The Solid State Polymerization of Trioxane by the Simultaneous Sublimation of the Monomer and Iodine[*]

By Hajime MIYAMA and Mikiharu KAMACHI

(Received July 12, 1963)

Recently, Kargin et al.[1] published an interesting method of polymerization by the simultaneous condensation of the vapors of monomers and inorganic substances on a strongly cooled surface. The present authors have now applied Kargin's method to the system of trioxane and iodine, both of which can be easily sublimed, and have thereby obtained polyoxymethylene of a high degree of polymerization in a good yield.

Although many reports[2-10] about the solid state polymerization of trioxane have been published, the method of polymerization catalyzed by iodine in the solid state has not been reported as far as the authors know. Also, the present method of polymerization is very different from other methods. Therefore, it seems worthwhile to report the details of our experimental results.

Experimental

The experimental method is as follows. Commercial trioxane (Eastman Kodak and American Celanese) is purified by several sublimations in a high vacuum and then introduced, at the pressure of $10^{-4}\sim10^{-5}$ mmHg, into an ampoule cooled by liquid nitrogen. At the same time, the desired quantity of iodine, which has also been purified by several vacuum sublimations, is introduced into the ampoule. This ampoule, containing the mixture produced by the simultaneous sublimation of trioxane and iodine, is sealed off and placed into a thermostat of a definite temperature. After being left for the definite time, the ampoule is opened. Then monomer and iodine are removed by benzene, and the undissolved polymer is washed two times with benzene.

The ESR spectra of the polymerization system are measured with a Varian V-4500 spectrometer. Also, the temperature-rise of the system during the polymerization is followed by a thermistor inserted into the reaction ampoule.

The inherent viscosity of the polymer obtained is measured in a *p*-chlorophenol solution (0.1 g./100 ml.) containing 2% of α-pinene by using an Ostwald viscometer at 60°C. The softening temperature is measured by a Kofler's Micro-Hot-Stage. Also, the X-ray diffraction of the polymer is measured by using a Rigaku Denki D-5C diffractometer.

Results

In order to conduct the polymerization, it is necessary to keep the pressure as low as possible. The existence of air, oxygen and other radical scavengers inhibits this reaction. Therefore, all measurements are conducted at the pressure of $10^{-4}\sim10^{-5}$ mmHg. The results obtained are shown in Table I and Figs. 1—4. As Figs. 1 and 2 show, the polymerization yield increases with time, but it reaches a limit only after a few ten minutes. Also, the yield increases with the increase in the temperature and in the iodine concentration. Although the inherent viscosity does not change with the polymerization time regularly, it decreases with the increase in the temperature and in the iodine concentration, as is shown in Figs. 3 and 4, where inherent viscosity is measured for the polymers obtained

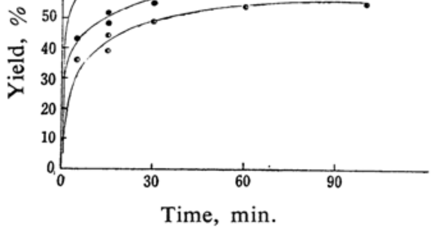

Fig. 1. Change of yield with time at various temperatures. Weight % of iodine is 0.67%.
○ 42.2°C ● 34.2°C ◐ 26.7°C

---

[*] An outline of this paper was presented at the 16th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1963 and will be published as a letter in *Journal of Polymer Science*.

1) V. A. Kargin, V. A. Kabanov, V. P. Zubov and I. M. Pupisov, *Polymer Sci.* U. S. S. R., **3**, 136 (1962).

2) W. Kern, H. Cherdron and V. Jaacks. *Angew. Chem.*, **73**, 177 (1961).

3) W. Kern and V. Jaacks, *J. Polymer Sci.*, **48**, 399 (1960).

4) V. Jaacks and W. Kern, *Makromol. Chem.*, **52**, 37 (1962).

