

Development of a New Advanced Process for Manufacturing Polyacetal Resins. Part III. End-Capping during Polymerization for Manufacturing Acetal Homopolymer and Copolymer

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SYNOPSIS

Conventionally, acetal homopolymer or copolymer is obtained by the polymerization of formaldehyde or trioxane, following the end-capping using acetic anhydride or unzipping of the unstable polymer end fraction. First, Asahi Chemical developed a new process to obtain an end-capped polymer during polymerization of highly purified formaldehyde using acetic anhydride as the chain-transfer agent. Use of highly purified formaldehyde and end-capping during polymerization using acetic anhydride as a chain-transfer agent or an end-capping agent will provide a simple process for manufacturing acetal homopolymer. The polymerization mechanism was confirmed by infrared spectroscopy analysis and proton NMR analysis of the polymer obtained. Second, for the acetal copolymer, purified trioxane was copolymerized with ethylene oxide in the presence of methylal, which gave an end-capped polymer with high thermal stability. Two new intermediates from the initiation reaction of the copolymerization, 1,3,5,7-tetraoxacyclononane (TOCN) and 1,3,5,7,10-pentaoxacyclododecane (POCD), were isolated and a new initiation mechanism was proposed.

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INTRODUCTION

Acetal resin (alternatively, polyoxymethylenes: sometimes called polyacetals or aldehyde resins) is a term used to describe high molecular weight polymers and copolymers or formaldehyde. First commercialized as a homopolymer in 1960 by DuPont, acetal resins are engineering thermoplastics that have found broad use in traditional metal applications.

In the early 1950s, after many years of casual research, DuPont launched an intensive investigation on the preparation, properties, and stability of these polymers. They discovered that tough solid polymers of formaldehyde, which they termed "acetal resin," were readily prepared from high-purity formaldehyde using ionic initiators. These resins

were stabilized by replacing the hydroxyl radicals on the polymer chain ends with ester groups. The resultant polymer, having excellent tensile, impact, and compression strengths and good abrasion and wear resistance, appeared capable of filling many applications then reserved for metals.¹⁻³ Announcement of this product was made in 1956 and commercial production began in 1960.

Shortly thereafter, Celanese (presently Hoechst Celanese) researchers developed an acetal resin based on the copolymerization of trioxane and cyclic ethers, such as ethylene oxide.⁴ In 1962, a commercial plant began producing this acetal copolymer. Since then, rapid expansion of acetal resin production has occurred worldwide.

Up to 1971, DuPont, Celanese, and Celanese joint ventures have been the sole producers of acetal resins. In 1972, Asahi Chemical started to produce acetal homopolymer by utilizing the world's third type of polyacetal technology.⁵ Asahi Chemical also industrialized acetal copolymer in 1985.

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Polyacetal resin is a mechanically well-balanced engineering plastic. Its use is growing steadily in the automobile and electronics industries. Acetal homopolymer can be obtained by the homopolymerization of formaldehyde or trioxane. However, only from formaldehyde polymerization is the acetal homopolymer industrially produced. At present, DuPont and Asahi Chemical are the only producers of the acetal homopolymer. Although the details of the process for making acetal homopolymer have never been made public, the general processing step can be outlined as monomer purification, polymerization, end-capping and finishing.^{6,7}

In this article, we will mention mainly the new technologies developed by Asahi Chemical, for the production of acetal homopolymer and copolymer. Features of Asahi Chemical's acetal homopolymer process are as follows: First, it uses highly purified formaldehyde gas as the monomer. Second, end-capping during polymerization uses highly purified formaldehyde as the monomer and acetic anhydride as a chain-transfer or end-capping agent.

Features of Asahi Chemical's acetal copolymer are as follows:

1. Trioxane synthesis and purification.
2. Polymerization, i.e., using highly purified trioxane and end-capping during polymerization. Design of the polymerization reactor is one of the significant features. This design was deduced from the copolymerization mechanism of trioxane and ethylene oxide.

The homopolymer is superior to the copolymer in mechanical properties, whereas the copolymer is superior to the homopolymer in processability. Production of both types of polymers provides Asahi with the ability to serve market segment needs for both polymers.

BACKGROUND FOR DEVELOPMENT OF THE NEW TECHNOLOGIES

There are two types of acetal resins: One is the acetal homopolymer and the other is the acetal copolymer. Conventional methods for the production of both types of polymers are shown in Figure 1.

Purified formaldehyde gas is first produced for the homopolymer. Formaldehyde is then polymerized into polyoxymethylene. The unstable —OH end group of the newly obtained acetal homopolymer is end-capped by acetic anhydride into a stable end group of CH_3COO —.

For the copolymer, trioxane is produced from aqueous formaldehyde and copolymerized with ethylene oxide. The thermally unstable end group $-\text{CH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{O})_l\text{H}$ of the newly obtained copolymer is then unzipped into a stable $-\text{CH}_2\text{CH}_2\text{OH}$ end group. Since its starting raw material is methanol, which is very cheap, acetal resin has a very promising future.

There are two important points to be considered in Asahi's development: First, polyacetal production requires a significant amount of energy, and the

