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The Mannich Reaction of Poly(acrylamide)

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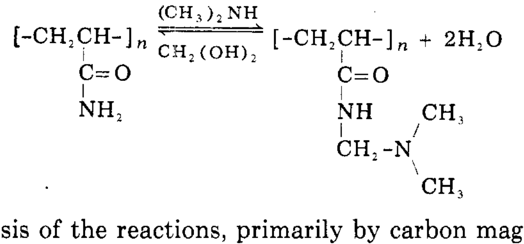
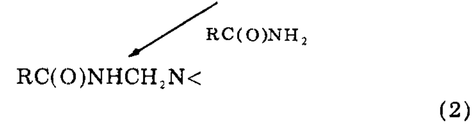
ABSTRACT: The Mannich reaction of formaldehyde and dimethylamine with a polymeric substrate, poly(acrylamide), was studied with carbon-13 nuclear magnetic resonance spectroscopy (^{13}C NMR). Reaction rates, equilibria, and the mechanism of conversion are characterized for the base-catalyzed reaction. The formation of the Mannich derivative is best described as a second-order process, involving the polymer and (dimethylamino)methanol, a rapidly formed product of dimethylamine and formaldehyde. The reaction exhibits a reversible equilibrium evidenced by a decrease in Mannich conversion with a molar excess of amine. A model equation describing this behavior gave estimates for the major equilibrium constants. Rate data, obtained in the absence of (dimethylamino)methanol, indicated that the reaction of the polymer with *N,N,N′,N′*-tetramethyldiaminomethane does not play a prominent role in the kinetics.

The Mannich reaction has been studied extensively and applied in the development of a wide range of compounds having commercial and synthetic importance.[1-4] This reaction involves the condensation of an amine, an aldehyde, usually formaldehyde, and a compound having a labile proton. The mechanism and reactive intermediates have been investigated, leading to some generalized conclusions. For example, it is now well accepted that the reaction normally involves the condensation of the *N*-hydroxymethylamine or methylenediamine with the labile hydrogen compound under both acidic and basic conditions.[3-7]

This study will describe the base-catalyzed Mannich reaction of dimethylamine and formaldehyde with a polymeric amide, poly(acrylamide). Direct spectroscopic analysis of the reactions, primarily by carbon magnetic resonance[8,9] (^{13}C NMR), has permitted a close examination of the kinetics of the transformation and the reaction equilibria and has confirmed the synthesis route as



$$[-CH_2CH(C{=}O)NH_2-]_n \underset{CH_2(OH)_2}{\overset{(CH_3)_2NH}{\rightleftharpoons}} [-CH_2CH(C{=}O)NHCH_2N(CH_3)_2-]_n + 2H_2O \qquad (1)$$



$$2CH_2(OH)_2 + 3{>}N\text{-}H \rightleftharpoons {>}NCH_2OH + {>}NCH_2N{<} + 3H_2O$$

$$\xrightarrow{RC(O)NH_2} RC(O)NHCH_2N{<} \qquad (2)$$

Table I
Polymer Characterization

	wt av mol wt
viscosity equation[12]	9.7×10^4
light scattering[a]	8.4×10^4

[a] Light scattering data, 628 nm; distilled water: 25 °C; $dn/dc = 0.182$.

Experimental Section

I. Polymer Synthesis. Poly(acrylamide) was prepared by a free radical solution polymerization initiated by the redox pair, sodium bisulfite–sodium persulfate. Initiator components were introduced simultaneously into a 20% nitrogen purged aqueous solution of Dow's acrylamide monomer. After the exotherm subsided the polymer was heated to 100 °C and allowed to cool slowly to ambient temperature to minimize unreacted monomer. The level of unsaturation left in the system was measured at less than 0.15% as determined by the bromate–bromide titration method.[10,11] The molecular weight, controlled by initiator level, was maintained below 100 000 to enable working with a low viscosity solution of the polymer derivative having greater than 20 wt % solids. The weight average molecular weight was measured by light scattering and with a viscosity equation.[12] These data are listed in Table I.

II. NMR Data. A. 25 MHz ^{13}C NMR Data. Fourier transform ^{13}C NMR were obtained at 25.2 MHz using a Varian XL-100 NMR spectrometer equipped with a Digilab FTS/NMR3 data system and a Varian V-6040 variable temperature controller. During operation, the spectrometer was locked on an external ^{19}F signal (C_6F_6). Protons were decoupled with broad band radio frequency noise.