5) S. Okamura, K. Hayashi and Y. Kitanishi, *J. Polymer Sci.*, **58**, 925 (1962).

6) S. Okamura, T. Higashimura and K. Takeda, *Makromol. Chem.*, **51**, 217 (1962).

7) K. Hayashi and S. Okamura, ibid., **47**, 230 (1961).

8) K. Hayashi, Y. Kitanishi, M. Nishii and S. Okamura, ibid., **47**, 237 (1961).

9) W. Wilson and H. May, *Chem. & Ind.* **1962**, p. 412.

10) O. L. Hammick and A. R. Boeree, *J. Chem. Soc.*, **121**, 2738 (1922).

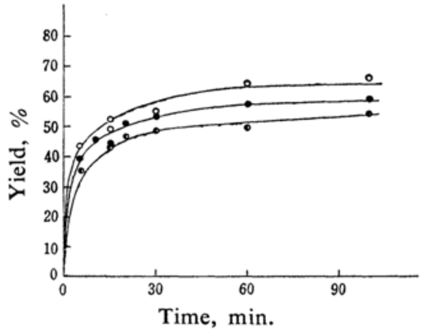

Fig. 2. Change of yield with time at various iodine concentrations at the reaction temperature of 34.2°C.
○ I_2 : 0.67 wt. %
● I_2 : 0.33 wt. %
◐ I_2 : 0.13 wt. %

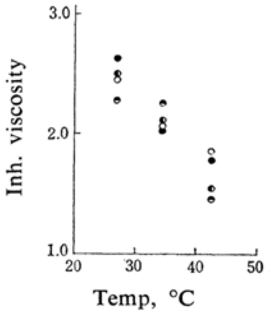

Fig. 3. Change of inherent viscosity with temperatures. Weight % of iodine is 0.67%.
○ Polym. time 5 min.
◐ Polym. time 15 min.
◓ Polym. time 60 min.
● Polym. time 120 min.

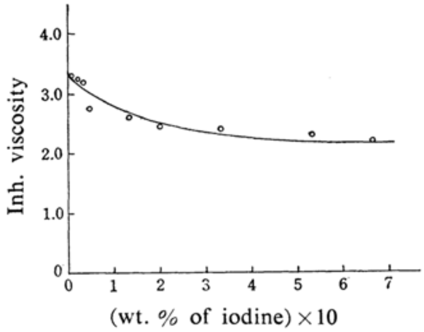

Fig. 4. Change of inherent viscosity with weight % of iodine. Reaction temperature is 34.2°C.