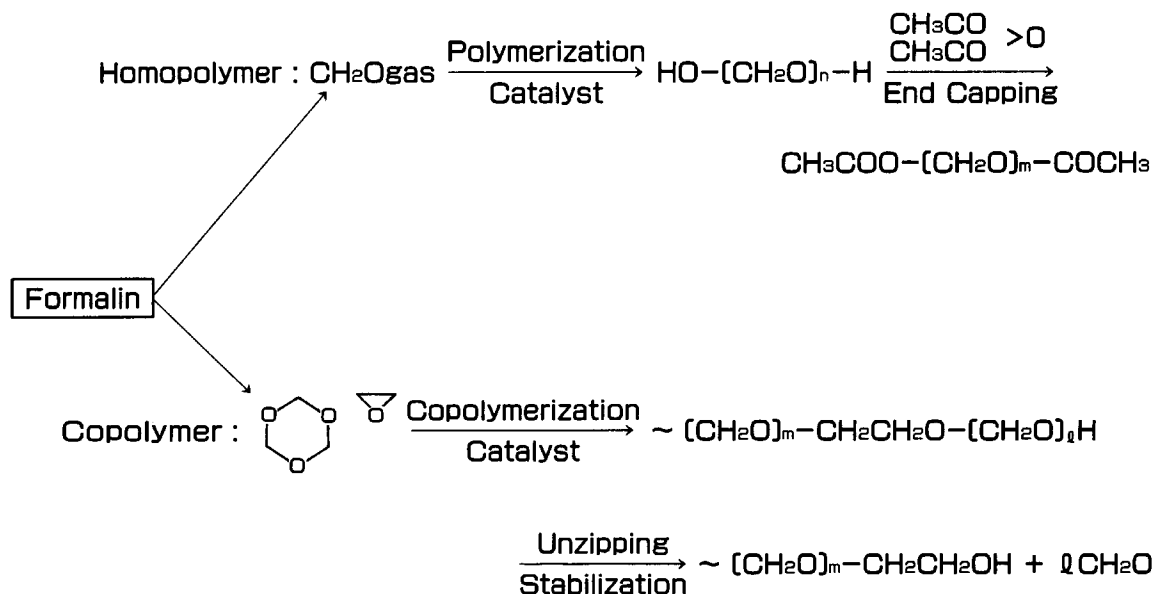


Figure 1 Conventional method for production of acetal resin.

conversion cost from formalin to polyacetal is high. The main reason why acetal resin needs so much energy is the high energy requirement to obtain purified monomer, i.e., purified formaldehyde and purified trioxane from formalin. Second, in the polymer-stabilizing step, several units of the polymer are lost. For example, in the case of the homopolymer, about 10% of the polymer is lost during acetylation, and in the case of the copolymer, from 5 to 10% of the polymer is lost due to unzipping of the unstable polymer end group.

The targets in developing an advanced process at Asahi Chemical were as follows:

1. A monomer process using highly concentrated aqueous formaldehyde solution. This target was mentioned before.⁸
2. The use of highly purified formaldehyde and end-capping during polymerization, using acetic anhydride as a chain-transfer or end-capping agent. An end-capped polymer with a stable acetyl group can be obtained by a chain-transfer reaction.
3. Asahi uses highly purified trioxane for the production of high-quality acetal copolymer. From this highly purified trioxane, an end-capped polymer with a stable methoxyl group can be obtained by a chain-transfer reaction using methylal as the chain-transfer agent or molecular weight regulator during polymerization.

DETAILS OF DEVELOPMENT

To illustrate Asahi Chemical's acetal homopolymer and copolymer process, as an example, the copolymer process is given in Figure 2. The starting raw material is methanol. Methylal is manufactured from methanol and the unreacted dilute aqueous formaldehyde solution that is produced as a by-product in the trioxane synthesis step. Methylal is then oxidized, and 3 mol formaldehyde and 1 mol water are formed. Thus, a 70 wt % aqueous formaldehyde solution is obtained.⁸ Trioxane is synthesized and purified from this highly concentrated aqueous formaldehyde solution. Unreacted aqueous formaldehyde is recycled back to the methylal synthesis step. Purified trioxane is copolymerized with ethylene oxide in the presence of a chain-transfer agent. Methylal is used as the chain-transfer agent or end-capping agent. Thus, the end-capped polymer with a stable methoxyl group can be obtained. For the acetal homopolymer, purified formaldehyde is

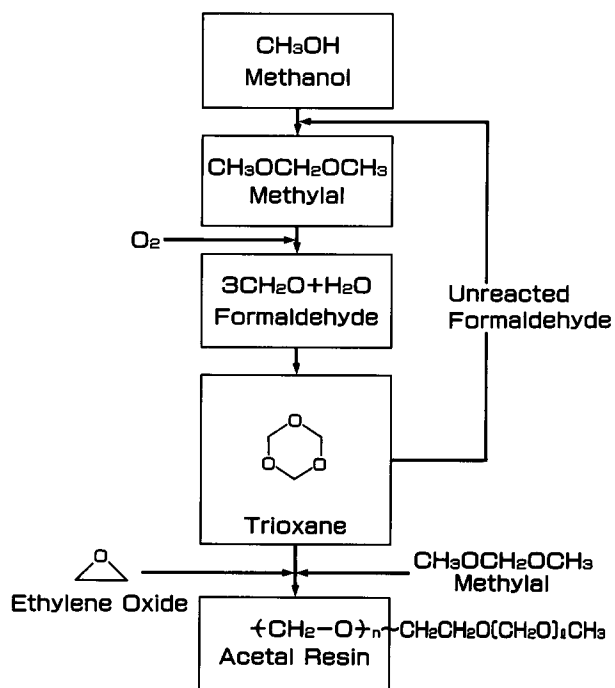


Figure 2 Asahi Chemical's acetal copolymer process.

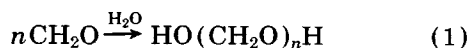
used as a monomer and acetic anhydride is used as the chain-transfer agent.

End-capping during Polymerization of Formaldehyde

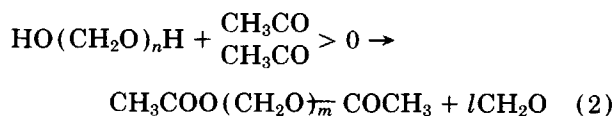
The limited solubility of the highly crystalline polymer yields a situation with many physical variables not present in a homogeneous system. For example, a typical polymerization in an inert solvent at room temperature or above involves the continuous introduction of sparingly soluble, gaseous formaldehyde (bp, -19°C) in proportion to its rate of polymerization. Thus, formaldehyde gas, formaldehyde solution, and a solid polymer phase are all present. Absorption of the monomer by the polymer and diffusion of the monomer to an active site are obviously important physical factors. Control of the particle size of the product is also important for subsequent isolation, washing, etc. The nature of the initiator, the solvent, contaminants, reaction conditions, and equipment design all contribute to the physical characteristics of the polymer slurry.⁹

Blair of DuPont¹⁰ proposed the use of bisquaternary ammonium salt as the initiator for polymerization. The use of a bifunctional quaternary ammonium salt is favorable for the growth of polymer particles that are easy to handle.