Repetitive 30° (8 μs) pulses applied at 250 Hz to the low frequency of Me_4Si were used to generate the carbon-13 free induction signals, which were filtered (15 kHz single side band crystal, 6.2 kHz RC, and 12 kHz Butterworth), digitized at a rate of 10 560 points/s (5280 Hz bandwidth), and accumulated in

Table II
^{13}C NMR Spectral Assignments

	chemical shift, δ (Me_4Si)[a]				
	CH_2	CH	CO	NCH_2	NCH_3
$(CH_2C(CONH_2)H)_n$	35.4	42.8	180.3		
$(CH_2C(CONHCH_2OH)H)_n$	36.0	43.0	178.5	64.0	
$(CH_2C[CONHCH_2N(CH_3)_2]H)_n$	36.2	43.4	178.0	61.7	42.2
$(CH_3)_2NH$					38.1
$(CH_3)_2NCH_2OH$				80.8	41.7
$(CH_3)_2NCH_2N(CH_3)_2$				83.3	44.0

[a] Secondary reference 1,4-dioxane at an assigned shift of δ 67.4 (Me_4Si).

computer memory. After accumulation, the digitized data were weighted using an exponential apodizing function with a 1.0 s time constant and fast-Fourier transferred to provide absorption spectra. Pulse repetition rates of 1.29 s^{-1} (4096 points) and 2.58 s^{-1} (2048 points) were used.

Samples were run as aqueous solutions in 12-mL precision NMR sample tubes. A consistent set of ^{13}C NMR chemical shifts was obtained by using *p*-dioxane as an internal reference having an assigned shift of δ 67.4 (Me_4Si).

B. 15 MHz ^{13}C NMR Data. Fourier transform ^{13}C NMR data were also obtained at 15 MHz using a JEOL FX-60 NMR spectrometer. The free induction signals were generated with a 65° (6 μs) pulse applied at 100 Hz to the low frequency of Me_4Si and a bandwidth of 3012 Hz (4096 points) was collected.

C. ^1H NMR Data. ^1H NMR spectra were obtained at 100 MHz using a Varian XL-100 NMR spectrometer and at 60 MHz using a Varian EM-360 NMR spectrometer. A self-consistent set of ^1H NMR chemical shifts was obtained by using 3-(trimethylsilyl)tetradeuteriosodium propionate (TSP) as an internal reference with an assigned shift of δ 0. Five-millimeter NMR tubes were used to obtain the ^1H NMR data.

III. Kinetic Data. The kinetics of the Mannich transformation were examined with ^{13}C NMR. A typical procedure involved mixing the three reagents, equilibrated at a given temperature, at equivalent stoichiometry. The reaction vessel was placed in a water bath to minimize the exotherm developed when the reaction is carried out at a concentration of approximately 2 M. A sample of the equilibrated mixture was then placed in the probe of the spectrometer maintained at the given temperature. Data accumulation was begun for a predetermined number of transients, sufficient to give an adequate signal, and stored in the computer memory for later analysis.

Results and Discussion

I. Carbon Magnetic Resonance. This study describes the kinetics and product composition of the Mannich reaction of poly(acrylamide). The ability of ^{13}C NMR to distinguish the various chemical species in this complex reaction makes it well suited for this type of investigation.

In the ^{13}C NMR spectrum, peaks are observed which are due to a naturally occurring isotope of carbon (^{13}C abundance 1.1%). The peak position or chemical shift is sensitive to the magnetic environment; consequently, specific types of carbon atoms can frequently be distinguished. Table II lists the ^{13}C NMR chemical shifts and spectral assignments for compounds prominent in this study. They include the polymeric amide, amide methylol, Mannich derivative, and low molecular weight amine–formaldehyde reaction products.

The ability to distinguish between primary and secondary amide carbonyl carbons is an important feature illustrated by the data in Table II and in Figure 1. Secondary amide structures can be further resolved with the corresponding NCH_2 methylene carbon peaks.

Quantitative conversion of poly(acrylamide) to the Mannich derivative was obtained by comparing the intensities of the corresponding carbonyl carbon peaks. In general, these intensities are influenced by concentration, magnetic relaxation time (T_1, T_2), and nuclear Overhauser enhancements (NOE).[13,14] The Mannich and poly(acrylamide) carbonyl peaks were affected to similar extents by these factors. Thus, accurate relative molar concentrations can be calculated from unmodified peak intensity data.