TABLE I

Iodine conc. wt. %	Polym. time min.	Polym. temp. °C	Yield %	η_{inh}	Softening temp. °C
0.67	5	42.2	57.6	1.85	184∼186
0.67	10	42.2	64.2	1.57	183∼186
0.67	15	42.2	66.9	1.43	184∼186
0.67	30	42.2	72.3	1.44	184∼186
0.67	60	42.2	78.2	1.78	184∼186
0.67	100	42.2	78.6	1.48	184∼186
0.67	5	34.2	43.0	2.02	184∼187
0.67	15	34.2	48.4	2.05	184∼187
0.67	15	34.2	51.1	2.11	184∼187
0.67	30	34.2	55.0	2.12	184∼187
0.67	60	34.2	63.8	2.26	184∼187
0.67	100	34.2	66.9	2.56	184∼187
0.67	5	26.7	35.5	2.44	184∼187
0.67	15	26.7	39.2	2.20	185∼187
0.67	15	26.7	44.3	2.27	184∼187
0.67	30	26.7	39.0	2.44	184∼187
0.67	60	26.7	54.1	2.29	184∼187
0.67	100	26.7	54.2	2.61	184∼187
0.33	5	34.2	39.8	2.43	184∼187
0.33	10	34.2	44.8	2.51	184∼187
0.33	15	34.2	44.9	2.39	184∼187
0.33	20	34.2	50.5	2.44	184∼187
0.33	30	34.2	52.8	2.39	184∼187
0.33	60	34.2	56.5	2.47	184∼187
0.33	100	34.2	59.0	2.52	184∼187
0.33	5	26.7	34.2	2.47	184∼187
0.33	10	26.7	39.2	3.28	186∼188
0.33	15	26.7	40.1	3.49	185∼188
0.33	20	26.7	41.4	3.23	185∼188
0.33	30	26.7	43.3	3.53	184∼188
0.33	60	26.7	46.7	3.50	184∼188
0.33	100	26.7	48.2	3.79	186∼189
0.13	5	26.7	35.8	2.74	184∼183
0.13	15	26.7	42.6	2.72	184∼186
0.13	20	26.7	46.2	3.08	184∼186
0.13	30	26.7	48.6	2.57	184∼188
0.13	60	26.7	49.2	2.97	184∼186
0.13	100	26.7	53.7	2.71	184∼186
0.67	30	34.2	55.6	2.22	184∼186
0.53	30	34.2	54.1	2.31	184∼186
0.33	30	34.2	52.8	2.39	184∼186
0.20	30	34.2	48.3	2.44	184∼186
0.13	30	34.2	43.3	2.57	184∼186
0.046	30	34.2	41.4	2.72	184∼186
0.033	30	34.2	40.1	3.19	184∼186
0.020	30	34.2	38.7	3.23	184∼186
0.007	30	34.2	36.8	3.31	184∼186

by the 30-minute reaction.

The temperature-rise of the reaction system measured by a thermister placed into the ampoule with an internal diameter of 1.8 cm. and a height of 4.0 cm. is shown in Fig. 5. The temperature of the reaction system is not constant during the polymerization, rather, it reaches a constant temperature within 3∼4 min. after the ampoule is placed into the thermostat.

By ESR measurements of the reaction system at room temperature, the spectra shown in Fig. 6 are obtained. After opening the ampoule, the intensity of the spectra decreases with time.

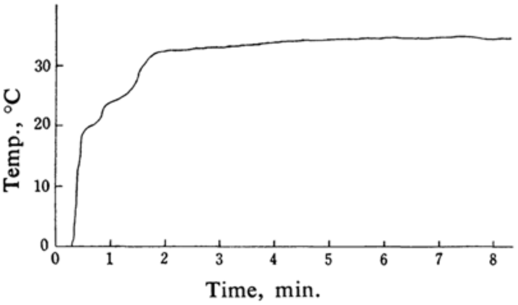

Fig. 5. Temperature change of the reaction system with time.
Reaction temperature ; 34.2°C

Although the ampoule is usually cooled with liquid nitrogen (−196°C) when both trioxane and iodine are sublimed into the ampoule, a higher condensation temperature may be obtained by using other freezing mixtures. As Table II shows, a small quantity of polymer is obtained even at 0°C, but the polymerization yield decreases as the condensation temperature increases. Therefore, all measurements are conducted at the condensation temperature of −196°C.

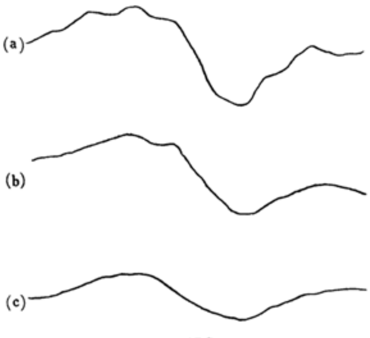

Fig. 6. ESR spectra of reaction mixture.
- a) during the polymerization,
- b) 10 minutes after the ampoule is opend,
- c) 2 days after the ampoule is opend.

