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Copolymerization of Formaldehyde and Succinic Anhydride in the Presence of Carbon Dioxide

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A Study of the copolymerization of formaldehyde and succinic anhydride was carried out in a liquid carbon dioxide solution without adding any catalyst. A copolymer, in which a small number of succinic units was inserted into the sequence of oxymethylene units because of the low rate of copolymerization of succinic anhydride, was formed. With enhancing the concentration of succinic anhydride, the content of succinic units in the copolymer slightly increased. At reaction temperatures up to 120°C, the molecular weight of the copolymer decreased with a rise in the temperature, whereas the content of succinic units increased to about 3 mol%. The copolymerization proceeded rapidly, so the reaction immediately reached equilibrium. From the results of the study by X-ray diffractiometry, the crystal structure of the copolymer can be said to be similar to that of polyoxymethylene, but the crystallinity of the copolymer decreased as the content of succinic units increased. The rate of thermal degradation, which started from the end-groups of the copolymer was decreased by ester linkgae. The thermal-degradation temperature was enhanced as the content of succinic units increased. The copolymer also showed a high resistivity to the folding of the film, even though it had not been treated so as thoroughly to esterify the endgroups of the copolymer.

The present authors have studied the polymerization of formaldehyde in a liquid carbon dioxide solution in the presence of acetic anhydride. They have thus determined that the resulting polyoxymethylene can easily and thoroughly be acetylated by discharging the unreacted monomer and carbon dioxide from the reaction system and then heating, *in situ*, the remains.[1] A perfect acetylation of the polymer end-groups is achieved with acetic anhydride, which is added, in advance of polymerization, into the reaction system at a concentration of only 5 mol% to the monomer. This fact suggests that the acetic anhydride added is selectively located in the neighborhood of the growing polymer chain end in the stage of propagation. If a cyclic acid anhydride is used instead of acetic anhydride, the formation of a copolymer in which the sequence of oxymethylene units is connected with both ends of the ring-opening acid anhydride may be inferred. This work is devoted to a study of how to prepare the copolymer composed of oxymethylene and ester units by the copolymerization of formaldehyde and succinic anhydride in the presence of carbon dioxide; it will also attempt to establish the properties of the copolymer.

Experimental

Preparation of Materials. The formaldehyde monomer was prepared by the pyrolysis of dried α-polyoxymethylene from 150 to 180°C in a stream of carbon dioxide, after which the gas mixture thus produced was cooled at -78°C in order to condense the formaldehyde and carbon dioxide, as has been described before.[2] The concentration of formaldehyde in the thus-prepared solution of carbon dioxide was 60.1 wt%. The succinic anhydride was purified by recrystallization from a chloroform solution.

Procedure of Polymerization. A stainless-steel pressure vessel, with a capacity of 30 m*l* was used for the polymerization. The weighed succinic anhydride was placed in the vessel, after which the vessel was evacuated at room temperature and then cooled by liquid nitrogen. The monomer solution, which had previously been prepared in a monomer reservoir, was fed into the evacuated pressure vessel through a tube connecting the vessel to the monomer reservoir. The amount of the monomer solution thus fed in was determined by weighing the vessels before and after the feeding. The polymerization was carried out by keeping the pressure vessel in an oil-bath controlled within ± 1°C. After the polymerization, the pressure vessel was cooled to 20°C; the unreacted monomer and carbon dioxide were then purged out.

After it had been cooled at -78°C, the product was

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[1] H. Yokota, M. Kondo, T. Kagiya and K. Fukui, This Bulletin, **41**, 1668 (1968).

[2] H. Yokota, M. Kondo, T. Kagiya and K. Fukui, *J. Polymer Sci.*, **A-1**, **6**, 425 (1968).

washed with ethyl ether cooled at −78°C and then with acetone. The succinic anhydride remaining in the resulting polymer was extracted with chloroform for 24 hr by using a Soxhlet extractor. The obtained polymer was dried *in vacuo* at room temperature.