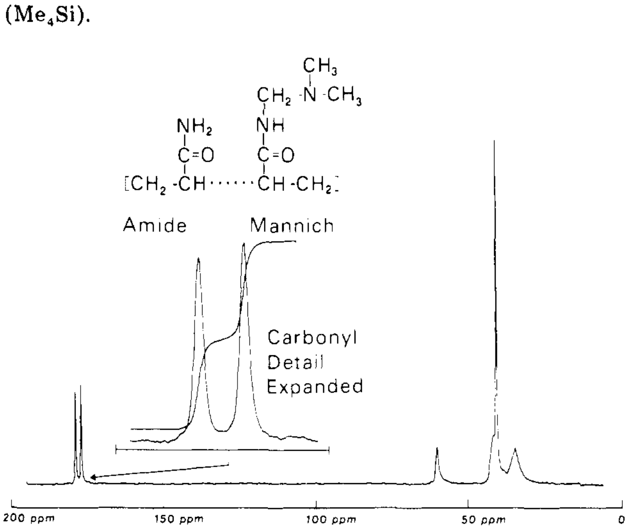


Figure 1. 15.3 MHz spectrum of Mannich polymer in aqueous solution. Composition: 50 mol % amide, 50 mol % Mannich.

Table III
^{13}C NMR Conversion for Various NMR Conditions

		calcd M conversion (%) to Mannich product	
decoupling	pulse interval, s	peak height	peak area
yes	0.33	52.9	53.5
yes	30.00	52.3	55.8
no	5.00	53.7	54.8

This is illustrated in Table III where the molar composition for a theoretical 50% converted Mannich polymer is listed for different decoupling conditions. These conversions agree to within an observed 3% relative error, demonstrating the essential equivalence of the NOE factors for these primary and secondary carbonyl carbons.

The equivalence of the two carbonyl carbon spin relaxation times (T_1), to within 10% relative error, was established by inversion–recovery experiments at 25 MHz (T_1 = 0.6 s) and at 15 MHz (T_1 = 0.35 s) at 25 °C. This was further evidenced by the fact that molar conversions obtained at pulse repetition rates of 0.33 and 30 s were equivalent. These data are also in Table III.

In Figure 2 the theoretical (based on stoichiometry) and ^{13}C NMR determined molar composition over a wide range of conversion to secondary amide are compared. ^1H NMR data comparing the primary and secondary amide resonance under conditions which minimize proton exchange[15] corroborated these carbon NMR conversions.

II. Kinetics. A number of kinetic studies have been made of the Mannich reaction in an effort to understand

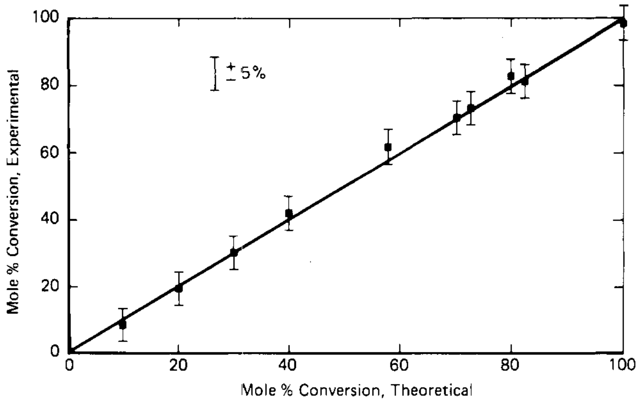


Figure 2. Experimental molar conversion (^{13}C NMR) to Mannich product vs. theoretical conversion, 25 °C.

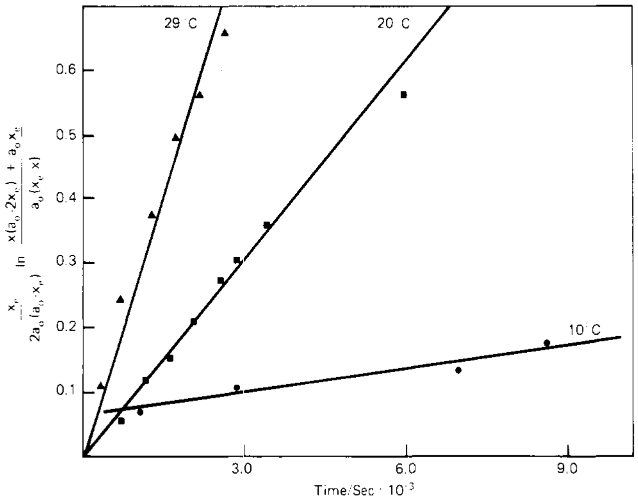


Figure 3. Second-order reaction plot of Mannich coversion of poly(acrylamide): temp, k [L/(mols)]: ●, 10 °C, 1.5×10^{-5}; ■, 20 °C, 9.6×10^{-5}; ▲, 29 °C, 2.4×10^{-4}. Arrhenius activation energy 22 ± 4 kcal/mol.

its mechanism.[16-19] ^{13}C NMR can be the basis for a similar approach. Spectra obtained over the course of the reaction furnish quantitative rate data as well as information identifying the most prominent intermediates.

