better the polymerizability. A critical difference of about 10–12 ppm was observed; i.e., those monomers with chemical shift differences less than 10 ppm polymerize well while those with values of 16 or more do not polymerize at all. Figure 1 gives the  $^{13}\text{C}$  spectra of the formamide and diallammonium chloride for comparison. Diallylformamide has a difference value of 15, and it is not surprising that polymerization does not occur.

### Polydiallylamine

Formation of this polymer involved two improvements over the procedures described in the earlier literature. First, it was found that isolation and purification of the diallylammonium chloride salt was not necessary. In fact, recrystallization led to loss of the monomer and involved handling a very hydroscopic salt. The salt is also oxidatively unstable and may yellow in air or upon heating for recrystallization. Careful distillation of diallylamine under nitrogen (necessary for generation of the HCl salt anyway) followed by immediate dissolution in the aqueous HCl polymerization solvent gave reproducible high yields of polymer with excellent properties.

The second improvement in the polymer synthesis was described previously by others and involves the use of a water-soluble azo initiator V-50.<sup>19</sup> We observed that an initiator concentration of 1–2% gave the best combination of polymerization rate (24–36 h) and polymer yield (> 80%). Most importantly, the polymer thus obtained (4) displayed excellent solubility in aqueous acid and contained no residual unsaturation which might lead to crosslinking. The

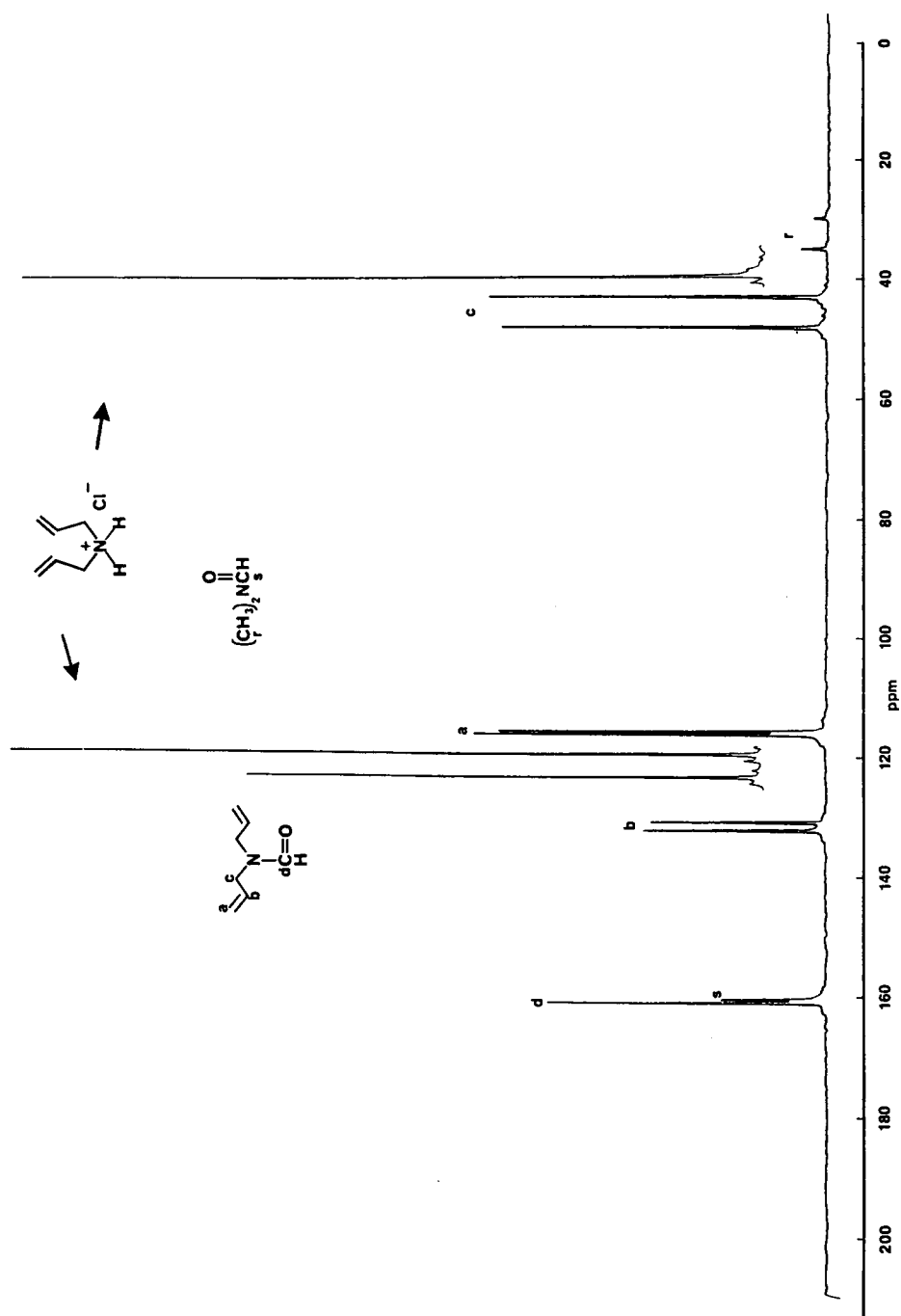
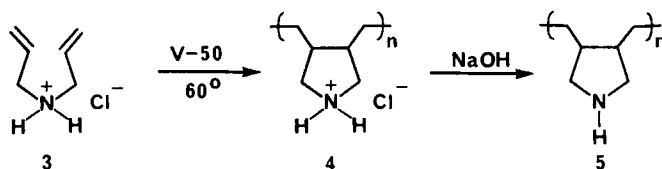


