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Some Aspects of the Reaction of Polyacrylamide with Formaldehyde

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ABSTRACT

The reaction of polyacrylamide with formaldehyde was studied in a neutral aqueous medium at equal initial molar concentrations of amide groups and of formaldehyde (0.05 mol/L) and in a range of temperatures from 45 to 75°C. The process was investigated by measuring the loss of free formaldehyde in the reaction mixture and the changes of the sum of free formaldehyde and methylol groups versus time. The addition of HCHO to an amide function of the polymer leads to its N-methylol derivative which may transform into the product of condensation between the latter and another amide group. Because of high dilution of polyacrylamide macromolecules in the reaction mixtures studied, cross-linking of the polymer chains with formaldehyde is rather unlikely. Therefore the disappearance of the N-methylols formed is probably due to some intramolecular reactions. It is believed that they involve the condensation of N-hydroxymethyls with neighboring amide groups which results in cyclic structures containing methylenediamide sequences. The occurrence of intramolecular reactions

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was confirmed by applying Flory's theory of gelation. The addition of HCHO to amide functions is a rate-determining stage in the case of polyacrylamide. For this reaction the rate constants were estimated and the corresponding activation energy was found to be 62 kJ/mol.

INTRODUCTION

Previous studies [1, 2] on the preparation of urea-formaldehyde (UF) resins of low HCHO emission showed that certain polymeric additives containing amine or amide functions can serve as excellent chemical traps for the formic aldehyde evolved whereas others may even stimulate its release from the resinous materials. For instance, opposite effects were observed in the case of polyacrylamide, an excellent inhibitor of formaldehyde emission, and chitosan, which in certain conditions augmented the evolution of HCHO from UF resins. Such differences in the behavior of various ingredients having similar reactive sites are probably due to the stability or instability of the final reaction products with HCHO. It was suggested that the spatial molecular structure of the polymer additive was in some way responsible for the type of formaldehyde derivative being formed. It seemed interesting to verify this opinion by performing some direct model reactions of the substances mentioned as components of the UF polycondensates. In particular, the present paper deals with one of the best HCHO emission inhibitors, i.e., polyacrylamide.

EXPERIMENTAL

Polyacrylamide

Polyacrylamide of intrinsic viscosity 1.88 dL/g (aqueous solution, 25°C) was prepared according to the method described elsewhere [3].

General Procedure for Kinetic Measurements

Measured quantities of neutral polyacrylamide aqueous solutions were introduced to a 500-mL reaction flask provided with a thermometer and a magnetic stirrer. The flask was placed in a thermostated water bath to maintain a selected constant temperature (i.e., 45, 60, and 75°C). After a constant temperature had been reached an aliquot of neutral formaline (38.2%) was added and this moment was considered zero time. The quantities of the formaldehyde and polyacrylamide solutions as well as the concentration of the latter were adjusted in such a way that the total volume of the reaction mixture was

400 mL and the concentrations of amide groups and of HCHO were both equal to 0.05 mol/L. Samples of 25 mL were taken at suitable intervals to analyze quantitatively the free unreacted formaldehyde and that bound in the form of N-hydroxymethyl groups.

Determination of Free Formaldehyde

A 25-mL aliquot of the reaction mixture was cooled to 4°C and made alkaline with 1 $\underline{M}$ Na_2CO_3 to pH 9.0. Then 2 mL of 1 $\underline{M}$ Na_2SO_3 were added immediately and the pH was adjusted immediately to 8.5 with several drops of 0.3 $\underline{N}$ HCl. The solution was left for 7 min and next acidified with 1 $\underline{M}$ CH_3COOH to obtain a pH of 4. The excess sulfite was neutralized with a 0.1 $\underline{N}$ iodine solution, using starch as the indicator. The product of the formaldehyde-bisulfite reaction was decomposed with 25 mL 2 $\underline{N}$ aqueous Na_2CO_3 at pH 9, and the liberated sulfite was titrated with 0.1000 $\underline{N}$ I_2 until the blue color of starch persisted.