Figure 3 shows a second-order plot obtained with ^{13}C NMR conversion data, that is by measuring relative peak areas for the primary and secondary amide carbonyl groups during the early stages of the reaction (<50 mol % conversion). The data are fitted to the equilibrium process,

$$A + B \rightleftharpoons C + D \tag{3}$$

where A and B are analogous to the polyamide and (dimethylamino)methanol, a rapidly formed reaction product of dimethylamine and formaldehyde. The integrated rate expression assuming equivalent stoichiometry in the reactants is

$$\frac{x_e}{2a_0(a_0 - x_e)} \ln \frac{x(a_0 - 2x_e) + a_0x_e}{a_0(x_e - x)} = kt \tag{4}$$

where a_0 represents the initial concentration of the reagents and x_e is the equilibrium concentration of product. The data provide a good fit to this kinetic model.

An equilibrium conversion, achieved within 20 h at the highest temperature, was within 5 mol % of a given stoichiometry. Since the rate of conversion was independent of whether the DMA and formaldehyde were prereacted, the rate-determining step was interpreted as the condensation of the N-hydroxymethylamine or related derivative with the polyamide. Evidence favoring this interpretation will be presented below.

Table IV
Equilibrium Molar Composition of
Amine-Formaldehyde Reaction Products

molar ratio of DMA/ CH_2O	mol % of (dimethylamino) methanol	tetramethyldiaminomethane	formaldehyde
0.66	65	~3	32
1.0	78	10	12
1.33	65	28	8
2.0	27	72	~1

The early stages of the Mannich reaction exhibit a strong exotherm which is associated primarily with the rapid formation of the amine-formaldehyde derivatives.[20] The influence of this exotherm on the kinetics was minimized by equilibrating the reaction mixture in a water bath prior to ^{13}C NMR measurements. This approach was effective in holding the exotherm to approximately the desired temperatures, although it did not altogether prevent an acceleration of the conversion rate in the early stages of the reaction. This heat history prior to kinetic measurement is most noticeable in the data at 10 °C where a nonzero intercept is observed. The effect is enhanced in this case because of both the relatively slow rate of conversion at 10 °C and large temperature dependence of the kinetics. The rate constants, calculated from the slope of the curves, are not influenced by this.

The time required to obtain a spectrum with adequate signal (~20 min) should be considered in the evaluation of rate constants with Fourier transform ^{13}C NMR. Equation 3 best described the data when the reaction does not proceed by an amount greater than experimental error (±5%) during the acquisition time. This condition is satisfied at the lower temperatures. The reaction, however, proceeds at the highest temperature fast enough to have a significant change in Mannich conversion over the collection interval. Data reduction taking account of this factor indicate an error of approximately 3% in the rate constant determined with eq 3. Hence, rate data and related thermodynamic parameters can readily be evaluated with this technique. All kinetic data were plotted at the midpoint of the acquisition time.

III. *N*-Hydroxymethylamine and Related Derivatives. The reaction of dimethylamine and formaldehyde gives primarily two products: (dimethylamino)methanol and N,N,N',N'-tetramethyldiaminomethane.[20,22-24] The relative composition depends on the molar ratio of the starting reagents. Table IV contains the approximate molar percentages of the products formed with various initial concentrations of DMA and formaldehyde as measured by ^{1}H NMR. These data were obtained with the anhydrous form of the amine mixed with crystalline formaldehyde at ambient temperature in D_2O to give a solution that was about 25% solids. The resolved methylene proton peaks in the ^{1}H NMR spectra were integrated to determine the molar composition within a 5% relative error. Spiking with commmercially available anhydrous N,N,N',N'-tetramethyldiaminomethane and formaldehyde enabled peak identification.

It is of interest to determine the molar conversion of poly(acrylamide) to its Mannich product as a function of the alcohol amine reagent composition. Both amine components could take part in the reaction forming the secondary amide. Information intended to clarify the role of each will be discussed below.

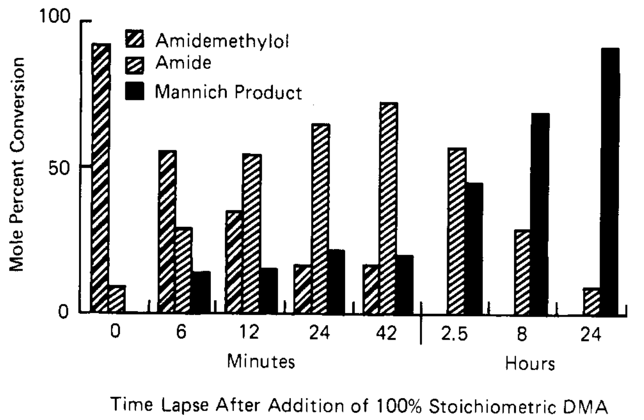


Figure 4. ^{13}C NMR kinetic data: poly(amidemethylol) conversion to Mannich product.