Fig. 1.  $^{13}\text{C}$ -NMR spectra of  $N,N'$ -diallylformamide (full lower spectrum) and diallylammonium chloride (upper inserts).

azo initiator did not cause polymer discoloration as found for peroxide and redox initiators. Presumably, elimination of the colored functionality (probably carbonyl groups as indicated by  $^{13}\text{C-NMR}$ ) also reduces the likelihood of product contamination by undesired reactive functionality.



Scheme 3

Polymer purification involved careful neutralization of the aqueous polymerization mixture to give **5** followed by extensive washing of the precipitated product with type I deionized water. IR and  $^{13}\text{C-NMR}$  spectra of the polymer redissolved in aqueous HCl are given in Figures 2 and 3. The latter clearly shows a pair of peaks for each carbon of the polymer corresponding to *cis* and *trans* substitution of the pyrrolidine units. No evidence of six-membered ring formation was observed.<sup>6,7</sup>

### Acetamide Derivative

The major difficulty with derivatization of the pyrrolidine polymer (**5**) is insolubility in most organic solvents. In fact, the only two common solvents that **5** was soluble in were ethanol and chloroform. Both have drawbacks. The former is reactive to most amide-forming reagents, and the latter does not give completely clear solutions. Chloroform also shows evidence of a slow reaction with the amine polymer that may involve carbene formation and/or nitrogen substitution resulting in crosslinking. However, if the amidation reaction is sufficiently rapid, good conversion to the functionalized polymer is observed.

The acetamide derivative (**6**) was obtained by reacting a threefold excess of acetic anhydride with the partially dissolved polymer in  $\text{CHCl}_3$  at room temperature. The reaction was complete in 18 h. Polymer purification involved reprecipitation from  $\text{CHCl}_3$  into dry ether and/or dialysis in water followed by freeze drying. The final polymer was readily soluble in water and many organic solvents including alcohols and chloroform. The latter was used to obtain an intrinsic viscosity of 0.50 at  $25^\circ\text{C}$ . The Huggins and Kraemer constants for this data were almost ideal at 0.353 and  $-0.14$ , indicating that this is a well-behaved polymer in terms of solution properties in organic solvents.