Procedure for Measuring Properties of the Copolymer. The inherent viscosity, η_i was determined by an Ostwald viscometer; the starting solution contained 0.5 g of the copolymer in 100 m*l* of *p*-chlorophenol in which 2% of α-pinene had been dissolved at 60°C.

The thermal stability of the copolymer was evaluated by the first-order reaction rate constant, k_{222} for thermal degradation at 222°C in an inert atmosphere. By heating the copolymer in a nitrogen atmosphere, which was kept at 222°C by means of a vapor bath of boiling methyl salicylate, the weight loss of the copolymer was followed continuously. The rate constant was estimated from the slope of the linear relation between the heating time and the logarithm of the weight loss of the polymer.

The folding endurance was represented by the number of creasing cycles which the copolymer film withstood before breaking when a film 120 μ thick was subjected to the creasing test of ASTM D-643-43. The film was prepared by pressing under heating.

The X-ray diffraction spectra were measured by the powdered-crystal method with a Rigaku-Denki DF-3 automatic X-ray diffractiometer. Filtered Cu$K\alpha$ radiation was used in this study.

Differential thermal analysis was carried out by a Shimadzu DT-10 differential thermoanalyzer. The powdered copolymer was dispersed in α alumina at a concentration of 20 wt%.

Determination of Copolymer Composition. The mole fraction of the copolymers was determined by measuring the infrared absorption intensity at 1737 cm^{-1} of the carbonyl group of the ester linkage. The absorption intensity at 1740 cm^{-1} of the carbonyl group, which was divided by the absorption intensity at 2930 cm^{-1} of the methylene group in order to eliminate the influence of sample thickness, was measured at a variety of compositions in a mixture of polyoxymethylene and methyl succinate, and the calibration curve thus obtained served to quantify the carbonyl group in the resulting copolymer. The infrared spectrum was measured by using a Hitachi EPI-2 infrared spectrometer. The polymer sample was molded as a KBr pellet or film. The film was prepared by pressing the copolymer powder at room temperature.

Results and Discussion

Influence of the Monomer Composition on the Copolymerization. The influence of the monomer composition on the copolymerization of formaldehyde and succinic anhydride in a liquid carbon dioxide solution at 100°C was investigated; the results are shown in Table 1.

Figure 1 shows a typical example of the infrared spectrum for the resulting polymer, in which the absorption band of the carbonyl group is exhibited only at 1740 cm^{-1}. This band was ascribable to the ester carbonyl group. This fact indicates that succinic anhydride gives ester linkage in the copolymer by means of ring-opening reaction. The present authors have already presented the following equation for the relation of the inherent viscosity, η_i and the number-average degree of polymerization, $\overline{P}_n$ to polyoxymethylene2):

$$\eta_i = 2.14\times10^{-2}\overline{P}_n^{0.61}$$

Assuming this equation to be applicable also in the case of a copolymer containing a low content of succinic anhydride as a comonomer, the number-average degree of polymerization of the copolymer shown in Figure 1 was found to be 1500. On the other hand, the determined content of succinic units in the copolymer was 0.71 mol%. Admittedly, the concentration of succinic units was about six times that of the polymer end-groups, the latter figure having been calculated from the number-average degree of polymerization.

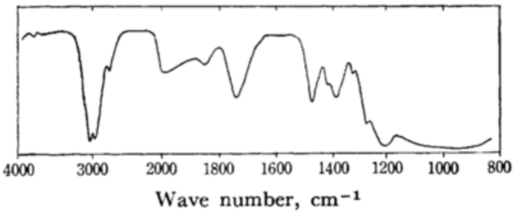


Fig. 1. Infrared spectrum of formaldehyde-succinic anhydride copolymer.
The sample; η_i 1.6 d*l*/g, succinic unit content 0.71 mol%.

TABLE 1. INFLUENCE OF MONOMER COMPOSITION ON COPOLYMERIZATION

CH_2O g	SAH[*1] g	SAH/CH_2O mol ratio	CO_2 g	Polymer yield g	Conversion[*2] wt%	η_i d*l*/g	k_{222}[*3] %/min	Content of succinic unit, mol%
0.5	5.8	3.0	0.3	0.26	4.3 (52.0)	1.4	6.3	0.49
1.9	2.8	0.50	1.2	1.13	24.1 (59.5)	1.6	5.2	0.62
3.5	1.1	0.091	2.4	2.17	47.2 (62.0)	1.3	7.1	0.59
2.7	0.11	0.012	1.8	1.55	55.4 (57.4)	1.6	6.7	0.71

Reaction conditions; temperature 100°C, time 60 min.

