BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1688—1693 (1969)

Polymerization of Formaldehyde in Liquid Carbon Dioxide. I. The Cause of the Polymerizability of the Monomer

Tsutomu Kagiya, Masatsune Kondo,*1 Kōzō Narita and Kenichi Fukui

Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received November 4, 1968)

The cause of the polymerizability of formaldehyde in liquid carbon dioxide was studied in connection with the preparation conditions of the monomer. A liquid carbon dioxide solution of the monomer was prepared by two different methods, by means of the pyrolysis of α-polyoxymethylene and by means of that of the hemiformal of polyethylene glycol, under a carbon dioxide stream. By adding various sodium salts to the pyrolysis system of α-polyoxymethylene, the polymerization rate, without the addition of any catalyst, of the monomer thus obtained was found to decrease with an increase in the pK_a value of the conjugated acid of the salt. The polymerization rate also decreased with the amount of sodium carbonate added. The hemiformal of polyethylene glycol was prepared by bubbling the gas evolved by the pyrolysis of paraformaldehyde into polyethylene glycol. The amount of acid present in the hemiformal thus obtained increased linearly with the pyrolysis time. The polymerization rate of the monomer obtained by the pyrolysis of the hemiformal increased in proportion to the acid content in the hemiformal. On the basis of these results, the initiation mechanism in the polymerization of formaldehyde without any additional initiator in a liquid carbon dioxide solution was discussed.

In respect to the polymerization of formaldehyde, many papers have been reported. It is well known that formaldehyde is so reactive that it can be polymerized easily by the initiating action of an impurity in a monomer solution, even at the temperature of −78°C.1) For this reason, little reproducibility of experimental results is observed in the polymerization. Little attention has, however, been paid to the cause of this phenomenon.

The present authors have already reported that the polymerization rate of formaldehyde is remarkably retarded by the addition of carbon dioxide,2) and that reproducible results can be obtained in a formaldehyde polymerization in a liquid carbon dioxide solution.3,4)

As has previously been reported, a liquid carbon dioxide solution containing 60 wt% of monomer is obtained when α-polyoxymethylene is pyrolyzed under a carbon dioxide stream and the mixed gas thus obtained is cooled at −78°C.3)

In the present paper, the cause of the polymerizability of formaldehyde in this solution will be studied quantitatively in connection with the preparation conditions of the monomer solution; the initiation mechanism in the polymerization of formaldehyde without any additional initiator will also be discussed.

Experimental

Materials. Commercially available α-polyoxy methylene (α-POM; the degree of polymerization *ca.* 100) and paraformaldehyde (paraform; the degree of polymerization is from 10 to 100) are used without further treatment. The calcium carbonate, sodium carbonate, sodium hydroxide, sodium acetate, sodium sulfate, sodium cyanide, and sodium chloride were commercially obtained. Commercial polyethylene glycol (PEG; average molecular weight is 380 to 420) was used after removing a volatile fraction of PEG by heating it at 200°C for one hour under normal pressure. Commercial carbon dioxide was dried by passing it through two drying tubes packed with phosphorus pentoxide.

Preparation of Monomer. *Direct Method by the Pyrolysis of α-POM.* The monomer was prepared directly by the pyrolysis of α-POM. 100 g of α-POM or a mixture of 100 g of α-POM and a measured amount of various sodium salts was put into a 300 m*l* decomposer (A) and then decomposed by heating at 150 to 180°C under a carbon dioxide stream (flow rate: 160 m*l*/min) (Fig. 1.1). The resulting mixture of formaldehyde and carbon dioxide was condensed in the monomer reservoir (B) at −78°C. The solution thus obtained was homogeneous and contained 59 to 61 wt% of the monomer and 39 to 41 wt% of carbon dioxide.

Two-steps Method by Pyrolysis of the Hemiformal of PEG. The hemiformal was prepared by the reaction of PEG with the monomer produced by pyrolyzing paraform

---

[*1] Present address: Sumitomo Chemical Co., Ltd., Takatsuki.

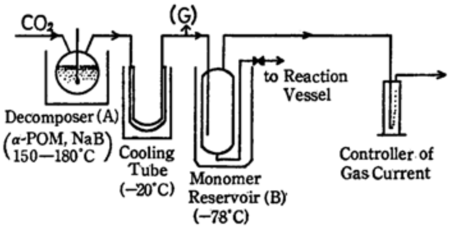
1) J. F. Walker, "Formaldehyde", 3rd Ed., Reinhold, New York (1964), pp. 46, 52.