Spectral characterization involved both IR and NMR. No residual amine groups were observed in the IR of a carefully dried sample (Fig. 4). The  $^{13}\text{C}$  spectrum displayed the same ratio of *cis*-to-*trans* substituted rings as in the starting polymer (Fig. 5). The residual acetic acid observed in this spectrum



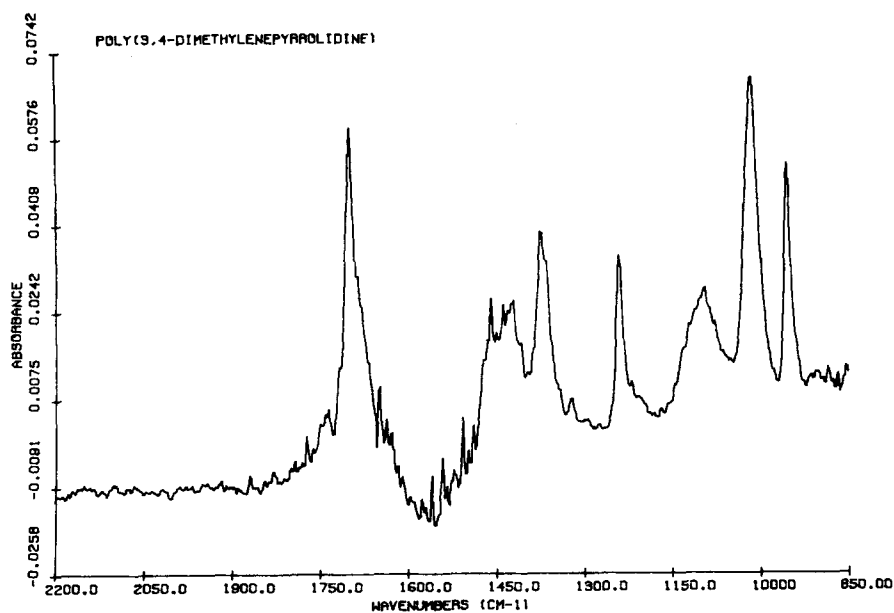


Fig. 2. FT-IR spectrum of poly(3,4-dimethylenepyrrolidine) in dilute aqueous HCl.

POLY(3,4-DIMETHYLENEPYRROLIDINE)

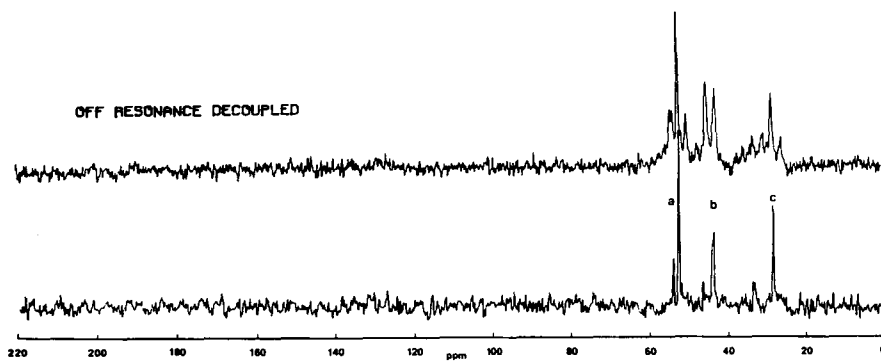
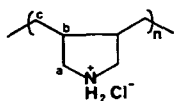


Fig. 3.  $^{13}\text{C}$ -NMR spectra of poly(3,4-dimethylenepyrrolidine) in dilute aqueous HCl: (lower spectrum) fully decoupled; (upper spectrum) off resonance decoupled.