Determination of the Sum of Free Formaldehyde and Methylol

To a 25-mL reaction mixture sample, 10 mL 2 $\underline{N}$ NaOH and 50 mL 0.1 $\underline{N}$ I_2 were added. It was then cooled in an ice-water bath for 1 h and then acidified with 2 $\underline{N}$ H_2SO_4. The excess iodine was titrated with thiosulfite solution.

RESULTS AND DISCUSSION

Figure 1 is a graphic illustration of the course of the reaction between polyacrylamide and formaldehyde in neutral (pH 7.0) aqueous medium at three different temperatures. In each case the initial molar ratio of polymer amide groups to HCHO is 1:1. The kinetic curves correspond to the decrease of the free formaldehyde concentration, F, and to the diminution of the sum of unreacted HCHO and N-methylols formed, F_{f+m}. The experiments were run at a relatively high dilution of polymer macromolecules (about 4.6×10^4 L/mol) so any cross-linking reactions leading to methylene bridges between polyacrylamide chains were only slightly probable. In this respect a somewhat similar situation takes place when the polymer used as the additive to a UF resin is dispersed in a cured solid phase. In such conditions it can be anticipated that the reaction of polyacrylamide with formaldehyde may lead to the formation of intramolecular cyclic structures according to

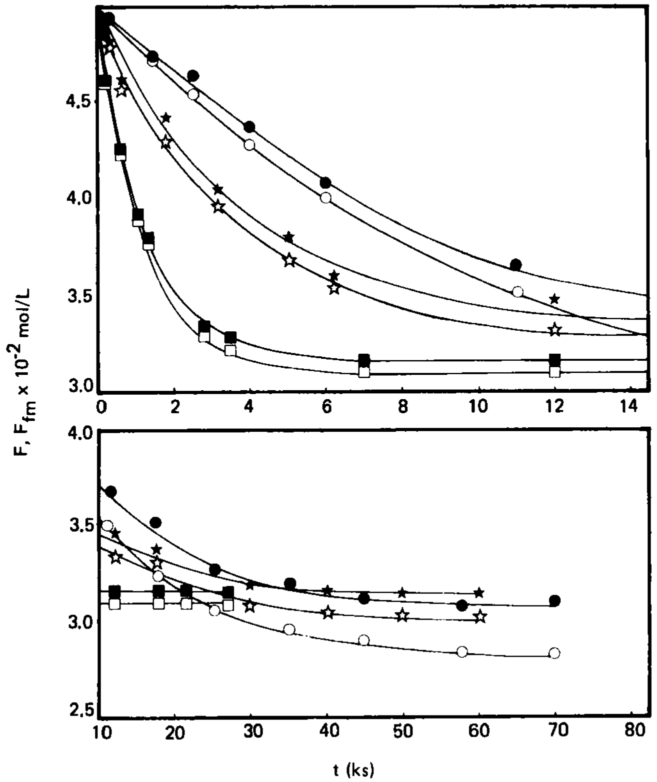
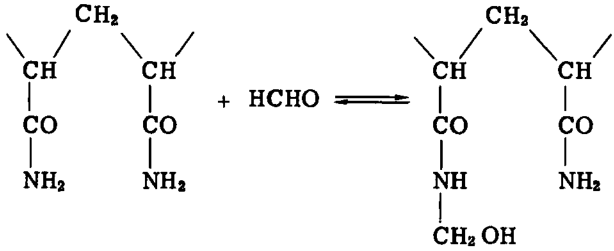
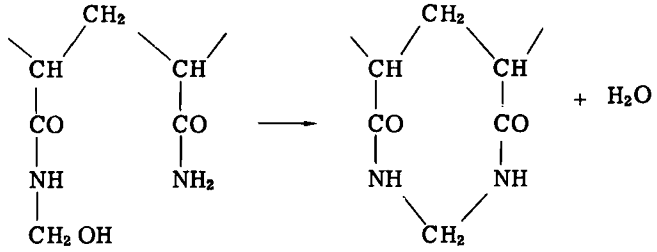