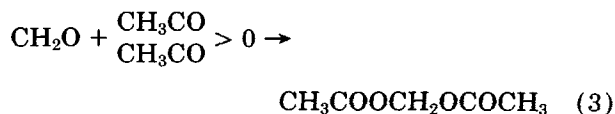
Conventionally, formaldehyde contains some impurities such as water, and when water acts as a chain-transfer agent, polymer end groups are the thermally unstable hydroxyl groups [eq. (1)]:



In this case, polymer end groups are acetylated by acetic anhydride at elevated temperature from 130–160°C [eq. (2)]:

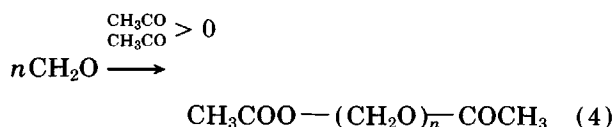


However, about 10% of the polymer is lost during acetylation due to unzipping from the unstable polymer end group, and methylene diacetate is formed as a byproduct by a side reaction [eq. (3)]:



Ten percent of the polymer loss will lead to a byproduct of methylene diacetate, nearly 50% (by weight) of the final product, i.e., gigantic amounts of byproducts.

Masamoto of Asahi Chemical proposed the use of highly purified formaldehyde and acetic anhydride as a chain-transfer or end-capping agent to cap the polymer ends during polymerization [eq. (4)].¹¹ Thus, polymer loss and byproduct formation can be minimized during stabilization:



We confirmed this not only in the laboratory scale but also in the commercial plant scale. Polymerization apparatus used in the laboratory scale is shown in Figure 3.

Highly purified formaldehyde in which any water and methanol can be detectable by gas chromatography was fed to the hexane solution using dimethyl distearyl ammonium acetate as the initiator and acetic anhydride as the chain-transfer agent. Gaseous formaldehyde was continuously fed to the hexane polymer slurry, which was intensively stirred.

Hexane solution containing the initiator and a small amount of acetic anhydride was continuously

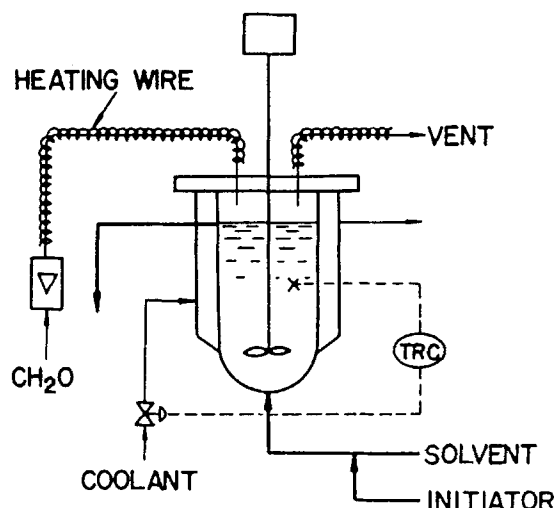


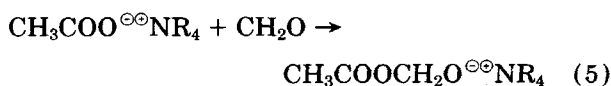
Figure 3 Polymerization apparatus.

fed to the polymerization reactor, and polymer slurry was continuously withdrawn, and thus polymer content in the slurry was adjusted about 20 wt %. The polymerization temperature was maintained at 50°C by a controlling thermal jacket. Withdrawn polymer slurry was filtered and washed with methanol and acetone and then dried in a nitrogen atmosphere.

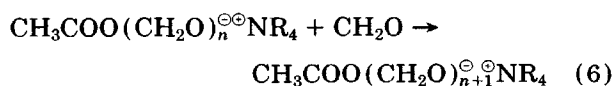
Figure 4 shows the infrared spectrum of the obtained polymer. Absorption of the acetyl group¹² was clearly found at 1755 cm⁻¹, which should be attributed to the chain-transfer reaction of acetic anhydride to the polymer chain end according to eq. (7).

In this case, the polymerization scheme using quaternary ammonium salt as the initiator can be written as follows:

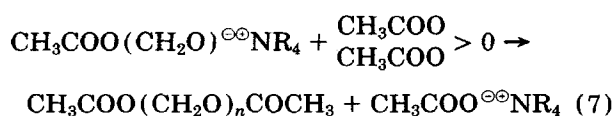
Initiation



Propagation



Chain transfer



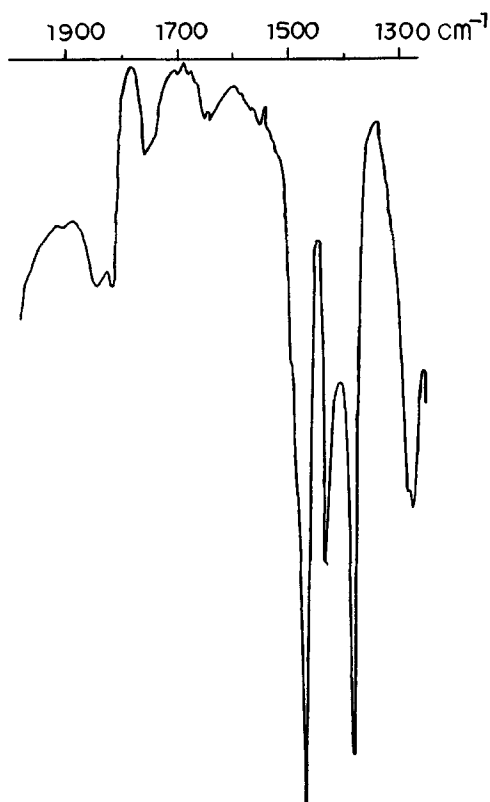


Figure 4 Infrared spectrum of the polymer: η_{sp}/c , 3.0.

