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Cationic Polymerization of Formaldehyde in Liquid Carbon Dioxide. III. Thermal Stabilization of the Resulting Polymer*1

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We investigated the acetylation of the endgroups of the polymer chain resulting from the polymerization of formaldehyde in liquid carbon dioxide in the presence of acetic anhydride. The thermal stability and the toughness of the resulting polymer were examined. All of the endgroups of polymer chains were satisfactorily acetylated by means of heating, between 140 and 150°C, the solid polymer, which was separated by discharging the unreacted monomer and carbon dioxide after polymerization. The acetic anhydride which was added in the beginning of the polymerization at a concentration of 5 mol% per monomer, was sufficient to stabilize the polymer thermally. On the acetylating of the polymer, the presence of air or acetic acid in the amount used to initiate the polymerization had no effect on the properties of the acetylated polymer. A simplified purification procedure for the acetylated polymer was presented.

Polyoxymethylene, ended with hemiformal groups, can be subjected to degradation by several processes; stepwise thermal depolymerization from the chain ends, autoxidative degradation leading to chain scission (observed at temperatures above 170°C), acidolytic scission of the acetal linkages of the main chain, and thermal chain scission at temperatures higher than 270°C.[1,2] In order to stabilize the polyoxymethylene by means of preventing the stepwise thermal depolymerization, acetylation,[3-5] etherification,[2,6,7] and other methods have been proposed. However, these stabilizing treatments must be carried out in separated processes. Wagner *et al.* have proposed a process of polymerizing formaldehyde in acetic anhydride as a solvent, followed with heating, *in situ*, the resulting polymer.[8] The acetic anhydride which is used in this process must, however, be drastically purified in order to remove the acid present in it.

The authors have previously reported on a cationic polymerization of formaldehyde in liquid carbon dioxide to produce high-molecular-weight polyoxymethylene.[9,10] The present work was

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carried out in order to simplify the stabilization process by means of acetylating the polymer by acetic anhydride, which had already been added to the system at the beginning of the polymerization of formaldehyde in liquid carbon dioxide.

Experimental

Materials. The formaldehyde monomer was prepared as has been previously described.[9] The acetic anhydride was purified only by distillation at normal pressure, so that it usually contained acetic acid in a concentration slightly above 1 wt%. The amount of acetic acid used as a catalyst was, therefore, determined with due regard to this concentration. In the case of adding a large quantity of acetic anhydride, it was necessary to use extremely-purified acetic anhydride so that excess acetic acid did not mix in the polymerization system. The acetic anhydride was, therefore, purified from acetic acid by reacting it with carbodiimide, thus producing a non-volatile compound.[11] That is, acetic anhydride was mixed with dicyclohexylcarbodiimide, kept at 100°C for one hours and then distilled (bp 51.7°C/60 mmHg). The concentration of acetic acid in the acetic anhydride thus prepared was found to be less than 0.1 wt%.

Procedures for Polymerization and Stabilization. The polymerization was carried out in the same manner as has been described in the previous papers,[9,10] except that the reaction temperature was not carefully controlled.

After the unreacted monomer and carbon dioxide has been discharged, the resulting polymer was taken out from the the autoclave in an atmosphere of carbon dioxide or air, and transferred into a glass tube which was afterwards sealed. Then, the sample was held in an oil bath kept at a fixed temperature. The polymer which resulted from the polymerization or which was obtained after heat treatment was washed with cooled ethyl ether and with acetone, and dried *in vacuo*.

In the some experiments, the polymer was heated as it was in the autoclave after the inner pressure had been reduced. Then, the polymer was purified by removing the unreacted acetic anhydride and other compounds only by means of evacuating the autoclave under heating.

Measurements of the Properties of the Resulting Polymer. The degree of polymerization was determined by viscosity measurements in a manner which has previously been described.[9]

The thermal stability of the resulting polymer was determined by the continuous measurement of the thermal degradation in a nitrogen atmosphere, which was kept constant at 222°C in a vapor bath of boiling methyl salicylate; it was represented as a first-order reaction rate constant. When a plot of the log of the weight per cent under composed versus the time gave two straight lines, the rate constants, k_{222}, calculated from each straight line are listed together with the range of decomposition (noted in parentheses).