FIG. 1. Changes of molar concentrations F (○, ☆, □) and F_{f+m} (●, ★, ■) as a function of time of reaction of formaldehyde (F_0 = 0.05 mol/L) with polyacrylamide (A_0 = 0.05 mol/L) in neutral aqueous solution at temperatures of 45 (○, ●), 60 (☆, ●), and 75°C (□, ■).



$$\begin{array}{c} \diagdown \underset{\substack{| \\ CO \\ | \\ NH_2}}{CH} \diagup \overset{CH_2}{} \diagdown \underset{\substack{| \\ CO \\ | \\ NH_2}}{CH} \diagup \end{array} + HCHO \rightleftharpoons \begin{array}{c} \diagdown \underset{\substack{| \\ CO \\ | \\ NH \\ | \\ CH_2OH}}{CH} \diagup \overset{CH_2}{} \diagdown \underset{\substack{| \\ CO \\ | \\ NH_2}}{CH} \diagup \end{array} \qquad (1a)$$



(1b)

Indeed, no gelation of the product was observed while conducting the reaction experiments. According to Flory's theory [4], it is known that if intramolecular cyclization had not taken place, the gel would have appeared at the critical extent of reaction of amide groups, p_c, given by

$$p_c = \alpha_c/r \qquad (2)$$

In this equation α_c is a critical value of the branching coefficient at the moment of gelation. In our case it means that there is the probability that two amide functions were linked to one with another by a methylene bridge. To find α_c, the following expression is used:

$$\alpha_c = \frac{1}{f - 1} \qquad (3)$$

where f is a functionality of the substrate subject to cross-linking. If the functionality of an amide group is taken as unity, f will be equal to the number-average degree of polymerization, D_n, of the polyacrylamide. $D_n = 2300$ was obtained from the relation given by Collinson and co-workers [5]:

$$[\eta] = 6.8 \times 10^{-4}\,\overline{M}_n^{\,0.66} \qquad (4)$$

where $[\eta]$ is the intrinsic viscosity of an aqueous solution of the polymer at 25°C (1.88 dL/g in our case) and $\overline{M}_n$ is the number-average molecular weight of polyacrylamide. From these data α_c is found to be 4.35×10^{-4}. In Eq. (2), r stands for the molar ratio of the two kinds of active functions of the reagents, i.e., in our case a ratio of amido groups to formaldehyde. Here, the functionality of the carbonyl

TABLE 1. Experimentally Found Extents of Reaction (p_e, p_e' and p_A) for Various Temperatures

Temperature (°C)	p_e	p_e'	p_A
45	0.83	0.55	0.76
60	0.79	0.53	0.78
75	0.78	0.52	0.76

group is 2, which means that r = 0.05. Thus the theoretical value of p_c becomes 2.95×10^{-2}. Table 1 provides the extents of reaction of amido groups, p_e, found experimentally from Eq. (5) at the time when no more changes of F and F_{f+m} were observed:

$$p_e = (2F_o - F_{f+m} - F)/A_o \tag{5}$$

where A_o and F_o are the initial molar concentrations of amide and formaldehyde, respectively. In each case p_e exceeds $p_c = 2.95 \times 10^{-2}$ significantly, which supports the opinion that some intramolecular reactions must have taken place. It is then quite possible that such reactions follow Schemes (1a) and (1b).

According to Carother's theory [6], which admits the possibility of intramolecular cyclizations, an infinite tridimensional network is formed when the extent of reaction of all the functional groups taking part in the process reaches a critical value p_c' given by

$$p_c' = 2/f' \tag{6}$$

where f' is an overall average functionality of the two reagents. For the process under consideration, p_c' is theoretically equal to 0.667, which is more than the experimental values of p_e' (Table 2) found from

$$p_e' = 2(2F_o - F_{f+m} - F)/(A_o + 2F_o) \tag{7}$$

Here p_e' signifies the extent of reaction of all the functional groups at the state of equilibrium. From the above it follows that in some favorable conditions the reaction mixtures should be able to form a gel. In-

TABLE 2. Dissociation Constants (K) of N-Methylol Groups as Products of Formaldehyde Addition to Polyacrylamide and Rate Constants (k' and k'') for Various Temperatures

Temperature (°C)	K (mol/L)	10^3 k' (L/mol·s)	10^3 k'' (L/mol·s)
45	0.10	0.97	0.91
60	0.24	2.2	1.8
75	0.33	5.5	5.1

deed, after storing the said solutions in an open vessel at ambient temperature for several days, a thin insoluble film could be detected on the surface of the liquid phase.