2) H. Yokota, M. Kondo, T. Kagiya and K. Fukui, *J. Polymer Sci., A-1*, **5**, 3129 (1967).

3) H. Yokota, M. Kondo, T. Kagiya and K. Fukui, *ibid.*, **6**, 425 (1968).

4) H. Yokota, M. Kondo, T. Kagiya and K. Fukui, *ibid.*, **6**, 435 (1968).

1.1. Direct method



1.2. Two-steps method

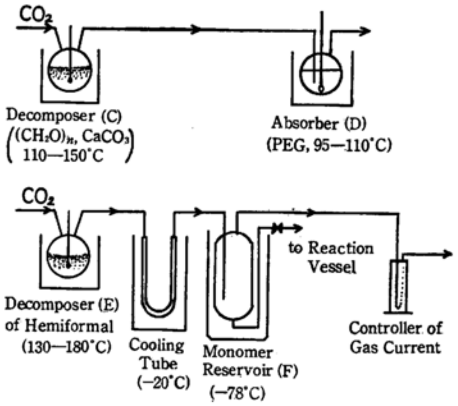


Fig. 1. Preparation apparatus of the carbon dioxide solution of formaldehyde.

(Fig. 1.2). 500 g of the paraform and a measured amount of the additive were placed in a 1000 m*l* decomposer (C) and decomposed by heating at 110 to 150°C under a carbon dioxide stream (flow rate: 160 m*l*/min). The mixed gas thus obtained was then ıtroduced into a 1000 m*l* absorber (D) (95—110°C) ontaining 500 g of PEG to give the hemiformal. The formaldehyde content in the hemiformal was found to be *ca.* 25 wt%.

The monomer was prepared by the pyrolysis of the hemiformal (Fig. 1.2). 500 g of the hemiformal were put into a 1000 m*l* decomposer (E) and pyrolyzed at 130 to 180°C under a carbon dioxide stream (flow rate: 160 m*l*/min). The resulting mixture of formaldehyde and carbon dioxide was passed through a tube cooled at −20°C and then liquefied in the monomer reservoir (F) at −78°C.

Polymerization Procedure. A stainless-steel autoclave with a capacity of 30 m*l* (16 mmϕ × 150 mm) was used as the reaction vessel. Into the vessel, which has been degassed *in vacuo* and cooled with liquid nitrogen, 10 m*l* of a carbon dioxide solution of formaldehyde was charged; this solution was maintained at 20±1°C for one hour. After the polymerization, the unreacted monomer and carbon dioxide gas were purged out. The white powdery polymer thus obtained was washed sufficiently with cooled diethyl ether, dried *in vacuo* at room temperature, and weighed.

Analysis. *Measurement of the Acid Content in the Hemiformal of PEG.* 10 m*l* of a 0.1 N NaOH aqueous solution was added to 10 m*l* of the hemiformal, and the excess of sodium hydroxide was titrated with a 0.1 N HCl aqueous solution using phenolphthalein as the indicator.

Measurement of the Number-average Degree of polymerization of the Polymer. The inherent viscosity measurement of a solution containing 0.5 g of the polymer in 100 m*l* of *p*-chlorophenol containing 2% of α-pinene was carried out with the use of an Ostwald viscometer at 60°C. The number-average degree of polymerization of the polymer was calculated by the following equation.[3)]

$$\eta_i = 2.14\times10^{-2}\ \bar{P}_n^{\,0.61} \qquad (1)$$

Measurement of the Adsorption of Acid by Sodium Salts. A measured amount of sodium salt was added to a PEG solution containing a measured amount of formic acid. After the solution had been kept standing for one hour at room temperature, 10 m*l* of this PEG solution was titrated back with a 0.1 N HCl aqueous solution.

Gas Chromatographic Analysis of the Impurities Involved in the Monomer. The impurity content in the gas produced by the pyrolysis of α-POM was determined by gas chromatography (Yanagimoto, Type GCG-3D) using a diglycerol column. The gas sample was collected in a micro-syringe from a side arm (G) (*cf.* Fig. 1.1) through a rubber stopper.