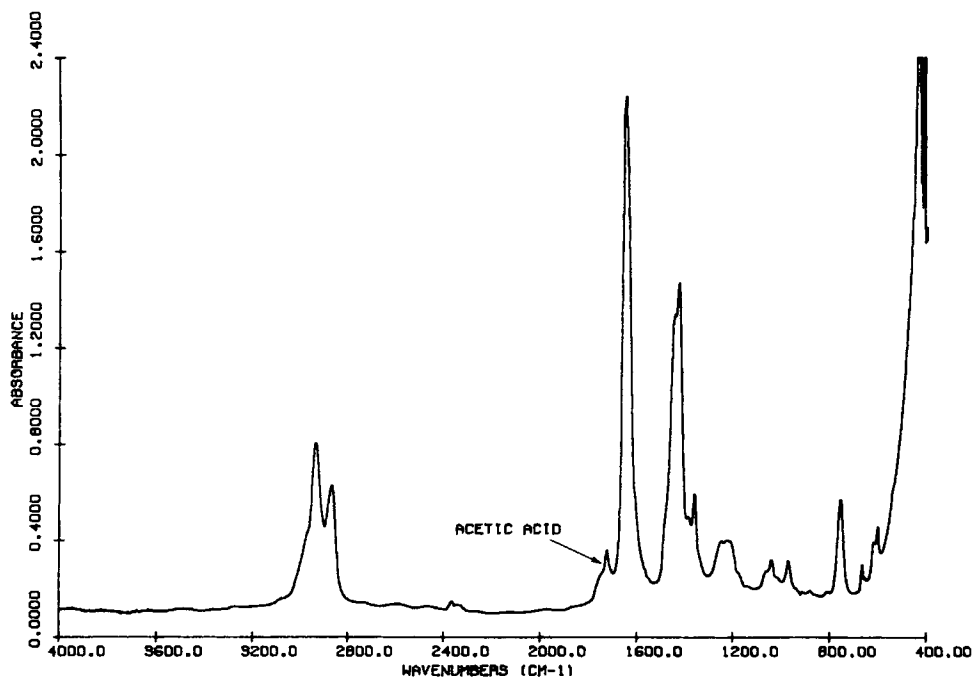
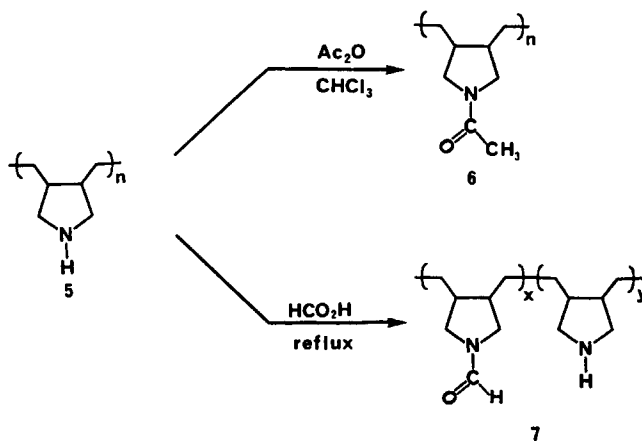


Fig. 4. FT-IR spectrum of poly(diallylacetamide) thin film cast on NaCl plate.

was readily removed by dialysis to give pure polymer.



Scheme 4

### Formamide Derivative

Conversion of the pyrrolidine groups to the corresponding formamide units (7) was not as clean or easy as for acetamide formation. Refluxing formic acid with continuous water removal was employed in an attempt to drive the reaction to completion. In all samples examined, however, there was evidence