The kinetic curves in Fig. 1 show that at the beginning of the reactions F_{f+m} decreases almost at the same rate as does the concentration of the free formaldehyde. This suggests that the addition of HCHO to the amide function is slow in this case as compared with the velocity of the condensation of the resultant N-methylol derivative with another amide group. The final reaction products, i.e., the methylenediamide bridges, are stable structures, so the cyclization process (1b) should be almost quantitative. The actual high yield of this reaction is presumably the main reason for the efficiency of polyacrylamide when used as an inhibitor of formaldehyde emission from UF resins. If the intramolecular cyclization (1b) is fast in comparison with the first reactional stage (1a), then, from a statistical point of view, 87.5% of all amide groups will take part in the ring-forming process. The real fractions of $-NH_2$ functions linked with methylenes, p_A, found from the experimental data after the time when no more changes of F and F_{f+m} are observed, are summarized in Table 1. These values are slightly lower than the above-mentioned theoretical one, perhaps because of some carboxyl group content formed by hydrolysis of $-CONH_2$ functions in the polyacrylamide samples used. Another reason may be a decrease of the flexibility of the polymer backbone as the number of the side rings formed is augmented. At that time the cyclization reactions may occur with more difficulty.

The N-hydroxymethyl groups formed during Process (1a) continue to react according to Eq. (1b) unless they neighbor rather rigid and passive methylenediamide ring systems on both sides. The final concentration of these N-methylol functions depends on their dissociation constant K whose approximate values for different temperatures are given in Table 2. The following expression was employed for the calculations of K at the equilibrium state:

$$K = F(A_o - 2F_o + F + F_{f+m})/(F_{f+m} - F) \tag{8}$$

The first stage of reaction, (1a), is rate-determining. Initially, as the concentration of the N-hydroxymethyl functions is very small, the effect of reversible dissociation on the kinetics of the overall process is not significant. Then the following kinetic equations may be proposed:

$$-dF/dt = kFA_a \quad \text{or} \quad -dF_{f-m}/dt = kF_{f+m}A_a \tag{9}$$

where k is the initial rate constant of (1a) and A_a is a concentration of amide groups capable of taking part in the subsequent reaction stage (1b) after time t. In practice, it is possible that the constant k changes to some extent as the process continues. At the beginning, A_a does not differ significantly from the total concentration of amide groups, A. Then the rate constant k may be estimated from the relation $k'' < k < k'$, k' and k'' satisfying the equations

$$-\frac{dF}{dt} = k'F[A_o - 2(F_o - F)] \tag{10}$$

$$-\frac{dF_{f+m}}{dt} = k''F_{f+m}[A_o - 2(F_o - F_{f+m})] \tag{11}$$

The numerical values of k' and k'' are depicted in Table 2. On the basis of these data the approximative value of the corresponding activation energy was determined graphically from an Arrhenius plot. In either case (of the k' and k'' temperature-dependence series) it was equal to 62 kJ/mol. As expected, this order of magnitude is typical for the addition of formaldehyde to amide groups [7, 8].

SUMMARY AND CONCLUSIONS

At sufficiently high dilutions of polyacrylamide macromolecules (for instance, 4.6×10^4 L/mol) in neutral aqueous solutions, the reaction with formaldehyde proceeds in two stages. At first HCHO adds to amide groups with the formation of the N-methylol derivative, and then it is quite probable that condensation between the N-hydroxymethyl groups and their amide neighbors occurs. In the latter stage ring structures are formed in which the nitrogen atoms are linked with each other by methylene bridges. The velocity of the process is controlled by the addition reaction whose activation energy is approximatively 62 kJ/mol. The formation of stable, practically undissociable ring methylenediamide fragments on the polyacrylamide backbone is believed to be responsible for the high efficiency of this polymer in reducing the emission of formaldehyde from UF resins.

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