The acetyl and hydroxyl groups of the resulting polymer were determined by means of a study of the infrared spectrum, which was measured with a polymer film prepared by cold pressing. The degree of acetylation was calculated as the molar ratio of the acetyl endgroup to the total endgroup, which was estimated by the following equation;

$$\text{Degree of acetylation} = \frac{D_{C=O}}{\alpha D_{OH} + D_{C=O}} \quad (1)$$

Here, $D_{C=O}$ and D_{OH} are the absorption intensities of the carbonyl group at 1750 cm^{-1} and of the hydroxyl group at 3500 cm^{-1} respectively; they were measured on the infrared spectrum of a polymer film. An α factor, which is a ratio of the molar extinction coefficient of the two bands, was experimentally determined on six samples; it was 2.46 ± 0.05.

The degree of toughness was measured by the folding endurance test described below. The polymer, which was mixed with 1% portions of both 4,4'-butylidene-bis-(6-tertiary butyl metacresol) and polyamide, was heated under compression to mold a film 120 μ thick. The folding endurance test was carried out using an MIT folding endurance tester according to ASTM D 643—43. The number of creasing cycles until the film breaks off is referred to as the "degree of toughness." The value indicated in the table is the mean value for five runs.

Result and Discussion

Influence of Acetic Anhydride Concentration. In order to establish the effect of the acetic anhydride concentration on the acetylation of the resulting polymer in the stabilizing process, the monomer was polymerized in liquid carbon dioxide at 30°C, using acetic acid as the catalyst. After polymerization, a part of the unwashed resulting polymer was transferred into a sealed tube in an atmosphere of carbon dioxide and then heated at 140°C. The results are shown in Table 1.

It was found that the polymer yield in the polymerization was reduced by increasing the concentration of acetic anhydride, and that a part of the resulting polymer had already been acetylated. Acetic anhydride at a concentration above 5 mol% was also found to be sufficient to acetylate all of the endgroups of the polymer chain. Moreover, the film which was molded from the polymer mixed with the antioxidants exhibited satisfactory degree of toughness.

Influences of Heating Temperature and Time. The effects of the temperature and the time in the stabilization process on the properties of the polymer were studied by an experiment in which the polymer produced in the polymerization in the presence of acetic anhydride (5 mol%) was divided into sealed tubes in an atmosphere of carbon dioxide and then heated. The results are shown in Table 2. The heating temperature at 120°C was too low to perform sufficient acetylation, whereas the decomposition of the polymer was appreciable at 160°C. As a result, the optimum operation temperature in the stabilization process was in a range of 140 to 150°C, and a reacton time of more than 2 hr was not required.

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TABLE 1. INFLUENCE OF ACETIC ANHYDRIDE CONCENTRATION ON ACETYLATION OF THE RESULTING POLYMER

I) Polymerization[a)]

Run No.	Acetic anhydride mol%/monomer	Polymer yield wt%	Degree of polym.	k_{222} %/min	Degree of acetylation mol%
1-1	0.5	76.8	1860	4.21	18
2	1.0	56.5	1680	5.2 (0—34%) 2.6 (34—%)	17
3	5.0	53.4	1580	4.99(0—27%) 1.48(27—%)	27
4	50.0	51.7	1520	6.60(0—39%) 0.86(39—%)	21

a) monomer, 6 g, 60 wt% in CO_2; acetic acid, 0.1 mol%/monomer; temp., 30°C.; time, 2 hr.

II) Acetylation[b)]

Run No.	Acetic anhydride per polymer end, mole ratio	Recovery yield wt%	Degree of polym.	k_{222} %/min	Degree of acetylation, mol%	Degree of toughness
1-1	6.0	97	1910	1.92(0—23%) 0.54(23—%)	77	—
2	14.9	96	1720	0.76(0—9%) 0.32(9—%)	95	—
3	74	97	1540	0.27	100	2.5×10^5
4	735	97	1580	0.21	100	2.0×10^5

b) heating temp., 150°C.; time, 1 hr.

TABLE 2. INFLUENCE OF TEMPERATURE AND REACTION TIME ON ACETYLATION OF THE RESULTING POLYMER[a)]

Run No.	Time hr	Recovery yield wt%	Degree of polym.	k_{222} %/min	Degree of acetylation, mol%
		Temperature, 120°C			
2-1	1	90	1680	3.2 (0—51%) 0.76(51—%)	71
2	2	88	1730	1.8 (0—16%) 0.55(16—%)	88
3	5	85	1650	0.52(0—11%) 0.36(11—%)	99
		Temperature, 140°C			
4	1	87	1700	0.51(0—6%) 0.30(6—%)	99
5	2	86	1670	0.28	99
6	5	82	1550	0.25	100
		Temperature, 160°C			
7	1	79	1650	0.27	99
8	2	75	1560	0.34	100
9	5	71	1450	0.26	100

a) Polymerization:
monomer, 6 g, 60 wt% in CO_2; acetic acid, 0.1 mol%/monomer; acetic anhydride, 5 mol %/monomer; temp., 30°C; time, 2 hr.
Result:
polymer yield, 56.5%; degree of polym., 1710; k_{222}, 3.1%/min; degree of acetylation, 23.8 mol%.
The resulting polymer was divided in the ampules of 30 m*l*.