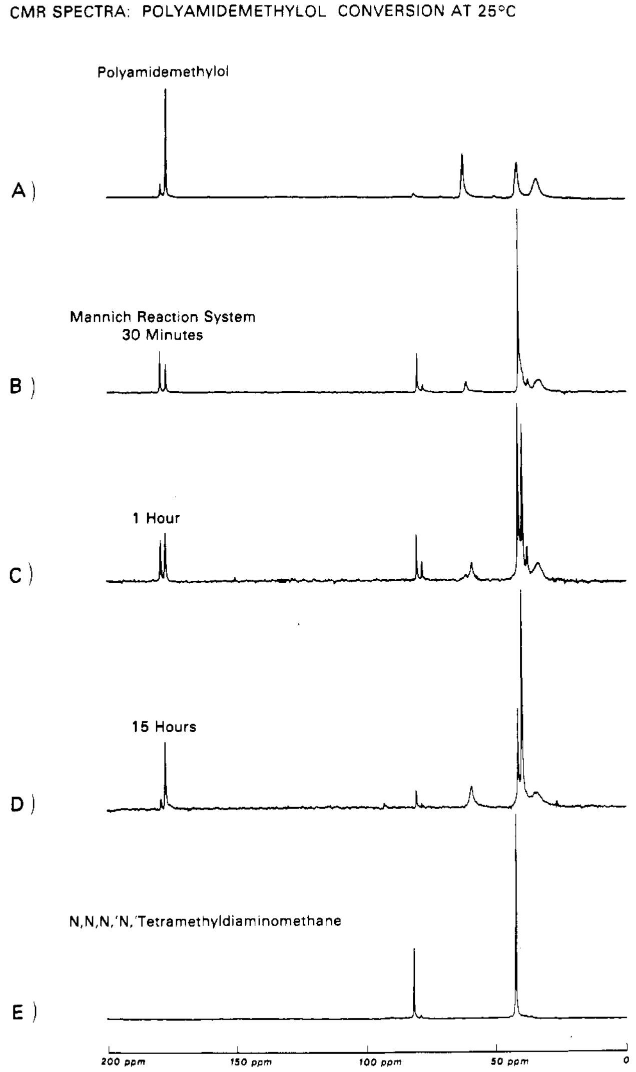
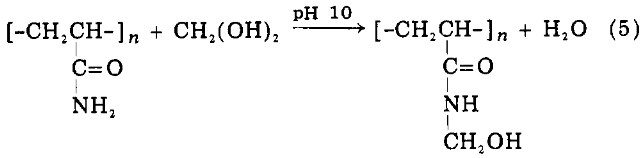


Figure 5. 15.3 MHz ^{13}C NMR spectra of the reaction of poly(amidemethylol) and dimethylamine, 25 °C: (a) 95% poly(amidemethylol) prior to addition of dimethylamine; (b) reaction mixture 30 min after dimethylamine addition (note appearance of primary amide and *N*,*N*,*N*′,*N*′-tetramethyldiaminomethane peaks); (c) reaction mixture 1 h after dimethylamine addition (note Mannich product methyl peak is discernable); (d) reaction mixture 15 h after dimethylamine addition (near equilibrium Mannich poly(acrylamide) product); and (e) 40% aqueous solution of *N*,*N*,*N*′,*N*′-tetramethyldiaminomethane.

IV. Mechanism. The kinetic data have suggested that the Mannich conversion of poly(acrylamide) with DMA and formaldehyde proceeds via a second-order process in which poly(acrylamide) reacts with the low molecular weight amine–formaldehyde derivative. More substantial evidence for this mechanism was developed by synthesizing a potential intermediate, the poly(amidemethylol),[25] and



$$[\text{-CH}_2\underset{\substack{|\\ \text{C=O}\\ |\\ \text{NH}_2}}{\text{CH}}\text{-}]_n + \text{CH}_2(\text{OH})_2 \xrightarrow{\text{pH } 10} [\text{-CH}_2\underset{\substack{|\\ \text{C=O}\\ |\\ \text{NH}\\ |\\ \text{CH}_2\text{OH}}}{\text{CH}}\text{-}]_n + \text{H}_2\text{O} \tag{5}$$

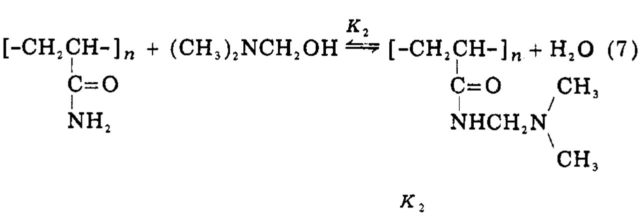
monitoring by ^{13}C NMR its conversion to Mannich derivative upon introducing a stoichiometric amount of dimethylamine. The transformations during the reaction are described by a block diagram in Figure 4, where the molar percent of three polymeric species, amidemethylol, acrylamide, and Mannich derivative, are characterized as a function of time after introduction of the amine.