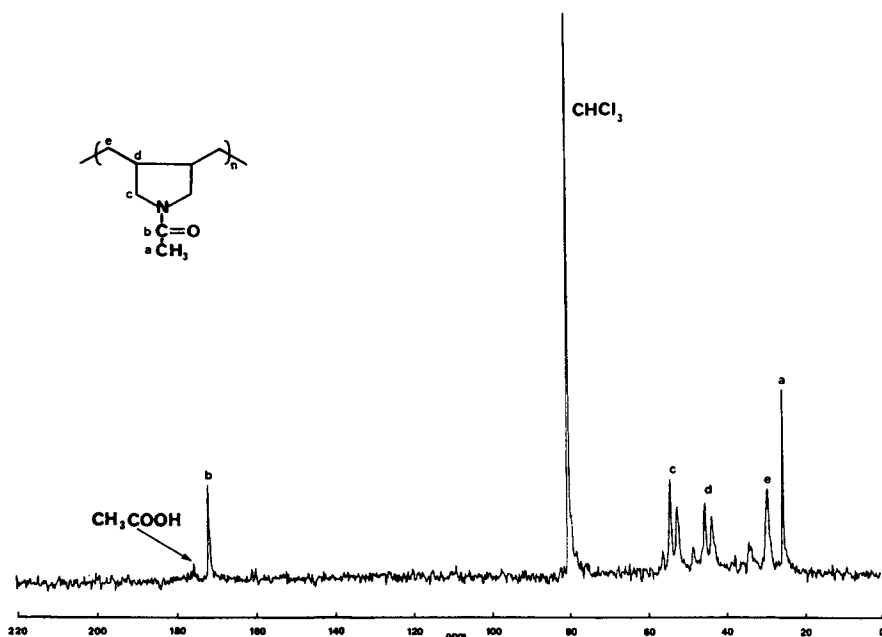


Fig. 5. <sup>13</sup>C-NMR spectrum of poly(diallylacetamide) in CHCl<sub>3</sub>.

for residual amine groups. For example, carefully dried polymer still displayed NH peaks in the IR (Fig. 6). <sup>15</sup>N-NMR was carried out using crosspolarization and showed two strong peaks for the NH groups of unsubstituted *cis* and *trans* repeat units in the ratio 4.5 to 1 at 338.0 and 336.7 ppm, respectively. Finally, the <sup>13</sup>C spectrum (Fig. 7) is more complex than that of the acetamide,

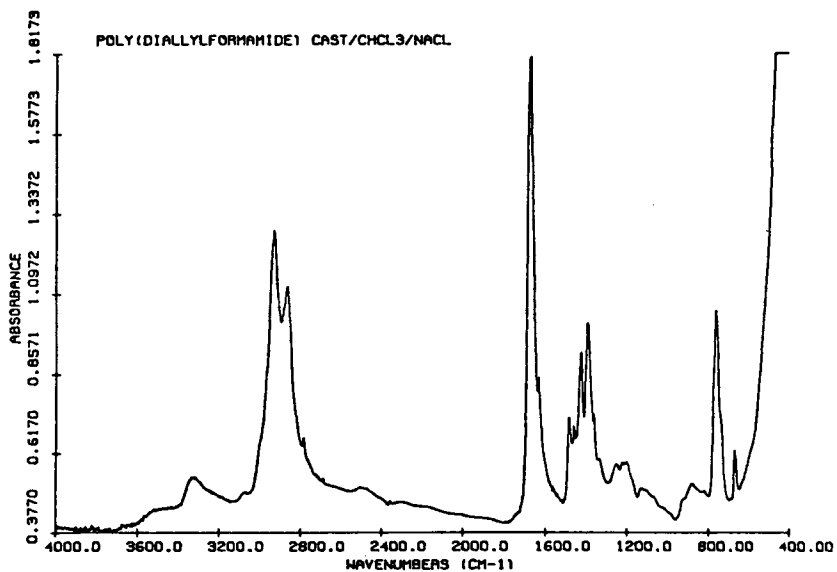


Fig. 6. FT-IR spectrum of poly(diallylformamide) thin film cast on NaCl plate.