TABLE 3. INFLUENCE OF THE ATMOSPHERE OF CARBON DIOXIDE AND AIR

I) Polymerization:
monomer; 6 g, 60 wt% in CO_2.
acetic anhydride; 5 mol%/monomer.
acetic acid; 0.1 mol%/monomer.
temperature; 30°C.
time; 2 hr.

Result:
polymer yield; 61.5 wt%.
degree of polym.; 1780.
k_{222}; 3.7 %/min.

II) Acetylation[a)]

Degree of polym.	k_{222} %/min	Degree of acetylation, mol%
	in carbon dioxide	
1740	0.51(0—6%) 0.32(6—%)	99
1560	0.32	100
	in air	
1550	0.55(0—5%) 0.30(5—%)	99
1730	0.76(0—11%) 0.32(11—%)	98

a) temp., 140°C; time, 2 hr.

Influence of Atmosphere. The crude polymer resulting from the polymerization was divided in an atmosphere of carbon dioxide or dry air into sealed tubes and heated 140°C for 1 hr. Table 3 shows these results. The presence of air caused the thermal stability of the resulting polymer to deteriorate somewhat, but this deterioration was not serious.

Influence of Acetic Acid. The polymerization of formaldehyde in liquid carbon dioxide is initiated by carboxylic acid as a catalyst, as has been described previously in this series. On the other hand, the acidolytic scission of acetal linkages of the main chain by carboxylic acid has been reported.[1] Therefore, the influence of acetic acid, as a sample of carboxylic acid, on the degree of polymerization and thermal stability of the resulting polymer in the stabilization process was investigated. The results are shown in Table 4. It was found that acetic acid reduced the thermal stability in a part of the resulting polymer, but 0.1 mol% per monomer, that is, the amount which was used as a catalyst, had no effect.

Table 4. Influence of acetic acid on acetylation

I) Polymerization[a]

Run No.	Acetic acid mol%/monomer	Polymer yield wt%	Degree of polym.	Degree of acetylation mol%
4-1	0.1	58.6	1210	27
2	0.1	57.8	1250	24
3	0.2	68.2	1070	21
4	1.0	74.1	640	26

a) monomer, 6 g, 60 wt% in CO_2; temp., 30°C; time, 2 hr; acetic anhydride, 5 mol%/monomer.

II) Acetylation[b]

Run No.	Recovery yield wt%	Degree of polym.	k_{222} %/min	Degree of acetylation mol%
4-1	89	1200	0.34	100
2	86	1140	0.25	100
3	83	1020	0.59(0—6%) 0.14(6—%)	99
4	62	660	1.53(0—13%) 0.35(13—%)	92

b) Crude polymer was divided in the atmosphere of carbon dioxide. temp., 140°C; time, 2 hr.

Procedure of Purifying the Resulting Polymer. After the unreacted monomer and carbon dioxide had been discharged, the polymer was a solid material and was wet with acetic anhydride. In addition to the polymer, the materials which exist in the stabilization process are acetic anhydride, carboxylic acid, carbon dioxide, and by-products which are volatile at the operating temperature. Therefore, these compounds can easily be removed by evacuating the reaction vessel under heating. The properties of the polymer purified by such a simple procedure were studied.

The polymerization was carried out under the condition shown in Table 5. After the autoclave had been heated at 150°C for 1 hour and then the inner pressure been reduced, the reaction vessel was evacuated under heating. The polymer, which was not washed or dried, exhibited satisfactory properties, as Table 5 shows. This result permitted the purification of the stabilized polymer to be simplified.

Table 5. Effect of evacuation on the purification of the resulting polymer

I) Polymerization
monomer, 6 g, 60 wt% in CO_2; acetic acid, 0.1 mol%/monomer; acetic anhydride, 5 mol%/monomer; temp., 30°C; time, 2 hr.

II) Acetylation
After purging out of the unreacted monomer and carbon dioxide, the polymer was heated at 150°C for 1 hr.

III) Results

Evacuation time at 150°C, min	Total polymer yield, wt%	Degree of polym.	k_{222} %/min	Degree of toughness
30	58.2	1680	0.31	24×10^4
60	57.4	1490	0.21	48