Reinitiation

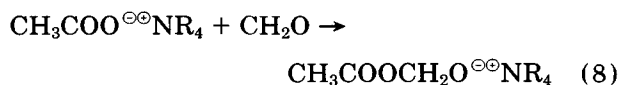


Figure 5 shows the effects of acetic anhydride on the reduced viscosity (η_{sp}/c) of the polymer obtained. The reduced viscosity was measured in *p*-chlorophenol tetrachloroethane mixed solvent at 60°C.

Acetic anhydride was dissolved in feed hexane solvent in which acetic anhydride content was varied from 400 to 1200 ppm. Nearly 100% of acetic anhydride in the feed solvent was confirmed to be consumed during polymerization. In withdrawn polymer slurry, acetic anhydride cannot be detectable by gas chromatography.

The acetyl group of the polymer chain end was detected by the infrared spectrum at 1755 cm^{-1} , and the main-chain oxymethylene unit was also detected by the infrared spectrum at 1470 cm^{-1} .¹² In Figure 6, the ratio of extinction of the carbonyl band ($\text{EC}=\text{O}$) at 1755 cm^{-1} and the reference band (ECH_2) at 1470 cm^{-1} , i.e., the ratio of the acetyl

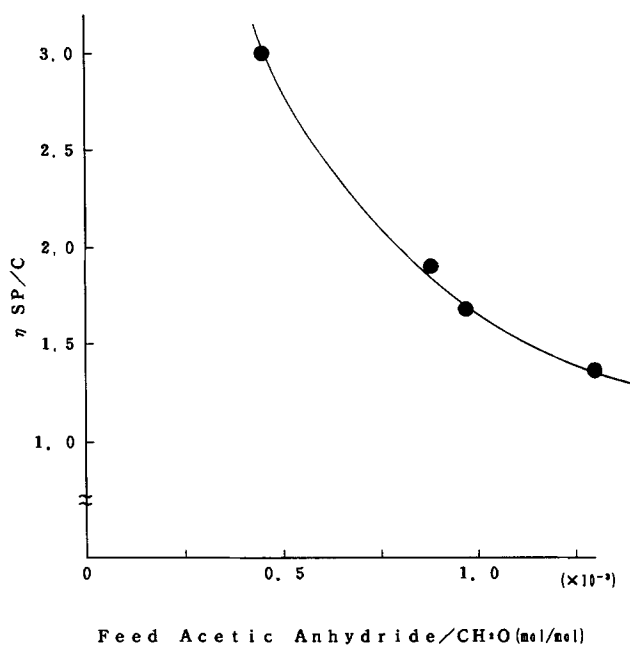


Figure 5 Effects of feed acetic anhydride on the reduced viscosity of polymer.

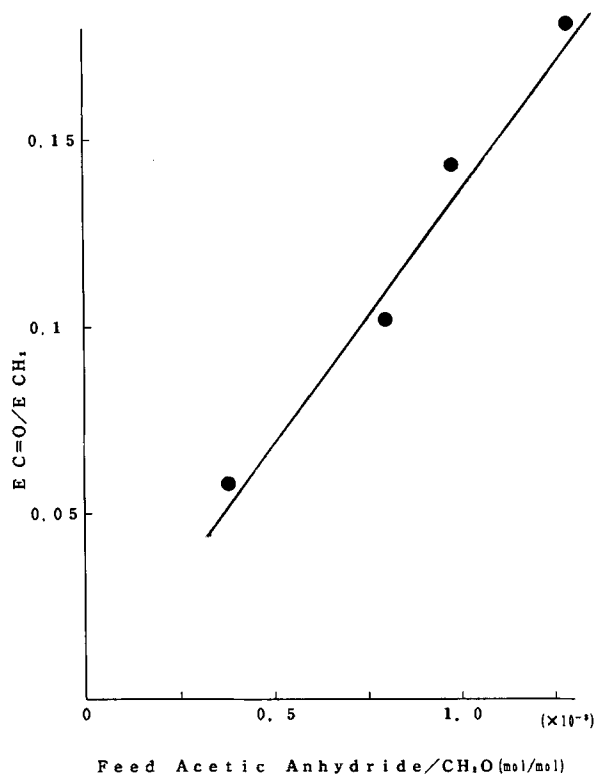


Figure 6 Relationships between feed acetic anhydride and the ratio of extinction of carbonyl band ($\text{EC}=\text{O}$) and reference band (ECH_2).