[*1] Succinic anhydride.

[*2] Values calculated to formaldehyde are shown in parentheses.

[*3] Values in an earlier stage of thermal decomposition.

TABLE 2. INFLUENCE OF REACTION TIME ON COPOLYMERIZATION

Reaction time min	Polymer yield g	Conversion wt%	η_i dl/g	k_{222}* %/min	Content of succinic unit, mol%
5	2.92	54.2	1.7	3.3	0.73
10	3.19	59.1	1.7	4.0	0.51
20	2.93	54.4	1.8	3.5	0.40
40	2.78	51.3	1.6	6.7	0.43
60	3.09	57.4	1.9	4.6	0.59
180	2.83	52.4	1.3	4.4	0.63

Reaction conditions: formaldehyde 4.3 g, succinic anhydride 1.1 g, carbon dioxide 2.9 g, temperature 100°C.
* The definition is the same as in Table 1.

TABLE 3. INFLUENCE OF REACTION TEMPERATURE ON COPOLYMERIZATION

Reaction temp. °C	Polymer yield g	Conversion*1 wt%	η_i dl/g	k_{222}*2 %/min	Mp °C	Content of succinic unit, mol%
20	2.43	56.4 (76.0)	2.7	2.6	173—178	0.091
50	2.28	53.0 (71.3)	2.2	3.4	174—179	0.19
80	2.33	54.2 (72.8)	1.5	7.4	167—174	0.34
100	2.10	48.8 (65.6)	1.3	5.2	168—174	0.64
120	2.48	58.7 (77.4)	0.98	8.1	166—171	2.04

Reaction conditions: formaldehyde 3.2 g, succinic anhydride 1.1 g, carbon dioxide 2.1 g, time 60 min.
*1 Values in parentheses are defined the same as in Table 1.
*2 The definition is the same as in Table 1.

Thus, it was concluded that succinic units are inserted at several places in the sequence of oxymethylene units.

The results shown in Table 1 indicate that the content of succinic units in the resulting copolymer increased slightly with an increase in the concentration of succinic anhydride, but the content was, in general, lower than 1 mol%. Regarding formaldehyde as M_1 and succinic anhydride as M_2, it seems that the monomer reactivity ratio r_1 is extremely large and that r_2 is nearly zero.

The polymer yield increased as the concentration of succinic anhydride became less. However, the polymer yield based on the formaldehyde monomer was almost independent of the concentration of succinic anhydride. The degree of polymerization was also constant in a like manner. These facts were ascribed to the fact that the addition polymerization of formaldehyde proceeded predominantly, because the monomer reactivity ratio r_2 was extremely small.

Influence of the Reaction Time. The influence of the reaction time on the copolymerization was also studied as is shown in Table 2. The degree of polymerization, the inherent viscosity, and the content of succinic units were not at all affected by the reaction time. Accordingly, it seems that the rate of polymerization was very large at the temperature of 100°C, so that the reaction immediately reached equilibrium.

Influence of the Reaction Temperature. Table 3 shows the influence of the reaction temperature on the copolymerization of formaldehyde with succinic anhydride. The inherent viscosity and the succinic-unit content of the resulting copolymer are plotted against the reaction temperature in Fig. 2. The succinic-unit content rapidly increased with an enhancement in the reaction temperature, although it was less than 3 mol% even in the copolymer resulted at 120°C. This fact indicates an increase in the monomer reactivity ratio r_2 with the reaction temperature. The copolymer yield was independent of the temperature, whereas the inherent viscosity decreased reciprocally with the temperature. It seems, therefore, that the initial concentration of initiating species increases with an enhancement of the temperature.