The immediate result of the above process is to increase the concentration of poly(acrylamide) by an apparent stripping of the formaldehyde from the polymer backbone. Tetramethyldiaminomethane dominates the low molecular weight reaction products formed apparently due to the excess dimethylamine relative to formaldehyde consistently present. A majority of the poly(acrylamide), approximate 70 mol %, is formed before substantial amounts of Mannich product develop.

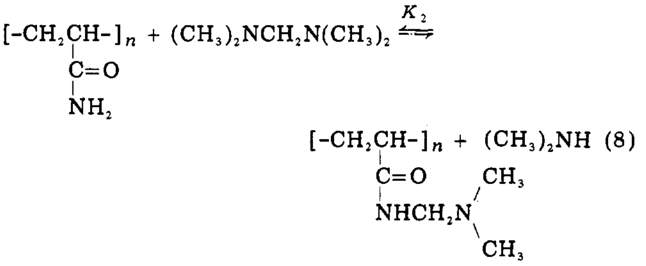
The spectral evidence documenting the above transformations is shown in Figure 5, where a series of ^{13}C NMR spectra, including tetramethyldiaminomethane, poly(amidemethylol), and intermediate states in the reaction, is presented. The development and disappearance of the amide carbonyl peaks and the two peaks associated with tetramethyldiaminomethane are the most prominent changes. The distinction between poly(amidemethylol) and the Mannich polymer is only resolved upfield where the methylene carbon next to the nitrogen appears at 64.0 and 61.7 ppm, respectively. The corresponding secondary amide carbonyl peaks cannot be resolved, though a peak ratio analysis is effective in subdividing the composite carbonyl peak into its components. Specifically, the ratio between the carbonyl and methylene carbon peaks in the highly converted poly(amidemethylol) was used to analyze the composite secondary amide carbonyl peak present during the Mannich transformation. This analysis was used in developing the block diagram in Figure 4.

V. Equilibra. The complex equilibria of the Mannich reaction with DMA and formaldehyde could be summarized in terms of the following reactions:

$$(\text{CH}_3)_2\text{NH} + n\text{CH}_2(\text{OH})_2 \overset{K_1}{\rightleftharpoons} (\text{CH}_3)_2\text{N}(\text{CH}_2\text{O})_n\text{H} + \text{H}_2\text{O} \tag{6}$$



$$[\text{-CH}_2\underset{\substack{|\\ \text{C=O}\\ |\\ \text{NH}_2}}{\text{CH}}\text{-}]_n + (\text{CH}_3)_2\text{NCH}_2\text{OH} \overset{K_2}{\rightleftharpoons} [\text{-CH}_2\underset{\substack{|\\ \text{C=O}\\ |\\ \text{NHCH}_2\text{N}\begin{smallmatrix}\diagup\text{CH}_3\\ \diagdown\text{CH}_3\end{smallmatrix}}}{\text{CH}}\text{-}]_n + \text{H}_2\text{O} \tag{7}$$



$$[\text{-CH}_2\underset{\substack{|\\ \text{C=O}\\ |\\ \text{NH}_2}}{\text{CH}}\text{-}]_n + (\text{CH}_3)_2\text{NCH}_2\text{N}(\text{CH}_3)_2 \overset{K_2}{\rightleftharpoons} [\text{-CH}_2\underset{\substack{|\\ \text{C=O}\\ |\\ \text{NHCH}_2\text{N}\begin{smallmatrix}\diagup\text{CH}_3\\ \diagdown\text{CH}_3\end{smallmatrix}}}{\text{CH}}\text{-}]_n + (\text{CH}_3)_2\text{NH} \tag{8}$$

$$(CH_3)_2NH + (CH_3)_2NCH_2OH \overset{K_4}{\rightleftharpoons} (CH_3)_2NCH_2N(CH_3)_2 + H_2O \quad (9)$$

Defining the molar concentrations with the following symbols, $[A] = (CH_3)_2NCH_2OH$; $[B] = (CH_3)_2NH$; $[C] = (CH_3)_2NCH_2N(CH_3)_2$; [M] = Mannich derivative; and [P] = poly(acrylamide), leads to the following equations:

$$[A] + [B] + 2[C] + [M] = [X] \quad (10)$$

$$[M] + [P] = [Y] \quad (11)$$

$$[A] + [C] = [P] \quad (12)$$

where [X] is the total amine concentration and [Y] is the total amount of polymer.