Results and Discussion

Polymerizability of the Monomer Obtained by the Pyrolysis of α-POM with the Addition of Various Sodium Salts. The polymerizability of the monomer obtained by the pyrolysis of a mixture containing 0.1 mol of sodium salts of various Brönsted acids in 100 g of α-POM was studied without any additional initiator. As shown in Fig. 2, the polymerization rate of the monomer thus obtained edcreased rapidly with an increase in the pK_a of the conjugated acid (HB) of sodium salt (NaB); the rate was almost constant above a pK_a of *ca.* 7. On the other hand, the degree of polymerization of the

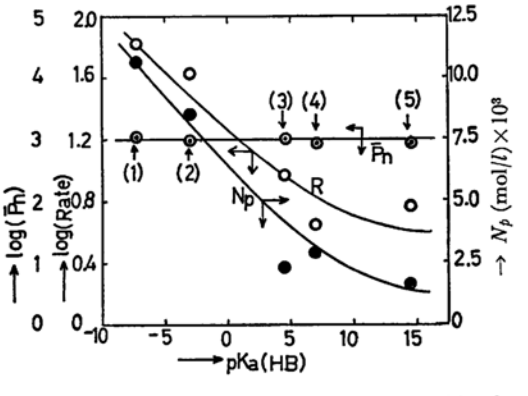


Fig. 2. Influence of pK_a of conjugated acid of sodium salts on the polymerization rate (*R*), the degree of polymerization ($\bar{P}_n$) and the number of moles of polymer chain (N_p). Pyrolysis condition: temperature, 150—180°C; time, 90 min; sodium salt/α-POM, 0.1 mol/100 g; Polymerization condition: temperature, 20°C; time, 60 min; monomer content, 60 wt-%; (1) NaCl, (2) Na$_2$SO$_4$, (3) NaOCOCH$_3$, (4) Na$_2$CO$_3$, (5) NaOH.

polymer was not affected by the addition of sodium salts. The number of moles of the polymer chain of the resulting polymer, which was defined as the ratio of the polymer yield (polymerized monomer mol/unit volume of reaction vessel) to the number-average degree of polymerization, was plotted against the pK_a, as shown in the same figure. The number of moles of the polymer chain also decreased with an increase in the pK_a of acid, almost reaching a constant above a pK_a of *ca.* 7. These results suggest that the quantity of initiating species decreases with an increase in the pK_a. Therefore, the decrease in the polymerizability of the monomer may be ascribed to the decrease in the amount of the initiator. These results lead to the conclusion that the polymerization is initiated by an acidic substance present in the monomer. In order to confirm the role of sodium salt, the adsorption of acids, such as formic acid, by sodium salt was examined. The amount of the acid adsorbed by sodium salt increased with an increase in the pK_a of the conjugated acid of the salt, as is shown in Fig. 3.

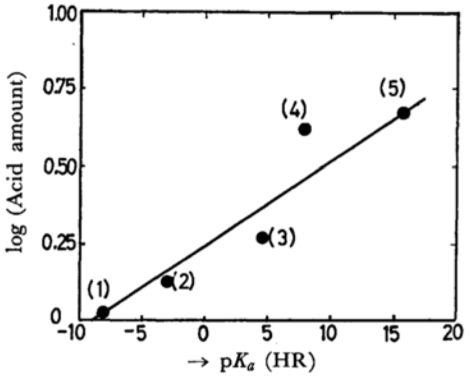


Fig. 3. Relationship between the amount of acid adsorbed by the salt and pK_a of conjugated acid of sodium salt. Formic acid content, 1.18 mol/*l* in PEG solution; reaction time, 1 hr; temperature, 20°C; (1) NaCl, (2) Na_2SO_4, (3) $NaOCOCH_3$, (4) Na_2CO_3, (5) NaOH.

From these results, it may be concluded that the sodium salt catches the Brönsted acid in the monomer, the polymerizability of the monomer was ascribed to the acid content of the monomer solution.

Effect of the Addition of Sodium Carbonate on the Pyrolysis of α-POM. As has been described above, the polymerizability of the monomer obtained by the pyrolysis of α-POM in the presence of sodium salts varied with the kind of sodium salts, and a remarkably depressing effect of the polymerizability was observed in the case of the addition of sodium carbonate. When the monomer was prepared by the pyrolysis of α-POM containing 0 to 10 wt% of sodium carbonate, the effect of the sodium carbonate content on the polymerizability of the monomer was examined.