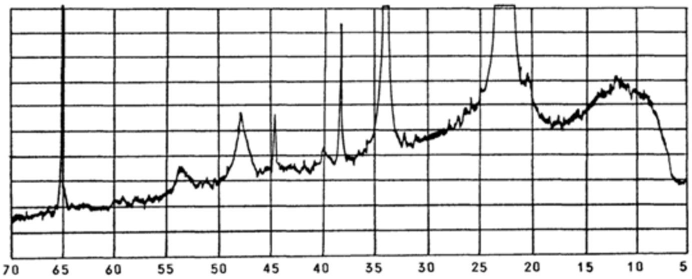

Fig. 7a. X-ray diffraction patterns of polymer obtained by the present method.

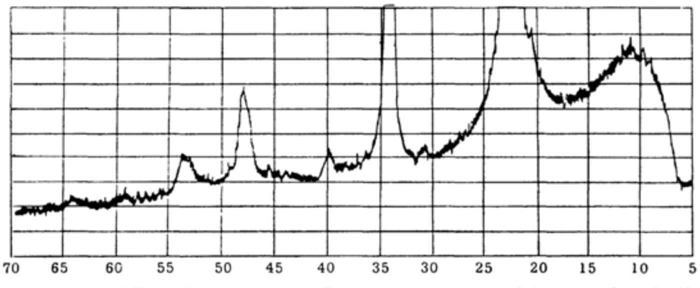

Fig. 7b. X-ray diffraction pattern of polymer made without using iodine.

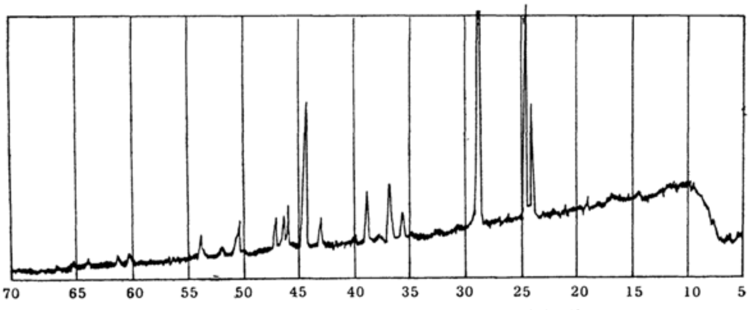

Fig. 7c. X-ray diffraction patterns of iodine.

TABLE II. POLYMERIZATION YIELDS AT VARIOUS CONDENSATION TEMPERATURES

Condensation temp., °C	Yield, %
−196	53.0
− 66	27.7
− 52	25.5
− 31	11.4
− 18	5.0
0	2.5

Here, the iodine concentration is 0.067 weight %, the polymerization time is 30 min., and the polymerization temperature is 42.2°C.

On the other hand, concerning the polymerization temperature (i. e., the temperature of the thermostat), the results shown in Table III are obtained.

TABLE III. POLYMERIZATION YIELDS AT VARIOUS POLYMERIZATION TEMPERATURES

Polymerization temp., °C	Yield
0	none
10	trace
15	26.8
20	32.6
23	42.8
26.7	49.0

Here, the iodine concentration is 0.67 weight %, and the reaction time is 30 minutes. From this result, it is obvious that the polymerization starts in the neighbourhood of 10°C.

No polymerization occurs in the liquid phase when 0.1 g. of iodine and 1.5 g. of trioxane are dissolved into 10 cc. of a solvent such as benzene or ethylene dichloride and heated to 40°C.

In order to confirm that the simultaneous sublimation is absolutely necessary, trioxane is placed into the ampoule first, without sublimation, and then iodine is sublimed into the ampoule. Table IV compares two methods where the iodine concentration is 0.67 weight %, the reaction time is 15 min., and the reaction temperature is 34.2°C.