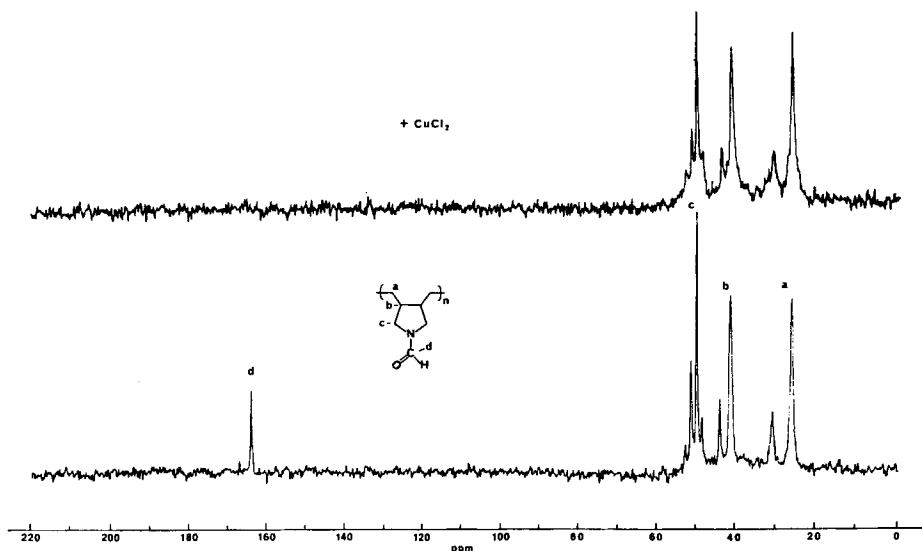


Fig. 7. <sup>13</sup>C-NMR spectra PDAF in water alone (lower trace) and with 8 mol% CuCl<sub>2</sub> (upper trace).

presumably because some of the peaks due to *cis* and *trans* units of the amide and free amine units overlap. It is not possible to assign these peaks with certainty at this time so that quantitative evaluation of the degree of substitution was not possible. However, IR evidence supports a fairly high degree of substitution ( $x > y$  in 7).

### Solution Behavior of the Formamide Polymer

Extensive evaluation of the viscosity behavior of this polymer was carried out in water, aqueous base, and methanol. Figure 8 gives the plot of reduced viscosity versus concentration and displays typical polyelectrolyte behavior. This was verified by replotting the data in a different format; i.e., the inverse of the reduced viscosity vs. the square root of the concentration. This gave a straight line with a correlation coefficient of 0.99, consistent with textbook examples of polyelectrolytes. A plot similar to that in Figure 8 was obtained in methanol and indicates that polyelectrolyte behavior occurs in this solvent also. When the polymer was evaluated in buffered water at a pH of 11.2, a normal viscosity plot was obtained with an intrinsic viscosity of 0.13 dL/g.

The repeat unit of PFAF is very similar in composition to *N*-vinylpyrrolidone. Both polymers are soluble in alcohols and water and insoluble in hydrocarbon solvents when dry. These factors suggested that poly(diallyl formamide) may have solution properties similar to poly(*N*-vinylpyrrolidone). The latter polymer is known to complex iodine and metals in solution and similar behavior was examined for the formamide polymer.

Figure 9 shows ultraviolet spectra of iodine in methanol with and without added poly(diallyl formamide). The spectrum of the polymer alone is also shown for reference. Addition of the polymer greatly increases the absorption