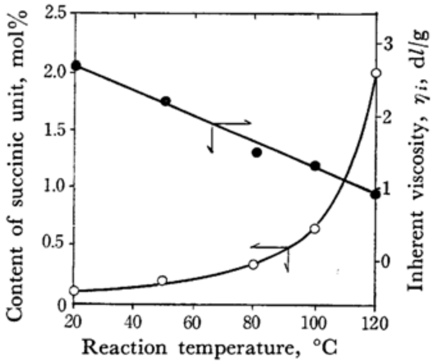
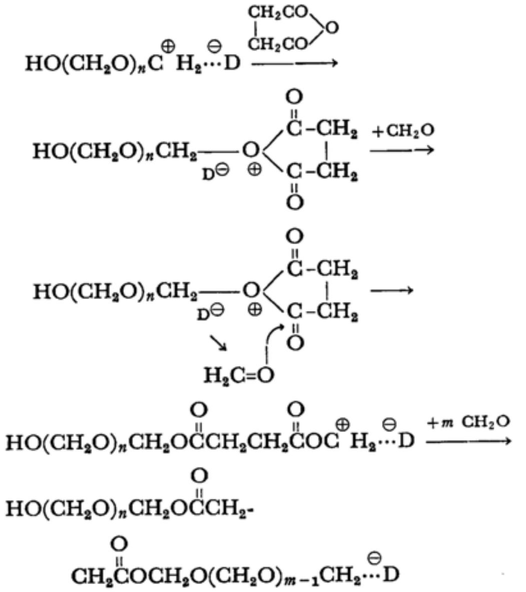


Fig. 2. Influence of reaction temperature on the degree of polymerization and succinic unit content of the copolymer.

Mechanism of Copolymerization. As has been mentioned above, formaldehyde and succinic anhydride copolymerized in a liquid carbon dioxide solution under pressure, while the addition polymerization of formaldehyde proceeded predominantly because of the low value of the monomer reactivity ratio r_2. Accordingly, it was concluded that an occasional insertion of succinic anhydride into the growing polyoxymethylene chain took place by means of the following schemes:



Structure and Properties of the Copolymer. It has been disclosed by infrared-spectrometric study that there is formed a copolymer into which succinic units are inserted in some places in the sequence of formaldehyde units. In this section, the structure and properties of the above copolymer will be discussed. The X-ray diffraction spectrum of the copolymer, which contained 0.68 mol% of succinic units, is shown in Fig. 3; the spectrum of α-polyoxymethylene, which was chosen as an example of the homopolymer of formaldehyde, is also shown in the same figure for the sake of comparison. The maximum peak for α-polyoxymethylene occurred at a scattering angle of 22.6°, whereas it occurred at 22.7° and there was an extra peak at 20.5° for the copolymer. The peak at 20.5° was ascribed to the amorphous part in the copolymer.[3] Furthermore, the crystallinity of the copolymers, which contained a variety of succinic units, was studied; the results are shown in Table 4. The crystallinity decreased as the succinic unit content rose. This fact indicates that a disturbance of the crystal lattice took place because of the insertion of succinic-units into the polymer chain.

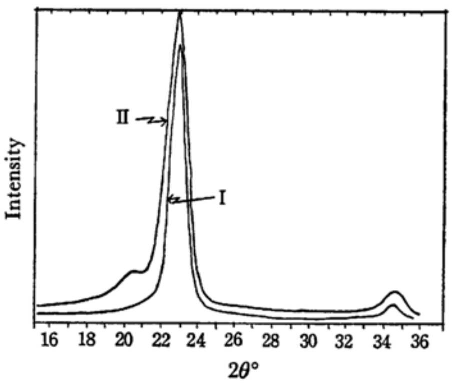


Fig. 3. X-ray diffraction spectra of the copolymer and α-polyoxymethylene.
(I) α-polyoxymethylene
(II) copolymer (succinic unit content, 0.68 mol%)

TABLE 4. INFLUENCE OF COPOLYMER COMPOSITION ON CRYSTALLINITY OF THE COPOLYMER

Content of succinic unit, mol%	η_i dl/g	Crystallinity %
0	0.95	98.0
0.40	1.79	94.6
0.67	1.75	88.7
1.1	0.30	82.1