As is shown in Fig. 4, both the polymerization rate and the number of moles of the polymer chain of the resulting polymer decrease with an increase in the amount of sodium carbonate, while the degree of polymerization is hardly affected by sodium carbonate. These findings indicate that the quantity of initiating species in the monomer decreases upon the addition of sodium salts.

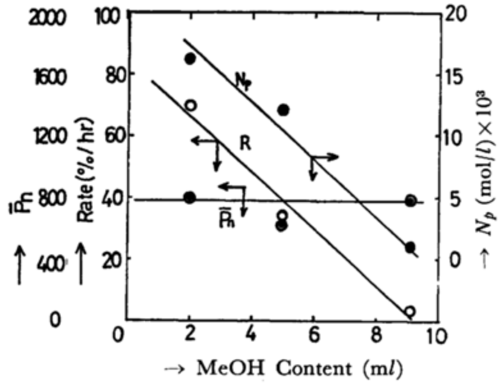


Fig. 4. Influence of the amount of sodium carbonate in decomposer (A) on the polymerization rate (*R*), the degree of polymerization ($\bar{P}_n$) and the number of moles of polymer chain (N_p). Pyrolysis and polymerization condition: the same condition as in case of Fig. 2.

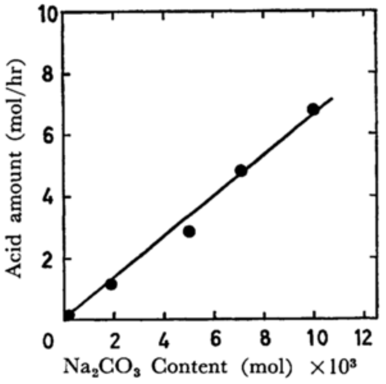


Fig. 5. Relationship between the amount of acid adsorbed by the salt and the amount of sodium carbonate. Formic acid content, 0.25 mol/*l*; reaction time, 1 hr; temperature, 20°C.

In order to make sure of the role of sodium salt, the ability of sodium carbonate to adsorb formic acid was also examined. As Fig. 5 shows, the amount of formic acid adsorbed by sodium carbonate increases proportionally with the amount of sodium carbonate.

These results are in accordance with the above finding that the polymerization caused by Brönsted acid is retarded by the adsorption of acid upon the addition of sodium salt.

Effect of the Impurities Present in the Monomer Gas on the Monomer Polymerizability. Gas chromatographic analysis of the pyrolyzed gas in the absence of sodium salts showed that the monomer contained methanol (0.45 mol%), water (0.35 mol%), and methyl formate (0.01 mol%) as impurities. In order to determine the influence of these impurities on the polymerization, the polymerizability of the monomer was examined in the presence of such additives as formic acid, methanol, water and methyl formate.

The results are shown in Table 1. Methyl formate had no influence on the polymerization, while water or methanol depressed the degree of polymerization but had no influence on the polymerization rate. On the other hand, both the polymerization rate and the degree of polymerization increased upon the addition of formic acid. These results show that formic acid acts as an initiator, while water and methanol act as chain transfer agents in the polymerization.

TABLE 1. INFLUENCE OF SUBSTANCES CONTAINED IN THE GAS OBTAINED BY THE PYROLYSIS OF α-POM ON THE MONOMER POLYMERIZABILITY

Substance	Rate (%/hr)	$R-R_0$ (%/hr)	$\bar{P}_n\times10^2$	$N_p\times10^3$ (mol/l)
Formic acid	21.9	18.4	20.0	3.8
Methanol	5.9	2.4	3.5	4.1
Methyl formate	5.2	1.7	5.9	1.8
Water	3.5	0	2.8	3.2
No additive	3.5	0	5.1	1.5

Polymerization condition: temperature 20°C, time 1 hr, substance/monomer (mole ratio) = 1/1000, R_0 is polymerization rate without any additive.

Formation of Acid. In order to clarify the acid formation quantitatively, the influence of the pyrolysis time and that of the addition of water on the acid formation in the pyrolysis of paraform were investigated.