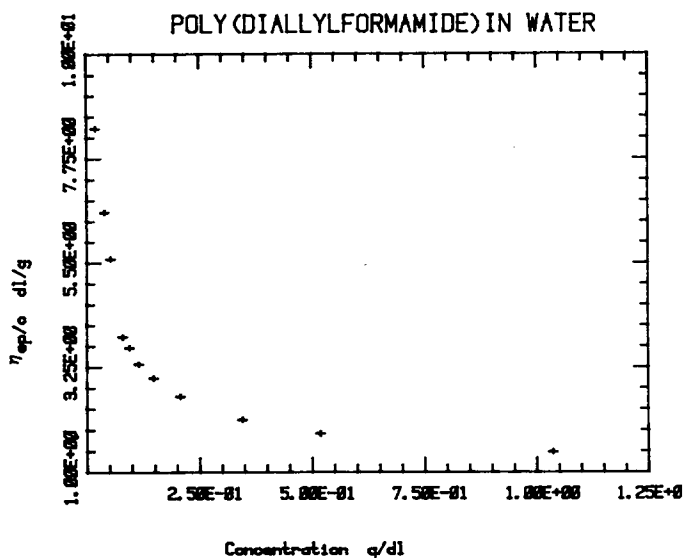


Fig. 8. Plot of  $\eta_{sp}/c$  (dL/g) vs.  $c$  (g/dL) for PDAF in water.

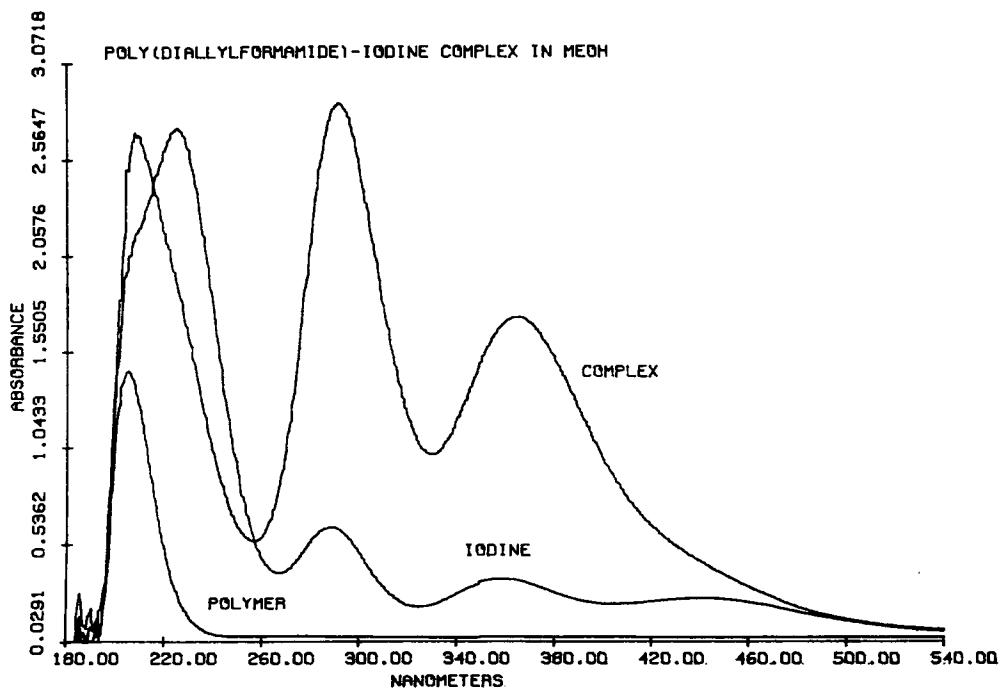


Fig. 9. UV spectrum of iodine in methanol with and without added PDAF.

