Correlating Viscosity in Urea–Formaldehyde Polymerization

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ABSTRACT: The objective of this study was to find a correlation for the viscosity changes during step polymerization of urea and formaldehyde. For this reason, a kinetic model for the condensation reactions was proposed, and using this model, a correlation for the kinematic viscosity changes of the solution during polymerization was obtained. Viscosity measurements of the samples during condensation reactions were carried out using Ubbelohde viscometers at intervals. The experimental data were curve fitted using our model, which was found to correspond very well. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci 69: 631–636, 1997

Key words: urea; formaldehyde; viscosity; polymerization; kinetic

INTRODUCTION

Urea–formaldehyde is mainly used as an adhesive in plywood and particle board industries. Two main steps are recognized in the reaction of formaldehyde with urea. The first is a simple addition of formaldehyde to introduce the hydroxymethl group and is catalyzed by either acids or bases. Hence, it takes place over the entire pH range.[1–12] The second step is a condensation reaction that involves the linking together of monomer units with the liberation of water to form a dimer, a polymer, or a vast network. The second reaction is only catalyzed by acids.

Tomita and Hirose[13] have shown that for formaldehyde-to-urea (F/U) molar ratios between 1.7 and 2.2 within the pH range 4–9, the following reactions take place:
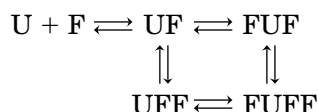
$$\text{U} + \text{F} \rightleftharpoons \text{UF} \rightleftharpoons \text{FUF}$$
$$\Updownarrow \qquad \Updownarrow$$
$$\text{UFF} \rightleftharpoons \text{FUFF}$$

where UF, FUF, UFF, and FUFF are monomethylolurea, N,N'-dimethylourea, N,N-dimethylolurea, and trimethylolurea, respectively.

This system was successfully observed by H NMR nuclear magnetic resonance spectroscopy on decomposition of both monomethylolurea and N,N'-dimethylolurea.[13] Methylolureas so formed undergo a series of condensation reactions with urea and themselves, giving rise to a series of products. These condensation reactions have been the subject of extensive studies, and several articles have been reported in the literature.[14–18] The following reaction scheme has been proposed, where M is the methylene bridge:

$$\text{UF} + \text{U} \rightarrow \text{UMU} \qquad (1)$$
$$\text{UF} + \text{UF} \rightarrow \text{UMUF} \qquad (2)$$
$$\text{UF}_2 + \text{UF}_2 \rightarrow \text{FUMUF}_2 \qquad (3)$$
$$\text{UF}_2 + \text{U} \rightarrow \text{UMUF} \qquad (4)$$
$$\text{UF}_2 + \text{UF} \rightarrow \text{FUMUF} \qquad (5)$$

It has been shown that the reaction between the amido methylol group and an amino group is bimolecular and hydrogen ion catalyzed. How-

ever, no buffer influence has been observed. The rate constant has been found to depend on the type of amide group or the amido methylene group.[18]

In this study, we have used the functional group approach in which we follow the polymerization by defining five reactive species. On the basis of this approach, a mathematical model is developed to predict the variation of polymer viscosity versus time, as discussed below.
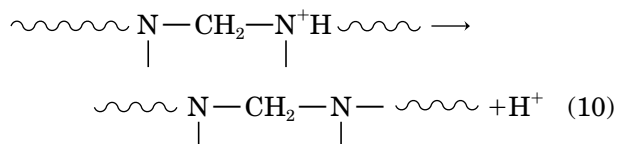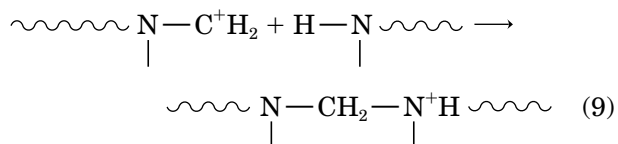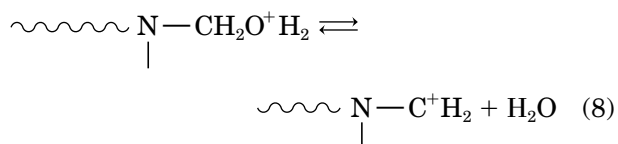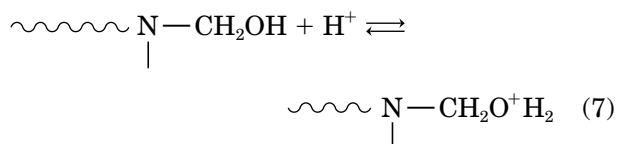
Kinetic Model for the Formation of Urea–Formaldehyde Polymer