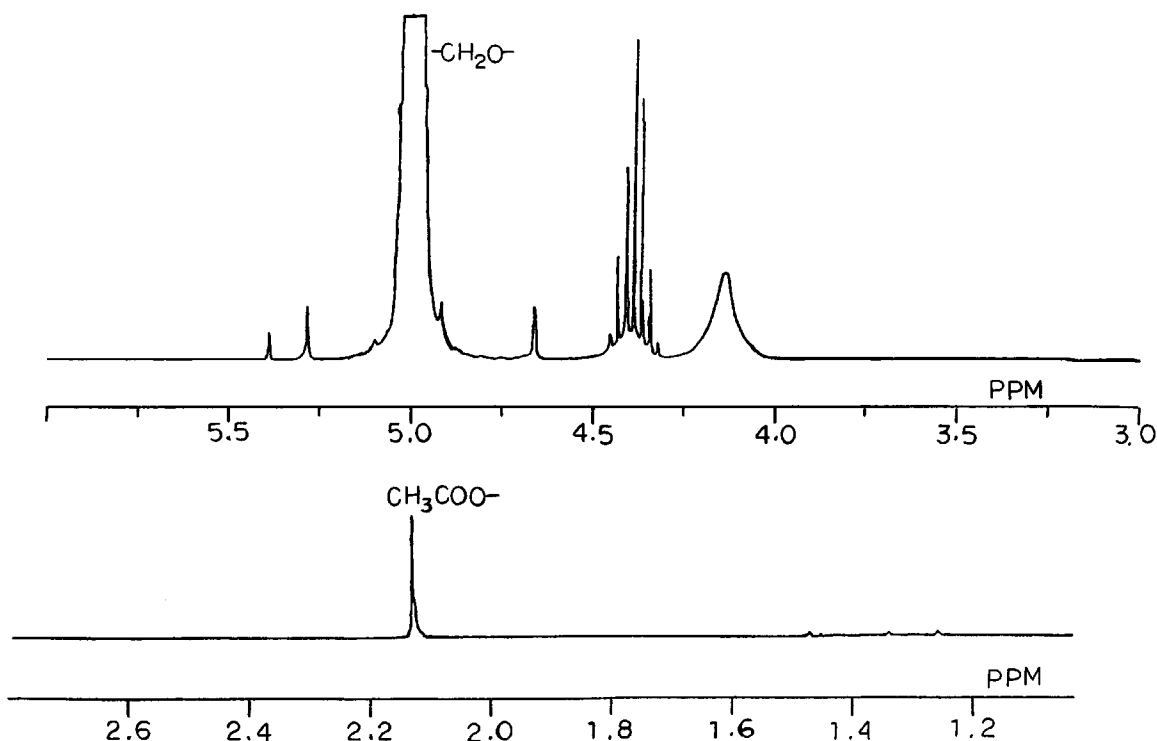


Figure 7 Proton NMR spectrum of the polymer.

end group to the polymer main-chain oxymethylene unit, is plotted vs. the acetic anhydride to formaldehyde ratio. Good linear relationships were observed.

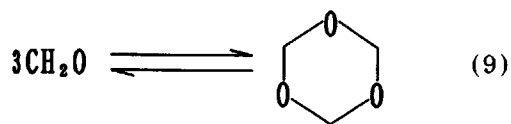
Figure 7 shows the proton NMR spectrum of the polymer ($\eta_{sp}/c = 1.7$). The proton NMR was measured in deuterated hexafluoroisopropyl alcohol at 55°C. The proton of the acetyl group was found at 2.1 ppm, and the proton of oxymethylene unit, at 5.0 ppm.

In this proton NMR spectrum, the mol fraction of the $-\text{OCH}_2-$ unit is 99.8%, and that of the $\text{CH}_3\text{COO}-$ group, 0.2%, which is in approximately good accordance with the ratio of the feed acetic anhydride to formaldehyde. The polymer obtained thus showed a negligible polymer loss at the following acetylation step and also showed a negligible generation of the byproduct of methylene diacetate.

End-capping during polymerization was confirmed not only in the laboratory scale but also at Asahi's acetal homopolymer plant, and the loss of polymer in the following acetylation step is negligible and generation of the byproducts, methylene diacetate, is also negligible.

Trioxane Synthesis and Purification

The reaction from formaldehyde to trioxane is as follows [eq. (9)]:



The key points of the Asahi's trioxane synthesis are the following: First, the solid acid. Conventionally, a corrosive catalyst such as sulfuric acid is used in the commercial production of trioxane,¹³ but Asahi Chemical developed a new reaction system employing a noncorrosive solid acid.¹⁴ Thus, Asahi established a solid acid reaction system with high selectivity and a high space time yield.

Second, the highly concentrated aqueous formaldehyde solution. The effect of the formaldehyde concentration on trioxane formation is shown in Figure 8. Since the reaction is based on an equilibrium, a high concentration of formaldehyde solution favors this reaction. Asahi uses the highly concentrated formaldehyde from the methylal oxida-

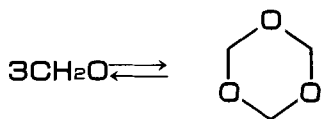
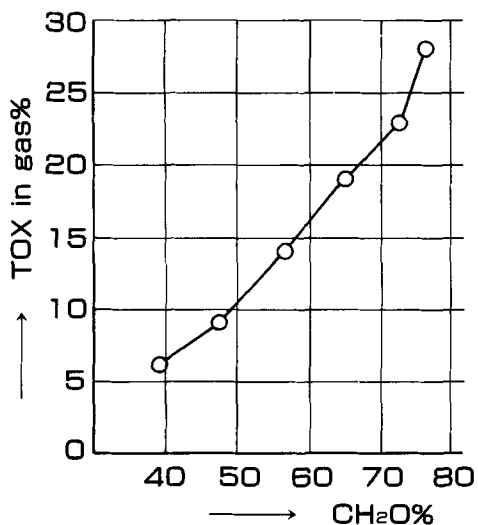


Figure 8 Effect of formaldehyde concentration on trioxane formation. TOX : trioxane.

tion.^{8,15,16} The trioxane thus produced is distilled and extracted by a water-insoluble organic solvent, such as benzene, methylene chloride, trichlorobenzene, or α -chloronaphthalene and fed to the purification step.

Asahi also developed a new system to obtain highly purified trioxane by a distillation technique.¹⁷⁻¹⁹ From this process, purified trioxane containing fewer than several parts per million impurities, such as water and formic acid, can be obtained. This purified trioxane is fed to the copolymerization section.

Mechanism and Kinetics of Trioxane Copolymerization

Even though boron trifluoride or its ether complex is used as the catalyst for the commercial production of the trioxane copolymer, there is no general agreement on the initiation mechanism of this monomer by the boron trifluoride ether complex. This polymerization has been characterized by the occurrence of an "induction period," during which formaldehyde is evolved without the precipitation of the crystalline polymer. The roles played by water as well as the formation of formaldehyde and cyclic formals during the induction period have been suggested. As for the

effects of water on the initiation mechanism, using boron trifluoride or its etherate catalyst, there are many different phenomena. Kern and Jaacks²⁰ reported that BF_3 coordinates directly with oxygen in the trioxane molecule. On the other hand, Iguchi²¹ reported that in a rigorously dried trioxane-cyclohexane solution trioxane cannot be initiated by $\text{BF}_3 \cdot \text{OBU}_2$.