TABLE IV. A COMPARISON OF TWO METHODS, WITH AND WITHOUT THE SIMULTANEOUS SUBLIMATION OF TRIOXANE

Method	Yield
Simultaneous sublimation	49.2%
Without sublimation of trioxane	trace

Also, in order to confirm whether the initiation of the polymerization occurs in the gas phase or in the solid phase, the alternating sublimations, wherein iodine vapor is removed during the sublimation of trioxane and trioxane vapor is removed during the sublimation of iodine, are compared with simultaneous sublimation in Table V. Here, the iodine concentration is 0.67 weight %, the reaction temperature is 34.2°C, and the reaction time is 30 minutes.

TABLE V. A COMPARISON OF ALTERNATING SUBLIMATION WITH SIMULTANEOUS SUBLIMATION

Method	No. of alterating repetitions	Yield
Alternating sublimation	2	49.4%
	6	52.0
Simultaneous sublimation	—	52.3

From this table, it is obvious that the polymerization does not start in the gas phase.

The inherent viscosity and softening temperature are also shown in Table I. The inherent viscosity is much higher than that (usually 1∼2) of polyoxymethylene obtained by conventional methods. Also, the X-ray diffraction patterns of the polymer obtained by the present method, of the polymer made without using iodine, and of the iodine are shown in Fig. 7. Obviously, a new peak is observed at the diffraction angle of 65°.

Discussion

Since the temperature of the polymerization system reaches the constant temperature after 3∼4 min., as Fig. 5 shows, the polymerization rates have been obtained from the slope of the curves after 4 minutes in Figs. 1 and 2, and the dependence of these rates upon the concentrations of monomer, iodine and polymer has been examined. Thus, it is found that the polymerization rate, V, is proportional to $[C]^{0.25}[M]^2/[P]^2$, as is shown in Fig. 8, where [M], [C] and [P] are weight percentages of the monomer, iodine and the polymer respectively. From the slope of the straight lines

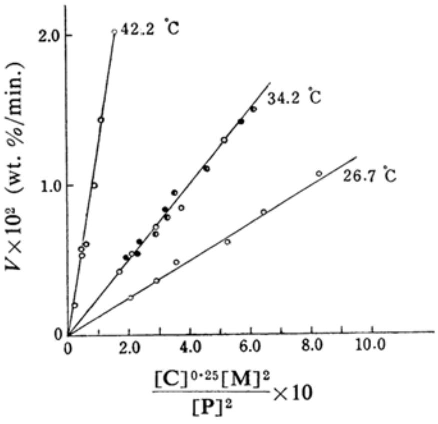

Fig. 8. Change of polymerization rate with $[C]^{0.25}[M]^2/[P]^2$.
○ I_2 : 0.67 wt. %
● I_2 : 0.33 wt. %
◐ I_2 : 0.13 wt. %

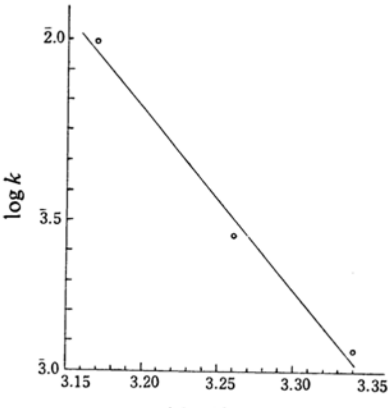

Fig. 9. Arrhenius' plot of $\log k$ via $1/T$.

in Fig. 8, the rate constants at various temperatures are obtained by means of the following equation;

$$V=k[\mathrm{C}]^{0.25}[\mathrm{M}]^2/[\mathrm{P}]^2$$

From the Arrhenius' plot of $\log K$ via $1/T$ shown in Fig, 9, the activation energy is found to be ca. 29 kcal./mol.

According to Kargin et al.,[1] the initiation takes place in the gas phase for the monomer-metal system, but in the solid phase for the monomer-salt and monomer-oxide systems. In our experiment, initiation occurs obviously in the solid phase. This may be due to some crystal defects or dislocations, as has been suggested by Kargin et al.,[1] Bamford et al.[11] and Semenov.[12] As Table II shows, the polymerization yield decreases as the condensation temperature increases. This result may be explained as follows by using their hypothesis. Since the rate of sublimation decreases as the condensation temperature increases, it is expected that number of crystal defects or dislocations produced by simultaneous sublimation will become smaller at a higher condensation temperature and that, therefore, the rate of polymerization will decrease.