The thermal properties of the copolymer were also investigated. A typical thermal degradation curve of a copolymer which had been constantly heated at 222°C in a nitrogen atmosphere is shown in Fig. 4. It was found that the rate constant of thermal degradation decreased with the heating time. The thermal degradation of polyoxymethylene, in general, follows a first-order rate equation; therefore, the rate constant does not vary

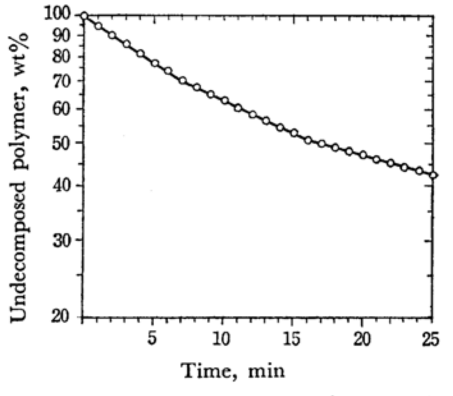


Fig. 4. Thermal decomposition of the copolymer in nitrogen atmosphere at 222°C.
Sample; η_i 1.34 dl/g, succinic unit content 0.64 mol%, initial rate constant of decomposition 5.2 wt%.

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[3] C. F. Hammer, T. A. Koch and J. F. Whitney, *J. Appl. Polymer Sci.*, **1**, 170 (1959).

with the time.④ On the contrary, the thermal stability of the copolymer investigated improved with heating. This may be ascribed to the fact that the successive degradation begun at the endgroups of the copolymer chain was lowered at the ester linkage, which is thermally more stable than the ether linkage.

Figure 5 shows the curves for the differential thermal analysis of the copolymer. With an increase in the content of succinic units, the melting point shown by the first peaks did not vary, but the degradation temperature by the second peaks increased. This may be caused by the thermal stability of the ester linkage in the copolymer chain.

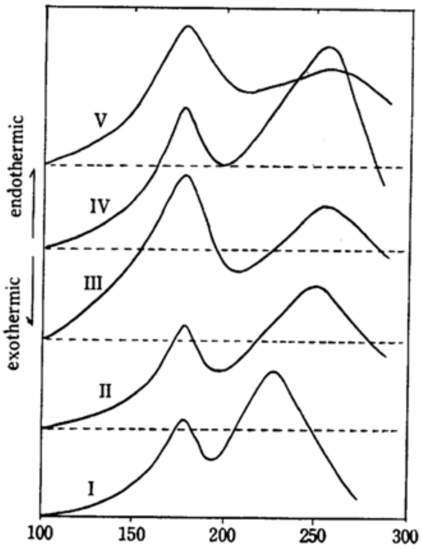

Fig. 5. DTA curves of the copolymer.
Succinic unit content and η_i of the sample: (I) 0.091 mol%, 2.7 dl/g; (II) 0.19 mol%, 2.2 dl/g; (III) 0.33 mol%, 1.5 dl/g; (IV) 0.64 mol%, 1.3 dl/g; (V) 2.04 mol%, 0.98 dl/g.

TABLE 5. FOLDING ENDURANCE OF THE COPOLYMER

Sample*[1]		Folding endurance*[2] $\times 10^{-3}$ times
Content of succinic unit, mol%	η_i dl/g	
3.5	1.8	87
2.0	1.8	78
1.1	1.7	92

*[1] Sample thickness 120 μ
*[2] Mean value for five runs

Lastly, the folding endurance of the copolymer film was studied; the results are shown in Table 5. Although there was no treatment for esterifying the endgroups in the copolymer, the film showed a high resistivity to folding. On the other hand, the folding endurance of polyoxymethylene diglycol has been reported to be less than 100 times.⑤ The high resistivity of the film to folding may be a characteristic of the copolymer.

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4) T. A. Koch and P. E. Lindvig, *ibid.*, **1**, 164 (1959).

5) R. N. MacDonald, U. S. Pat. 2768994 (1956).