According to the work of Smets and Borzee[19] on the condensation of monomethylolureas, both thermal and acid-catalyzed reactions occur together, and the rate equation is as follows.

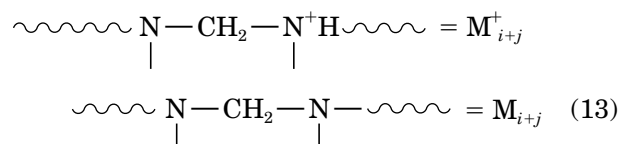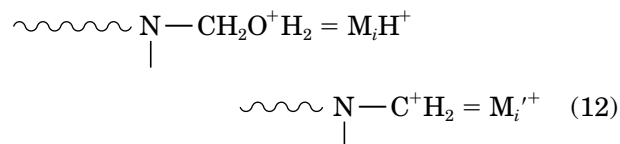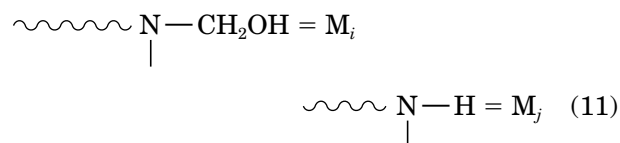$$-d[x]/dt = K[H^+][M]^2 + K'[M]^2 \quad (6)$$

where $[M]$, $[X]$, and $[H^+]$ are concentrations of monomethylolurea, methylol group, and hydronium ion, respectively. K and K' are rate constants.

In view of this, the following reaction mechanism has been proposed; eq. (9) is the rate-limiting step.

$$\sim\sim\sim N-CH_2OH + H^+ \rightleftharpoons$$

$$\sim\sim N-CH_2O^+H_2 \quad (7)$$

$$\sim\sim\sim N-CH_2O^+H_2 \rightleftharpoons$$

$$\sim\sim N-C^+H_2 + H_2O \quad (8)$$

$$\sim\sim\sim N-C^+H_2 + H-N\sim\sim\sim \longrightarrow$$

$$\sim\sim N-CH_2-N^+H\sim\sim\sim \quad (9)$$

$$\sim\sim\sim N-CH_2-N^+H\sim\sim\sim \longrightarrow$$
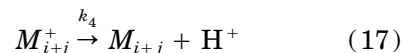
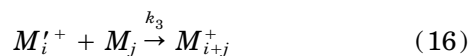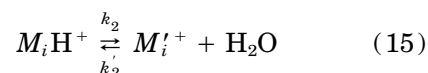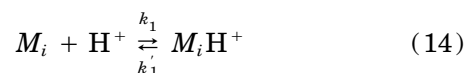$$\sim\sim N-CH_2-N-\sim\sim\sim +H^+ \quad (10)$$

Since the backward and forward rate constants of eqs. (7) and (8) are high with respect to eq.

(9), we may assume that they are at equilibrium. Let us apply the following notation:

$$\sim\sim\sim\sim N-CH_2OH = M_i$$

$$\sim\sim N-H = M_j \quad (11)$$

$$\sim\sim\sim N-CH_2O^+H_2 = M_iH^+$$

$$\sim\sim N-C^+H_2 = M_i'^+ \quad (12)$$

$$\sim\sim\sim N-CH_2-N^+H\sim\sim = M_{i+j}^+$$

$$\sim\sim N-CH_2-N-\sim\sim = M_{i+j} \quad (13)$$

Thus, we can write the above reaction mechanism as follows in which i and j denote the number of mono-, di-, or trimethylol molecules attached together.

$$M_i + H^+ \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} M_iH^+ \quad (14)$$

$$M_iH^+ \underset{k_2'}{\overset{k_2}{\rightleftharpoons}} M_i'^+ + H_2O \quad (15)$$

$$M_i'^+ + M_j \overset{k_3}{\to} M_{i+j}^+ \quad (16)$$

$$M_{i+j}^+ \overset{k_4}{\to} M_{i+j} + H^+ \quad (17)$$

$M_i'^+$ species can react with all M_j, but M_i^+ cannot.