According to Miki and co-workers,²² the mechanism of initiation may be different with media polarity. Although it was not clearly shown that the polymerization of trioxane was not initiated by $\text{BF}_3 \cdot \text{OEt}_2$ alone in nonpolar media (*n*-hexane or benzene), the strong accelerating effect of water was indeed demonstrated. This effect was much less pronounced in the more polar ethylene dichloride and disappeared completely in the highly polar nitrobenzene.

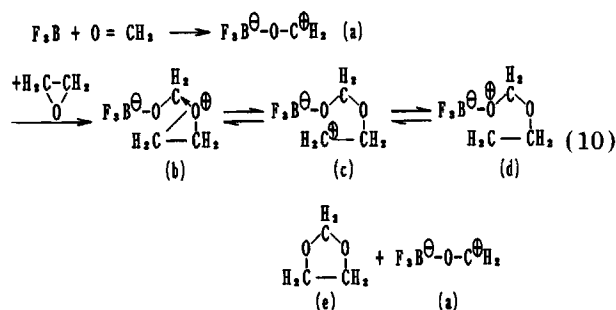
Collins et al.²³ reported that molten trioxane at 70°C initiated with $\text{BF}_3 \cdot \text{Bu}_2\text{O}$ did not polymerize at a low water concentration (< 17 ppm H_2O), and they concluded that the initiation of trioxane by $\text{BF}_3 \cdot \text{Bu}_2\text{O}$ in the presence of water occurs by rapid hydrolysis of BF_3 to form protonic acids that protonate trioxane in the primary initiation step. Lu et al.²⁴ reported proton NMR studies leading to the development of a more detailed mechanistic scheme for the initial process. Collins et al.²³ reported that water is necessary for the polymerization using the BF_3 ether complex as the initiator.

On the other hand, there are several reports that denied the role of water as a cocatalyst using $\text{BF}_3 \cdot \text{OBU}_2$. Chen²⁵ reported the result using rigorously dried trioxane, and polymerization started smoothly at 65°C without adding any substance. In almost every case, solidification occurred instantaneously within 0.5 min. Chen's result showed that homopolymerization of trioxane with $\text{BF}_3 \cdot \text{Bu}_2\text{O}$ without water polymerization can start smoothly. Moreover, Chen²⁶ also reported the polymerization of purified trioxane with dioxolane using $\text{BF}_3 \cdot \text{Bu}_2\text{O}$ as the catalyst. Catalyst/monomer mole ratios were varied from 0.85×10^{-5} to 10.0×10^{-5} (mol/mol) and solidification occurred in a short time (within ~ 1 min) at a reasonable catalyst concentration without adding any water. These results also showed that for the copolymerization of trioxane with dioxolane, using $\text{BF}_3 \cdot \text{Bu}_2\text{O}$ as the catalyst, water is not necessary for polymerization.

Studies conducted by Weissermel et al.^{27,28} on the copolymerization of trioxane and ethylene oxide revealed that an induction period, much longer than

observed in the case of the homopolymer, prevails. It has been established that during this period ethylene oxide is converted to 1,3-dioxolane and 1,3,5-trioxepane and to low molecular weight linear copolymers. Only after all of the ethylene oxide is so consumed does the solid polymer form.

Weissermel et al.²⁸ proposed the interception of formaldehyde with ethylene oxide to form dioxolane for the initiation mechanism of the copolymerization of trioxane and ethylene oxide [eq. (10)]:



Collins et al.²⁹ also reported the fundamental consideration concerning the copolymerization mechanism of trioxane and ethylene oxide initiated with boron trifluoride dibutyl etherate. They confirmed that ethylene oxide is converted to dioxolane and trioxepane.

Weissermel et al.²⁸ and Collins et al.²⁹ proposed the formation mechanism of dioxolane from ethylene oxide and formaldehyde, and this mechanism was thought plausible for a long time. However, Asahi Chemical researchers isolated novel cyclic compounds^{30,31} that are the reaction products of trioxane and ethylene oxide and proposed a new polymerization mechanism.

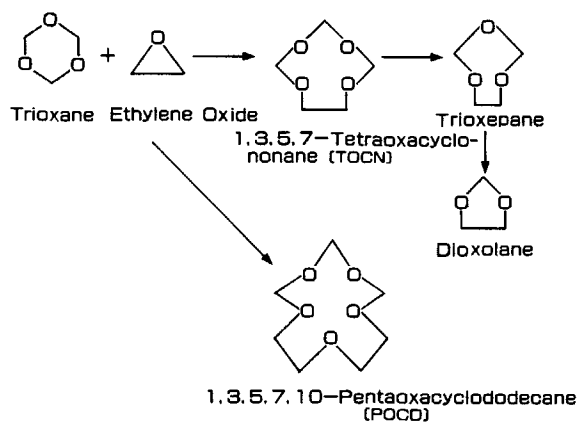


Figure 9 Initiation mechanism of copolymerization of trioxane and ethylene oxide.

Table I Time Required for Disappearance of Ethylene Oxide

	H ₂ O in Trioxane (ppm)		
	1	20	100
Time (s)	40	80	260

We will now discuss the newly discovered initiation mechanism for the copolymerization of trioxane and ethylene oxide. The previously held theory concerning the mechanism for the copolymerization of trioxane and ethylene oxide is based on much experimental data. Trioxane is decomposed to form formaldehyde, and the formaldehyde then reacts with ethylene oxide to produce dioxolane and trioxepane. These two chemicals then copolymerize with trioxane. Previous work shows only the results of the reaction in the last stable zone.

These are our new discoveries. Purified trioxane and ethylene oxide was introduced to the glass ampule and the glass ampule was immersed in the oil bath at definite temperature. A cyclohexane solution of boron trifluoride dibutyl ether was introduced from the cap of the glass ampule to the melt trioxane ethylene oxide mixture with a microsyringe and then the mixture was intensively shaken in the oil bath. The reaction mixture was then poured into the methanol solution containing a small amount of ammonium.

The precipitated polymerization products were separated, dried, and then analyzed. The solution part was also analyzed by gas chromatography.