Based on the above, the following relation is derived:

$$\frac{[P]^2K_2}{[M]K_4} + 2[P] - \frac{1}{K_4} - \frac{[M]}{[P]K_2} + [M] = [X] \quad (13)$$

where

$$K_2 = [M][H_2O]/[P][A] \quad (14)$$

and

$$K_4 = [C][H_2O]/[A][B] \quad (15)$$

This development describes the Mannich reaction system as a function of the amount of excess amine in terms of experimentally definable equilibrium constants.

Data characterizing the molar conversion of the polymer to its Mannich derivative as a function of excess amine are shown in Figure 6. Consistently, as the molar excess of the amine increases, the conversion to the Mannich product is reduced. The major byproduct in this regeneration of the poly(acrylamide) is tetramethyldiaminomethane. No detectable amounts of (dimethylamino)methanol were observed in the ^{13}C NMR spectra above an amine excess of 40 mol %.

Equation 13 can be fitted to these data to estimate quantitative values for the equilibrium constants represented in the above model. With the hydrolysis constant for tetramethyldiaminomethane (K_4 in eq 9) measured directly with ^1H NMR, again by quantitative evaluation of the methylene proton peaks, a nonlinear least-squares regression fit provides an estimate for K_2.[26] Since K_2 and K_4 are related,

$$K_2 = K_3K_4 \quad (16)$$

a calculated value for K_3 from the above data can be compared with the experimentally measured equilibrium constant (eq 8). The latter was obtained by reacting the anhydrous tetramethyldiaminomethane with the polymer at 25 °C and evaluating the molar conversion to secondary amide with ^{13}C NMR. The equilibrium constants found with these methods are tabulated in Table V. The comparison between K_3 values is reasonable, in accord with the model and approaches used to describe this reaction system.

Two routes to the Mannich derivative are suggested in the above scheme: reaction of the polymer with either (dimethylamino)methanol or tetramethyldiaminomethane. The data presented so far give no indication of the relative importance of these reactions in Mannich product formation. To clarify this the following information was developed.

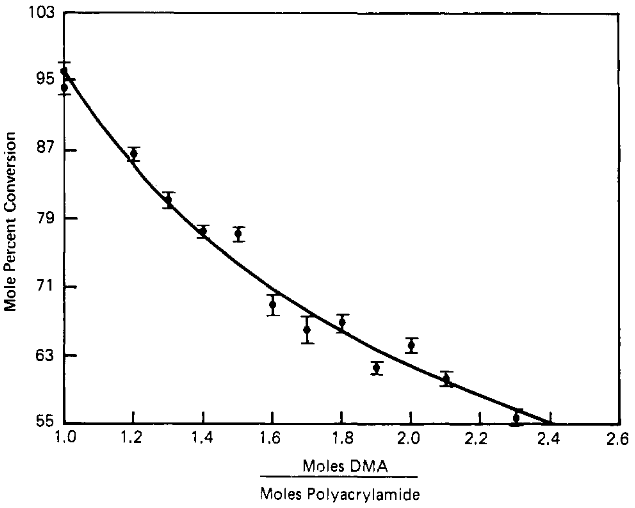


Figure 6. Mannich conversion vs. moles of excess dimethylamine: solid line nonlinear least-squares fit to eq 13.

Table V
Equilibrium Constants: Mannich Reaction (25 °C) of Poly(acrylamide)

	K_2	K_3	K_4
estimated by curve fitting	7.9×10^3	2.8	
estimated by ^1H NMR		2.9	2.8×10^3

The rate of hydrolysis of the tetramethyldiaminomethane to dimethylamine and (dimethylamino)methanol was found with ^1H NMR to be rapid, reaching 90% of its equilibrium hydrolysis level within 5 min at 25 °C. This fact renders ambiguous any measurement of comparative rates of polymer conversion with stoichiometric quantities of these reagents. Further, the rate of formation of the Mannich product in the presence of a threefold excess of the amine was found to be much slower than the corresponding reaction with equivalent molar quantities of polymer, formaldehyde, and amine. Only 17% Mannich product was formed in 24 h in 25 °C. These conditions, which shift the equilibria such that the formaldehyde exists predominantly in the form of tetramethyldiaminomethane, should enhance reaction 8. From the slow rate observed, it was concluded that this reaction plays a minor role in developing Mannich product.[27] In fact, the observed rate corresponds to what would be expected, based on the decrease in the concentration of (dimethylamino)methanol due to the excess amine as calculated by eq 9. The reversal of eq 8 is not influential until significant amounts of Mannich product are formed.