The reaction rate of different groups involved in the reaction are not the same, thus, k_3 not only is a function of temperature but also F/U ratio. In other words, k_3 is an average, the value of which is assumed constant within the measured viscosity range. Moreover, there is a thermal reaction path which is bimolecular, according to the work of Smets and Borzee.[19]

$$M_i + M_j \overset{k_t}{\to} M_{i+j} + H_2O \quad (18)$$
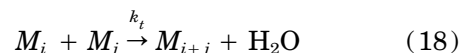
Here, k_t is also a rate constant that is a function of temperature and the F/U ratio.

Considering the proposed mechanism, we can write the rate equation for different species as follows:

$$\frac{d[M_1]}{dt} = -k_3[M_1] \sum_{i=1}^{\infty} [M_i'^{\,+}]$$
$$- k_t[M_1] \sum_{i=1}^{\infty} [M_i] \quad (19)$$

$$\frac{d[M_2]}{dt} = -k_3[M_2] \sum_{i=1}^{\infty} [M_i'^{\,+}] + k_4[M_2^{+}]$$
$$+ \frac{k_t}{2} [M_1]^2 - k_t[M_2] \sum_{i=1}^{\infty} [M_i] \quad (20)$$

$$\frac{d[M_3]}{dt} = -k_3[M_3] \sum_{i=1}^{\infty} [M_i'^{\,+}] + k_4[M_3^{+}]$$
$$+ \frac{k_t}{2} [M_1][M_2] + \frac{k_t}{2} [M_2][M_1]$$
$$- k_t[M_3] \sum_{i=1}^{\infty} [M_i] \quad (21)$$

$$\frac{d[M_4]}{dt} = -k_3[M_4] \sum_{i=1}^{\infty} [M_i'^{\,+}] + k_4[M_4^{+}]$$
$$+ \frac{k_t}{2} [M_1][M_3] + \frac{k_t}{2} [M_2][M_2]$$
$$+ \frac{k_t}{2} [M_3][M_1] - k_t[M_4] \sum_{i=1}^{\infty} [M_i] \quad (22)$$

The factor of $\frac{1}{2}$ appears in these expressions because the rate constant k_t is defined with respect to the rate of disappearance of the polymer molecules (two molecules of M_1 disappear for each molecule of M_2 formed in the reaction $M_1 + M_1 \rightarrow M_2$).

Since the reactions $M_1 + M_2 \rightarrow M_3$ and $M_2 + M_1 \rightarrow M_3$ are indistinguishable from each other, it follows that the rate of appearance of polymer M_3 by these thermal reactions may be represented as

$$\frac{d[M_3]}{dt} = \frac{k_t}{2} [M_1][M_2] + \frac{k_t}{2} [M_2][M_1] \quad (23)$$

Thus, the overall rate of appearance of any polymer M_P is

$$\frac{d[M_p]}{dt} = -k_3[M_p] \sum_{i=1}^{\infty} [M_i'^{\,+}]$$
$$+ k_4[M_p^{+}] + \frac{k_t}{2} \sum_{i=1}^{P-1} [M_i][M_{p-i}]$$
$$- k_t[M_p] \sum_{i=1}^{\infty} [M_i] \quad (24)$$

Summing up the above equations yields

$$\frac{d \sum_{j=1}^{\infty} [M_j]}{dt} = -k_3 \sum_{j=1}^{\infty} [M_j] \sum_{i=1}^{\infty} [M_i'^{\,+}]$$
$$+ k_4 \sum_{j=2}^{\infty} [M_j^{+}] + \frac{k_t}{2} \sum_{j=2}^{\infty} \sum_{i=1}^{j-1} [M_i][M_{j-i}]$$
$$- k_t \sum_{j=1}^{\infty} [M_j] \sum_{i=1}^{\infty} [M_i] \quad (25)$$