The initiation mechanism during the bulk copolymerization of trioxane and ethylene oxide using boron trifluoride dibutyl etherate as the initiator were carefully studied, and new intermediates or novel compounds isolated were 1,3,5,7-tetraoxacyclononane (TOCN) and 1,3,5,7,10-pentaoxacyclododecane (POCD), which disclosed the precise initiation mechanism as shown in Figure 9. First, ethylene oxide reacts with trioxane to produce TOCN, which is the reaction product of 1 mol ethylene oxide and 1 mol trioxane, and POCD, which is the reaction product of 2 mol ethylene oxide and 1 mol trioxane. Trioxepane and dioxolane result from the former compound and then are copolymerized with trioxane.

Experimental results are shown Figure 10. At first, as the ethylene oxide concentration decreased, TOCN and POCD appeared. After the ethylene ox-

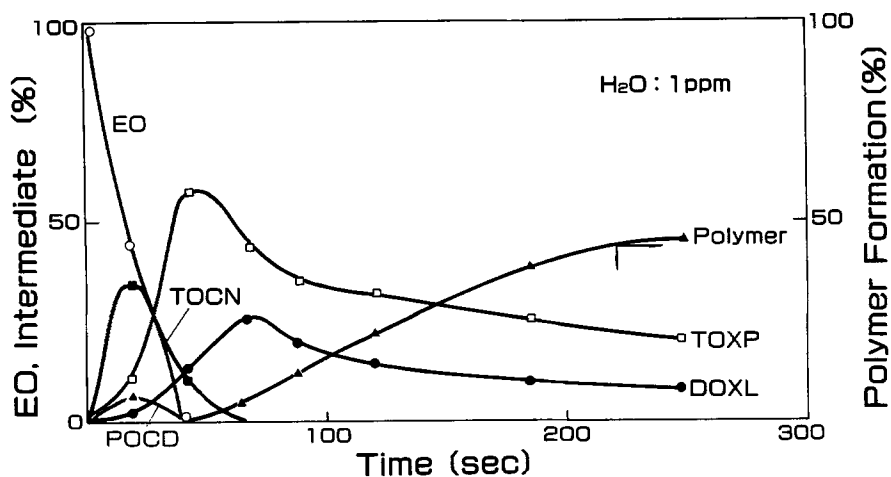


Figure 10 Concentration profile of reactants and intermediates in trioxane/ethylene oxide copolymerization (H_2O : 1 ppm). EO : ethylene oxide; TOCN : 1,3,5,7-tetraoxacyclononane; POCD : 1,3,5,7,10-pentaoxacyclododecane; TOXP : trioxepane; DOXL : dioxolane.

ide was consumed, polymerization started. As the concentration of TOCN decreased, the concentration of trioxepane increased. Soon after the appearance of trioxepane, dioxolane appeared, and the concentration of these two compounds decreased steadily with time. Now, we will refer to the effects of water on the initial copolymerization reaction of trioxane and ethylene oxide in more detail.

Figure 10 shows the concentration profiles of the reactants and intermediates when the water concentration in trioxane is about 1 ppm. Figure 11

shows the concentration profiles of reactants and intermediates when the water concentration in trioxane is 100 ppm. Consumption of ethylene oxide is prolonged, as is the appearance and consumption of TOCN and POCD. Therefore, the appearance of trioxepane is also prolonged. The appearance of dioxolane is not observed in this time period.

Table I shows the time required for consumption of ethylene oxide when the water concentration in trioxane is 1, 20, and 100 ppm. As the water concentration becomes high, the time required becomes

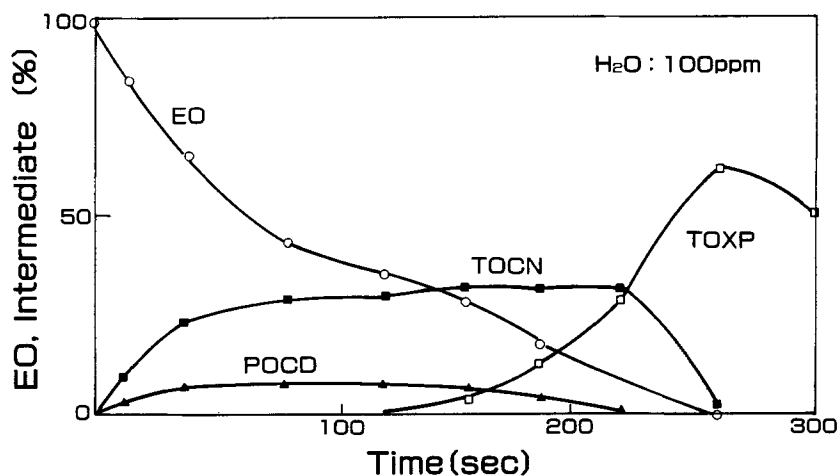


Figure 11 Concentration profile of reactants and intermediates in trioxane/ethylene oxide copolymerization (H_2O : 100 ppm). EO : ethylene oxide; TOCN : 1,3,5,7-tetraoxacyclononane; POCD : 1,3,5,7,10-pentaoxacyclododecane; TOXP : trioxepane.

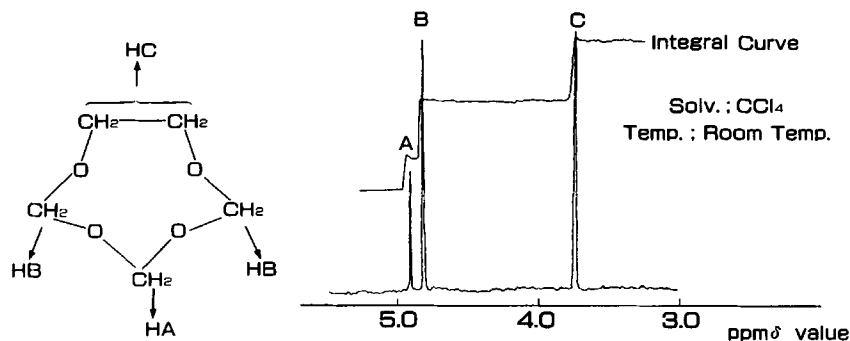


Figure 12 Proton NMR pattern of intermediate A (1,3,5,7-tetraoxacyclononane).

longer. From these experiments, we concluded the following about the induction period of copolymerization:

1. The induction period is a result of consecutive reactions of these intermediates, formed during the early stage of copolymerization.
2. The induction period is affected by the amount of impurities. For example, water prolongs the induction period.