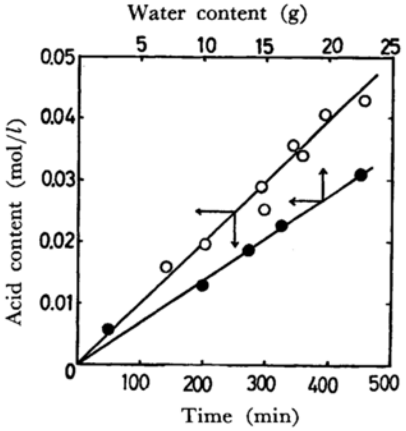


Fig. 6. Influence of the pyrolysis time and of the addition of water on the acid content of the hemiformal. Preparation condition: temperature, 95—115°C; PEG/paraform (weight ratio) = 1; $CaCO_3$/paraform (weight ratio) = 1; pyrolysis time, 110–150 min. (●).

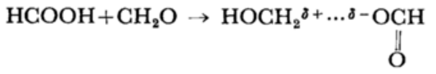
As Fig. 6 shows, the amount of acid in the hemiformal thus prepared increased linearly with the pyrolysis time of the paraform. This indicates that the acid is not contained in paraform as an impurity, but is produced by a side reaction in the course of pyrolysis. In addition, the amount of acid also increased linearly with the amount of water added. From these results, it may be considered that formaldehyde reacts with water as in Eq. (2) and produces the equivalent mole of formic acid and methanol;

$$2CH_2O+H_2O\rightarrow HCOOH+CH_3OH \qquad (2)$$

According to these results, it may be concluded that the polymerization is initiated mainly by the formic acid produced by the reaction of formaldehyde with the water which is originally present in the paraform used.

Influence of the Acid Content in the Hemiformal on the Monomer Polymeizability. The monomer polymerizability was studied in connection with the acid content in the hemiformal. Hemiformals containing different amounts of acid were prepared by varying the pyrolysis time of the paraform or by adding different amounts of calcium carbonate to the paraform.

It was found that the polymerization rate increased linearly with the acid content in the hemiformal (Fig. 7). From this, it may be concluded that the polymerization is initiated by formic acid as in Eq. (3) and that the monomer polymerizability depends on the amount of acid in the monomer.



$$HCOOH+CH_2O\rightarrow HOCH_2{}^{\delta+}\cdots{}^{\delta-}O\underset{\underset{O}{\|}}{C}H \qquad (3)$$

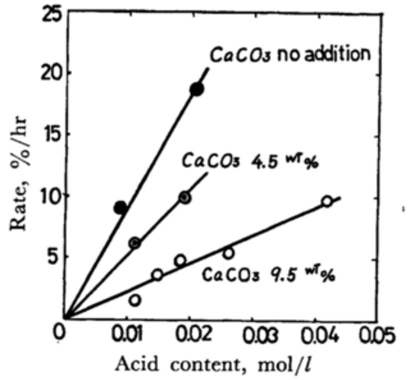


Fig. 7. Influence of the acid content of the hemiformal on the polymerization rate. Hemiformal preparation condition: the same condition as in case of Fig. 6; polymerization condition: the same condition as in case of Fig. 2.

On the other hand, straight lines with slopes differing with the amount of calcium carbonate were observed. That is, when a large amount of calcium carbonate was added to the paraform in the hemiformal preparation step, a great decrease in the polymerization rate was observed in spite of the higher acid content in the hemiformal.

In order to study the cause of this, hemiformals containing almost the same acid content (0.01 mol/*l*) were prepared by adding different amounts of calcium carbonate; the monomer polymerizability was then examined by the use of the monomer obtained by the pyrolysis of these hemiformals. As is shown in Fig. 8, both the polymerization rate and the degree of the polymerization of the resulting polymer decrease with an increase in the calcium carbonate content in the hemiformal preparation step, while the number of moles of the polymer chain increases.

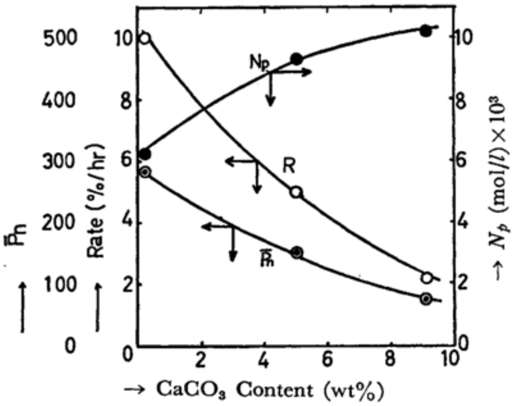


Fig. 8. Influence of the amount of calcium carbonate in the hemiformal preparation step on the polymerizability of monomer obtained by the pyrolysis of the hemiformals of the same acid content (0.01 mol/*l*).