Since eqs. (14) and (15) are fast and at equilibrium, it follows that

$$[M_i'^{\,+}] = \frac{k_2[M_i H^{+}]}{k_2'[H_2O]} \quad (26)$$

$$[M_i H^{+}] = \frac{k_1}{k_1'} [M_i][H^{+}] \quad (27)$$

Because of a large amount of water in the reaction media, we may assume that its concentration is constant, so we have

$$[M_i'^{\,+}] = \frac{k_2 \cdot k_1[M_i][H^{+}]}{k_2' \cdot k_1'[H_2O]} = K_e[M_i][H^{+}] \quad (28)$$

$$K_e = \frac{k_2 \cdot k_1}{k_2' \cdot k_1'[H_2O]} \quad (29)$$

When the expression given by eq. (28) is summed over all i ($i = 1, 2, 3, \cdots$), the following result is obtained:

$$\sum_{i=1}^{\infty} [M_i'^{\,+}] = K_e[H^{+}] \sum_{i=1}^{\infty} [M_i] \quad (30)$$

Considering eq. (28), we can write the rate equations for intermediate species M_j^{+}'s:

$$\frac{d[M_2^{+}]}{dt} = + \frac{k_3}{2} K_e[H^{+}][M_1]^2 - k_4[M_2^{+}] \quad (31)$$

$$\frac{d[M_3^{+}]}{dt} = \frac{k_3 K_e}{2} [H^{+}][M_1][M_2]$$
$$+ \frac{k_3 K_e}{2} [H^{+}][M_2][M_1] - k_4[M_3^{+}] \quad (32)$$

Since pH is constant during the condensation step, we can write, in general,

$$\frac{d[M_p^+]}{dt} = \frac{k_3 K_e}{2} [\mathrm{H}^+] \sum_{i=1}^{p-1} [M_i][M_{p-i}]$$

$$- k_4 [M_p^+] \quad (33)$$

$$\frac{d \sum_{j=2}^{\infty} [M_j^+]}{dt} = \frac{k_3 K_e}{2} [\mathrm{H}^+] \sum_{j=2}^{\infty} \sum_{i=1}^{j-1} [M_i][M_{j-i}]$$

$$- k_4 \sum_{j=2}^{\infty} [M_j^+] \quad (34)$$

Using the fact that all M_j^+ are consumed at approximately the same rate at which they are formed (the pseudo-steady-state approximation), we have

$$\frac{d \sum_{j=2}^{\infty} [M_j^+]}{dt} = 0 \Rightarrow \sum_{j=2}^{\infty} [M_j^+]$$

$$= \frac{k_3 K_e [\mathrm{H}^+]}{2k_4} \sum_{j=2}^{\infty} \sum_{i=1}^{j-1} [M_j][M_{j-i}] \quad (35)$$

The double summation in eq. (35) may be expressed as[19]

$$\sum_{j=2}^{\infty} \sum_{i=1}^{j-1} [M_i][M_{j-i}] = \left[\sum_{i=1}^{\infty} [M_i] \right]^2 \quad (36)$$

Combining eqs. (25), (30), (35), and (36) yields

$$\frac{d \sum_{j=1}^{\infty} [M_j]}{dt}$$

$$= - \left[\frac{k_3 K_e}{2} [\mathrm{H}^+] + \frac{k_t}{2} \right] \left[\sum_{j=1}^{\infty} [M_j] \right]^2 \quad (37)$$

The number-average degree of condensation is defined as

$$\bar{D}_n = \frac{\sum i[M_i]}{\sum [M_i]} = \frac{M_0}{\sum [M_i]} \quad (38)$$

in which M_0 is the total concentration of initial monomers. Therefore,

$$- \frac{M_0 d\bar{D}_n}{\bar{D}_n^2 dt} = - \left[\frac{k_3 K_e}{2} [\mathrm{H}^+] + \frac{k_t}{2} \right] \frac{M_0^2}{\bar{D}n^2} \quad (39)$$

EXPERIMENTAL

Chemicals

Commercial formalin was supplied by SINA Chemical Co. and was used as the source of formaldehyde. Its concentration was 39.37% when analyzed using the sulfite method.[21] The methanol content of formalin and its acidity were, respectively, 3.12% and 180 ppm using ASTM standards.[22] Commercial urea with a nitrogen content of 45.8% was used. Urea was supplied by Shiraz Petrochemical Co. A modification of the sulfite method[23] for formaldehyde solution was used for the determination of free formaldehyde.