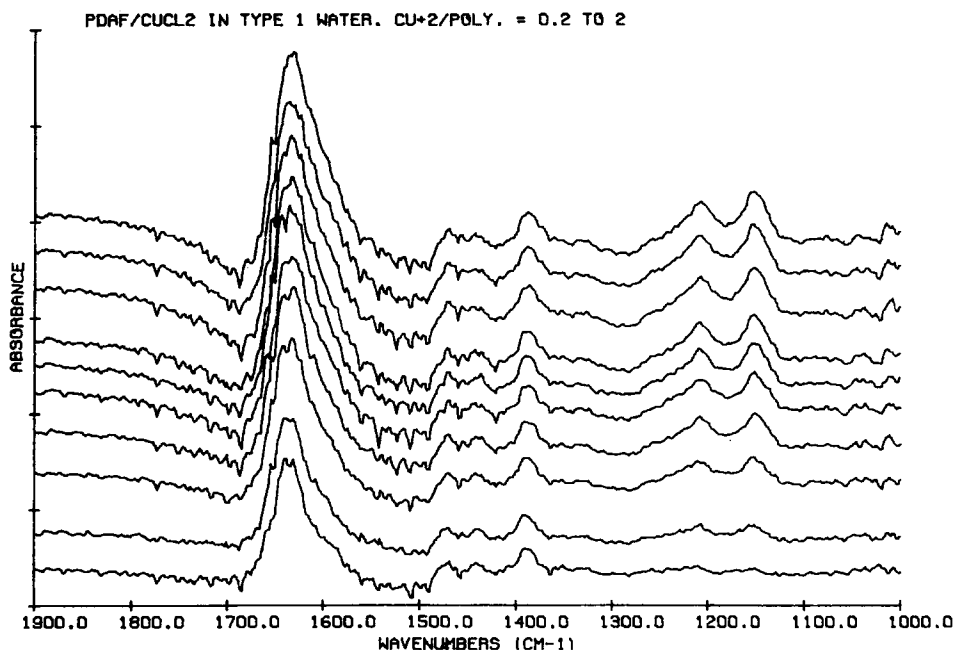


Fig. 10. FT-IR spectra of aqueous solutions of PDAF with increasing amounts of added  $\text{CuCl}_2$ ; increasing concentration from bottom to top.

due to iodine. The first derivative spectrum shows that the original spectrum has peaks at 277 and 323 nm, and addition of the polymer shifts these bands to 286 and 330 nm, respectively. This bathochromic shift in the iodine absorption is indicative of complexation with the polymer. Aqueous solutions of iodine plus PDAF are stable much longer than iodine solutions alone. This suggests that this polymer may have application in the development of new iodine-containing antiseptic solutions similar to Povidone-iodine, the commercial iodine solution containing poly(*N*-vinylpyrrolidone).<sup>23</sup>

Figure 10 shows a series of FTIR spectra of aqueous solutions of the polymer with varying amounts of cupric chloride. The spectra were obtained using a circular internal reflectance accessory for obtaining spectra of aqueous solutions. The ratio of copper ion to repeat unit in the polymer increases from 0.2 to 2.0 in going from the bottom to the top spectrum in the figure. The shape of the carbonyl peak changes, the peak grows in intensity, and a new set of peaks near 1200 and 1150  $\text{cm}^{-1}$  appears as the amount of copper increases. The carbonyl peak changes and the new peaks are attributed to complexation with the cupric ion.

<sup>13</sup>C-NMR spectra have also shown that addition of paramagnetic transition metal ions to polymer solutions selectively broaden the peaks of groups involved in complexation.<sup>24</sup> We have examined the effect of +2 ion salts of manganese, copper, cobalt, and nickel in water and methanol on PDAF. All four ions added to methanolic solutions of the polymer result in rapid precipitation of the complexed polymer, and no spectra were obtained. In water, however, the effect of the added metal salt on the intensity and broadness of the formamide carbonyl peak was monitored with respect to

concentration (see Fig. 7). The ratio of estimated amide repeat units to metal ion was varied from 100 : 1 down to 10 : 1. Strong interaction was observed for all four metals as determined by complete disappearance of the carbonyl peak at a characteristic salt concentration. Other carbon peaks were somewhat broadened but decreased in intensity very little compared to the carbonyl peak. The order of decreasing strength of interaction is that listed; i.e., the concentration of manganese ion required to reduce the intensity of the carbonyl peak to a given value was less than that for copper, cobalt, and nickel in that order. These observations are only qualitative since they do not take into account line widths, differences in  $T_1$ 's, nor the relative "paramagnetic strength" of the ions. In view of the selectivity of the broadening of the carbonyl peaks, it is clear that interaction between the polymer and the metal ions is strong and takes place selectively at the carbonyl oxygen.

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