Conclusions

^1H and ^{13}C NMR spectroscopy are effective in characterizing the equilibria associated with the base-catalyzed Mannich reaction of poly(acrylamide).

This Mannich reaction occurs primarily by condensation of poly(acrylamide) with a formaldehyde amine derivative, (dimethylamino)methanol, in a second-order kinetic process.

A model equation describing the equilibrium conversion as a function of excess DMA provides quantitative estimates for the equilibrium constants prominent in the system.

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Polymerization Modes of Tetracyanoquinodimethane and Vinyloxy Compounds

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ABSTRACT: Polymerization of tetracyanoquinodimethane (TCNQ) with *n*-butyl vinyl ether, isobutyl vinyl ether, 2-chloroethyl vinyl ether, phenyl vinyl ether, and vinyl acetate was studied in acetonitrile. The first two vinyl ethers homopolymerize in the presence of TCNQ and the last three compounds copolymerize in an alternating fashion with TCNQ. The two polymerization modes were correlated to electron-donating character of the monomers by Taft's substituent constants for vinyloxy compounds.

It has been pointed out that tetracyanoquinodimethane (TCNQ) can participate in radical copolymerizations as an acceptor monomer, causing a spontaneous alternating copolymerization with styrene (St).[1] On the other hand, Stille et al.[2] reported that TCNQ initiates the cationic homopolymerization of alkyl vinyl ethers in acetonitrile, indicating the powerful electron-accepting character of TCNQ. It was thus conceivable that the system composed of TCNQ and a donor monomer could change in its polymerization behavior from alternating copolymerization to cationic homopolymerization of the electron-donating monomer, as a function of the electron-donating character of the monomer.

The polymerization of TCNQ with *n*-butyl vinyl ether (nBVE), isobutyl vinyl ether (iBVE), 2-chloroethyl vinyl ether (CEVE), phenyl vinyl ether (PhVE), and vinyl acetate (VAc) was studied. The polymerization modes observed can be correlated with the electron-donating character of the vinyloxy compounds.

Experimental Section

1. Material. Commercial TCNQ was purified by recrystallization from acetonitrile and was sublimed (twice) (mp 294.5–295.5 °C). PhVE was prepared from phenol and dibromoethane according to the method of McElvain et al.[3] (bp 54 °C (17 mmHg)). CEVE (bp 109 °C), VAc (bp 71.0 °C), iBVE (bp 82 °C), and nBVE (bp 94.5 °C) were purified from commercial products by conventional methods.[4] The monomer purity was checked by gas chromatography (purity, 99.6–99.8%). α,α′-Azobis(isobutyronitrile) (AIBN) was purified by recrystallization from ethanol. Acetonitrile was refluxed with phosphorus pentoxide and then distilled at 82 °C. Dichloromethane was refluxed with calcium hydride and distilled at 39.5 °C. Boron trifluoride etherate was distilled at 125.5 °C under nitrogen.

2. Polymerization Procedure. TCNQ–iBVE and TCNQ–nBVE. TCNQ (0.1 g) and 1.0 g of iBVE (or 1.0 g of nBVE), 6.8 mg of AIBN (or 5.7 mg of AIBN for the TCNQ–nBVE system), and 10 mL of acetonitrile were placed in an ampule, which was then degassed (freeze–thaw cycle repeated three times) and sealed. The ampule was placed in a bath at 60 °C for 21.8 h (or 18.1 h for the TCNQ–nBVE system), cooled, and opened. The reaction solution was poured into excess methanol. The polymeric product was collected by filtration, dissolved in benzene, and reprecipitated in excess methanol. The yield of polymeric product was 166 mg (or 98 mg for the TCNQ–nBVE system). Anal. For the TCNQ–iBVE system Calcd for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: N, 0; C, 72.34; H, 11.35. For the TCNQ–nBVE system Calcd for $C_6H_{12}O$: C, 71.94; H, 12.08. Found: N, 0; C, 72.39; H, 11.68. The solution viscosity of these products in benzene was determined at 30 °C to be $\eta_{sp/c}$ = 0.067 dL/g (*c* 2.79 g/dL) for the product of the TCNQ–iBVE system and $\eta_{sp/c}$ = 0.062 dL/g (*c* 1.15 g/dL) for that of the TCNQ–nBVE system.

TCNQ–CEVE. Given amounts of TCNQ, CEVE, and AIBN and 10 mL of acetonitrile were placed in an ampule, which was then degassed as above and sealed. The ampule was heated at

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