Resin Synthesis

Commercial formalin was poured into a beaker. Its pH was adjusted to 5.1 with $0.1N$ NaOH. The required amount of urea was added to produce an initial F/U ratio of 1.94. The resulting solution was stirred for 4 min, and then the pH was adjusted to 8.5. This solution was charged to a three-necked reaction vessel placed in a water bath. The reaction vessel was equipped with a mechanical stirrer and a condenser. The reaction temperature was allowed to rise up to 89°C and free formaldehyde was periodically checked until equilibrium was reached (approximately about 35 min). After this time, condensation reactions were initiated at constant temperature of 85 ± 1°C by lowering the pH of the solution with formic acid to the desired value.

During condensation reactions, viscosity measurements were done using Ubbelohde viscometers at selected intervals. For this purpose, samples of about 25 mL were taken from the vessel and poured into a small beaker placed in an ice-water bath to lower the temperature of the sample to 25°C as soon as possible. The procedure was the same for all experiments except for pH and time of condensation reactions.

RESULTS AND DISCUSSION

Assuming that the relation between the logarithm of kinematic viscosity and the number-average
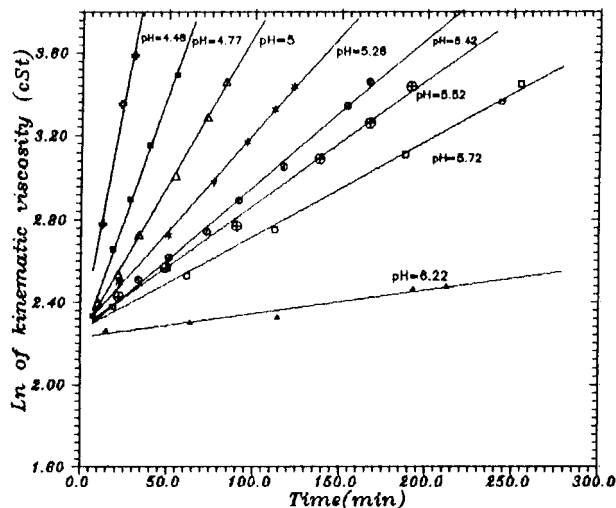
Figure 1 Kinematic viscosity changes during condensation reactions.

Figure 2 Plot of b versus hydronium ion concentration $[H^+]$.

degree of condensation is linear (this is a proposal)

$$\ln v = A + B\bar{D}n \tag{39}$$

we obtain

$$\frac{d(\ln v)}{Bdt} = \left[\frac{k_3K_e}{2}[H^+] + \frac{k_t}{2}\right]M_0 \tag{40}$$

Solving eq. (40) with the initial condition that at $t = 0$ and $v = v_0$, we obtain the following result:

$$\ln\left(\frac{v}{v_0}\right) = \left[\frac{BM_0k_3Ke[H^+]}{2} + \frac{BM_0k_t}{2}\right]t \tag{41}$$

$$v = v_0\exp(bt) \tag{42}$$

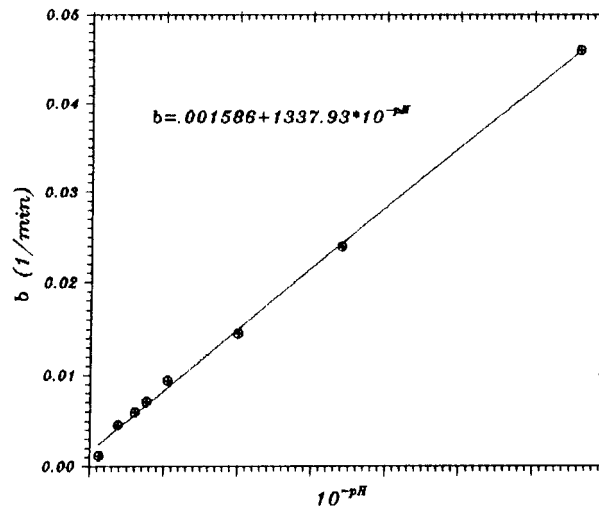$$b = \frac{BM_0k_3K_e[H^+]}{2} + \frac{BM_0k_t}{2} \tag{43}$$

According to eq. (42), kinematic viscosity varies exponentially with time during condensation reactions. Also, b is a linear function of hydronium ion concentration at constant temperature.