This indicates that when hemiformals with the same acid content are prepared, the amount of a substance which acts as both a retarding and a chain transfer agent in the hemiformal may increase with the calcium carbonate content in the hemiformal preparation step. On the other hand, methanol content in the hemiformal may increase with the calcium carbonate content, because the pyrolysis time must be long when the calcium carbonate content is large.

Influence of the Addition of Methanol to the Hemiformal on the Monomer Polymerizability. Methanol may be considered to react with formic acid in the hemiformal pyrolysis step. From this, it may be supposed that methanol acts as both a retarding and a chain transfer agent.

In order to determine the influence of the methanol in the hemiformal pyrolysis step on the monomer polymerizability, methanol was added to a hemiformal containing 0.13 mol/*l* of the acid; the polymerizability of the monomer obtained by the pyrolysis of these hemiformals was then examined. As Fig. 9 shows, both the polymerization rate and the degree of polymerization of the resulting polymer decreased proportionally with the amount of methanol added to the hemiformal, while the number of moles of the polymer chain increased.

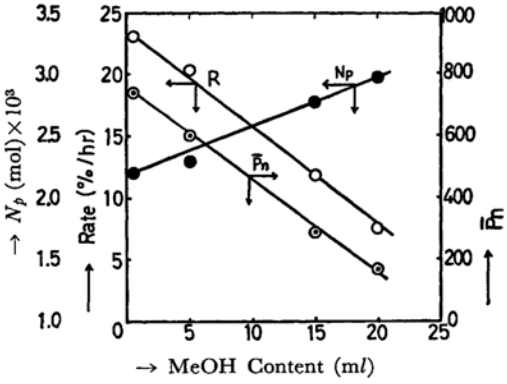


Fig. 9. Influence of the amount of methanol contained in the hemiformal on the rate of polymerization, the degree of polymerization and the number of moles of polymer chain. The hemiformal preparation condition: temperature, 100−115°C; time, 70 min; $CaCO_3$/paraform (weight ratio) = 0.1; acid content of the hemiformal, 0.3 mol/*l*.

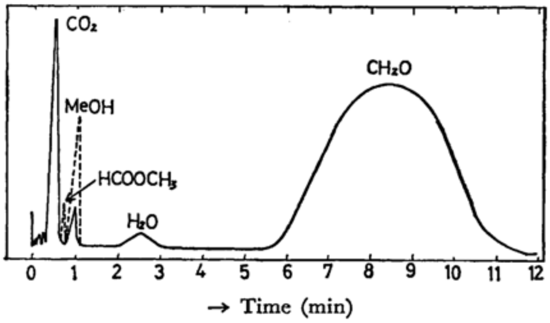


Fig. 10. Gas chromatography of the gas obtained by pyrolyzing the hemiformal. Pyrolysis condition: temperature, 135°C; measurement condition of gas chromatography: temperature, 120°C; carrier gas, He (74 m*l*/min); column, diglycerol.

On the other hand, from the results of the gas chromatographic analysis of the gas obtained by the pyrolysis of the hemiformal (Fig. 10), it was found that the amount of methyl formate formed increased with the amount of methanol in the hemiformal.

From these results, it may be concluded that methyl formate is produced by the reaction of methanol with formic acid present in the hemiformal during the course of the pyrolysis, and that the monomer polymerzability decreases in consequence of the decrease in the acid content of the monomer.

This is in accordance with the facts that both the polymerization rate and the degree of polymerization decrease, while the number of moles of the polymer chain of the polymer increases, with the amount of methanol in the hemiformal.

On the basis of these results, it may be concluded that, in the hemiformal preparation step, the addition of calcium salt to the paraform causes a decrease in the amount of an initiator (acid) in the hemiformal because of adsorption with the salt, and that then, in the hemiformal pyrolysis step, the addition of methanol to the hemiformal causes a decrease in the acid content of the monomer by means of a reaction with the alcohol.