The fact that the polymerization system must be heated up to 10°C for the reaction to occur suggests that the favorable orientation of the monomer is necessary for the chain propagation. According to the NMR measurements of Okamura et al.,[13] the movement of the trioxane monomer becomes active about 20°C. Therefore, there is a possibility that this kind of movement causes the orientation favorable to the polymerization. The obtained activation energy of 29 kcal./mol. is large compared with the activation energy of 5 kcal./mol.[14] in the in-source radiation polymerization of trioxane, but it is small compared with the 40 kcal./mol.[15] in the post radiation polymerization. Morawetz[16] obtained the activation energy of 25 kcal./mol. for the post-irradiation polymerization of acrylamide and considered this value to be the activation energy of the propagation step. Taking these results into account, our activation energy might correspond to that of the propagation step.

The ESR spectra shown in Fig. 6 are very close to those obtained by the radiolysis of commercial polyoxymethylene.[17] On the other hand, the results of X-ray diffraction suggest the existence of some interaction between iodine and the polymer. Therefore, it is very difficult to find whether active species of the initiating polymerization are produced from trioxane or from iodine, and no conclusive mechanism can be obtained from the above-described results. The existence of a free radical proved by ESR measurement and the inhibition of polymerization by air, oxygen and other radical scavengers do not support the radical mechanism conclusively. For this purpose, a quantitative agreement between kinetical data and ESR data is necessary. At present, the authors prefer to explain this reaction by assuming that the initiation of the polymerization takes place in association with crystal dislocations or defects caused by the simultaneous sublimation and that the propagation step starts somewhere between 0°C and 15°C.

Summary

It has been found that the polymerization of trioxane occurs in the solid state by subliming the monomers and iodine simultaneously on a cooled surface and raising the temperature over 10°C. This method gives a polymer of a high degree of polymerization in a good yield. As a result of chemical kinetic treatments, the polymerization rate has been found to be proportional to $[\mathrm{C}]^{0.25}$ $[\mathrm{M}]^2/[\mathrm{P}]^2$, where [C], [M] and [P] are the concentrations of iodine, the monomer and the polymer respectively. The reaction mechanism has been discussed in

---

11) C. H. Bamford, G. C. Eastmond and J. C. Ward, *Proc. Roy. Soc.*, **271**, 357 (1963).

12) N. N. Semenov, *J. Polymer Sci.*, **55**, 563 (1961).

13) K. Hayashi, K. Kamata, H. Yoshida, M. Nishii, Y. Nakase, K. Hayashi and S. Okamura, The 11th Symposium of the High Polymer Society of Japan, Osaka, Nov., 1962.

14) K. Hayashi and S. Okamura, The International Symposium on Radiation-Induced Polymerization and Graft-copolymerization, Columbus, Ohio, Nov., 1962.

15) K. Hayashi, Y. Nakase, H. Ochi, M. Nishii and S. Okamura, The 15th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1962.

16) F. A. Fadner and H. Morawetz, *J. Polymer Sci.*, **45**, 475 (1960).

17) M. Kashiwagi, unpublished work.

connection with the results of ESR and X-ray measurements.

The authors wish to express their thanks to Dr. Y. Kurita and Mr. Heisaburo Iguchi for their help in the ESR measurements to Dr. Yukio Kinoshita and Messrs. Toshio Mizushima and Masamichi Nakamura for their help in the X-ray diffraction measurements, and to Mr. Atsushi Takeda for his help in the experiment.

Basic Research Laboratories
Toyo Rayon Co., Ltd.
Tebiro, Kamakura