Equation (42) may be rewritten as

$$\ln v = \ln v_0 + bt \tag{44}$$

According to eq. (44), the logarithm of kinematic viscosity must be a linear function of time. In Figure 1, the logarithm of kinematic viscosity is plotted against time for each experiment. The slope b and intercept $\ln v_0$ for each experiment were calculated by the method of least squares and are shown in Table I. In Figure 2, b was plotted

Table I Results of Regression Analysis

Exp. No.	pH During Condensation Reactions	v_o (cSt)	b (1/min)	Average Temperature During Condensation Reactions (°C)	Correlation Coefficient
1	4.48	9.30	.046	86.5	0.994
2	4.77	9.00	.024	85.0	0.998
3	5.00	9.36	.015	85.1	0.999
4	5.28	9.65	.009	85.0	0.999
5	5.42	9.48	.007	85.0	0.998
6	5.52	9.71	.006	84.8	0.998
7	5.72	9.63	.005	84.8	0.997
8	6.22	9.30	.001	84.5	0.979

against hydronium ion concentration $[H^+]$. The graph shows a linear relationship, as we expect from eq. (43).

Also as shown in Table I, v_0 is approximately constant. Its average value is 9.43 cSt. Finally, we present the following experimental correlation for the estimation of kinematic viscosity during condensation reactions for the foregoing experimental condition.

$$\ln(v/9.43)$$
$$= (0.001586 + 1337.938 * 10^{-pH}) * t \quad (45)$$

REFERENCES

1. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **71,** 643 (1952).
2. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **71,** 661 (1952).
3. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **71,** 890 (1952).
4. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **72,** 88 (1953).
5. L. E. Smyte, *J. Am. Chem. Soc.,* **73,** 2735 (1951).
6. L. E. Smyte, *J. Am. Chem. Soc.,* **74,** 2713 (1952).
7. L. E. Smyte, *J. Am. Chem. Soc.,* **75,** 574 (1953).
8. L. E. Smyte, *J. Am. Chem. Soc.,* **75,** 1508 (1953).
9. L. Bettelhiem and J. Cedwall, *J. Svensk Kemisk Tidskirft,* **60,** 208 (1948).
10. G. A. Crowe and C. L. Lynch, *J. Am. Chem. Soc.,* **70,** 3796 (1948).
11. G. A. Crowe and C. L. Lynch, *J. Am. Chem. Soc.,* **71,** 3791 (1949).
12. G. A. Crowe and C. L. Lynch, *J. Am. Chem. Soc.,* **72,** 3622 (1950).
13. B. Tomita and Y. Hirose, *J. Poly. Sci.,* **14,** 387 (1976).
14. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **72,** 202 (1953).
15. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **72,** 207 (1953).
16. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **72,** 213 (1953).
17. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **72,** 1207 (1953).
18. J. I. DeJong and J. DeJonge, *Rec. Trav. Chim.,* **72,** 139 (1953).
19. G. Smets and A. Borzee, *J. Poly. Sci.,* **3,** 371 (1951).
20. C. D. Holland and R. F. Anthony, *Fundamentals of Chemical Reaction Engineering,* 2nd Ed., Prentice-Hall International, Inc., 1989.
21. American Society for Testing and Materials, *Concentration of Formaldehyde Solutions,* ASTM Designation D 2194-65, Annual Book of ASTM Standards, Vol. .06.03 1984.
22. American Society for Testing and Materials, *Methanol Content of Formaldehyde Solutions,* ASTM Designation 2380-79, Annual Book of ASTM Standards, Vol. .06.03 1984.
23. G. M. Kline, *Analytical Chemistry of Polymers,* Wiley, New York, 1963.