We confirmed the phenomenon that water prolongs the induction period not only in the laboratory scale but also in the bench and pilot scale. The two new intermediates A and B were separated and col-

lected by gas chromatography and then structures were confirmed by proton NMR. Figure 12 shows the proton NMR pattern of the new intermediate A, which is identified as 1,3,5,7-tetraoxacyclononane. From this figure, the integral value of HA to HB to HC is equal to 1 to 2 to 2. Figure 13 shows the proton NMR pattern of the new intermediate B, which is identified as 1,3,5,7,10-pentaoxacyclododecane. The integral value of HA to HB to HC is equal to 1 to 2 to 4. Figure 14 shows how the polymer changes with polymerization yield. Almost every ethylene oxide unit is trapped in the polymer chain during the early polymerization stage.

The reduced viscosity of the polymer is an interesting subject. A maximum value of reduced viscosity

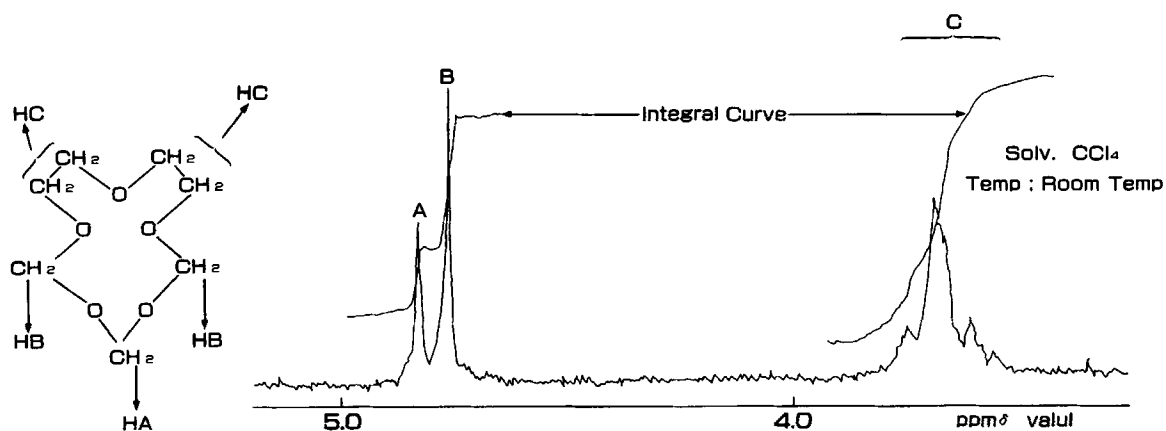


Figure 13 Proton NMR pattern of intermediate B (1,3,5,7,10-pentaoxacyclododecane).

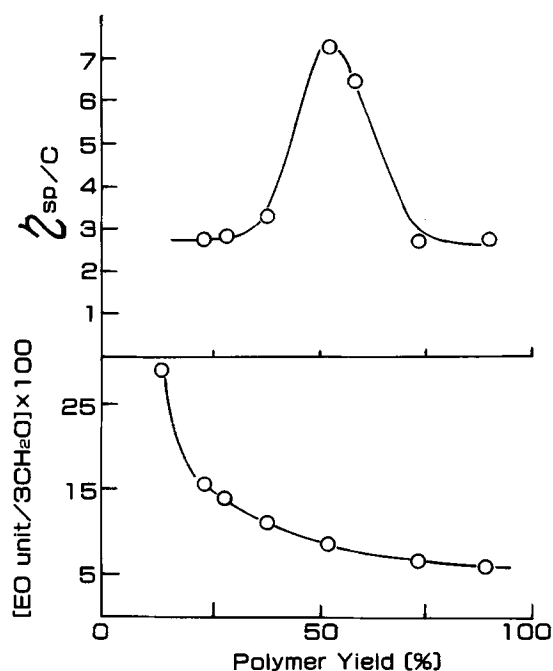


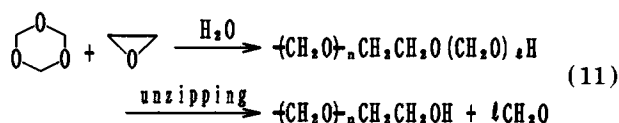
Figure 14 Transacetalization during polymerization.¹⁶
EO : ethylene oxide.

is observed around a polymer conversion of 50%. It then decreases to a constant value with polymer conversion. This phenomenon may be explained by transacetalization. At about a polymer yield of 50%, an ultrahigh molecular weight polymer is formed. However, the transacetalization reaction yields the most probable molecular weight distribution.

Therefore, reduced viscosity remains constant with polymer yield.

Polymerization Reactor and Stabilization

In the conventional technique, the polymerization-grade trioxane used includes some impurities such as water, methanol, and formic acid. For example, when the water acts as a chain-transfer agent, the unstable polymer end group $-\text{CH}_2-\text{CH}_2\text{O}-(\text{CH}_2\text{O})_n\text{H}$ is generated. This unstable end portion $-\text{CH}_2\text{CH}_2\text{O}-(\text{CH}_2\text{O})_n\text{H}$ is unzipped by the stabilization technique, and a polymer with a stable $-\text{CH}_2\text{CH}_2\text{OH}$ end group is obtained [eq. (11)]:



Various methods are proposed to remove the unstable portions via a controlled thermal process, i.e., subjecting the polymer to its melt temperature using compounding mill rolls³² or vented extruders.³³ Another method is to hydrolytically react the unstable hemiacetal end groups using basic conditions.³⁴ In these cases, the polymer losses during polymer stabilization are from 5 to 10%. On the other hand, the Asahi Chemical process uses highly purified trioxane containing less than several parts per million impurities and uses methylal as the chain transfer or end-capping agent.

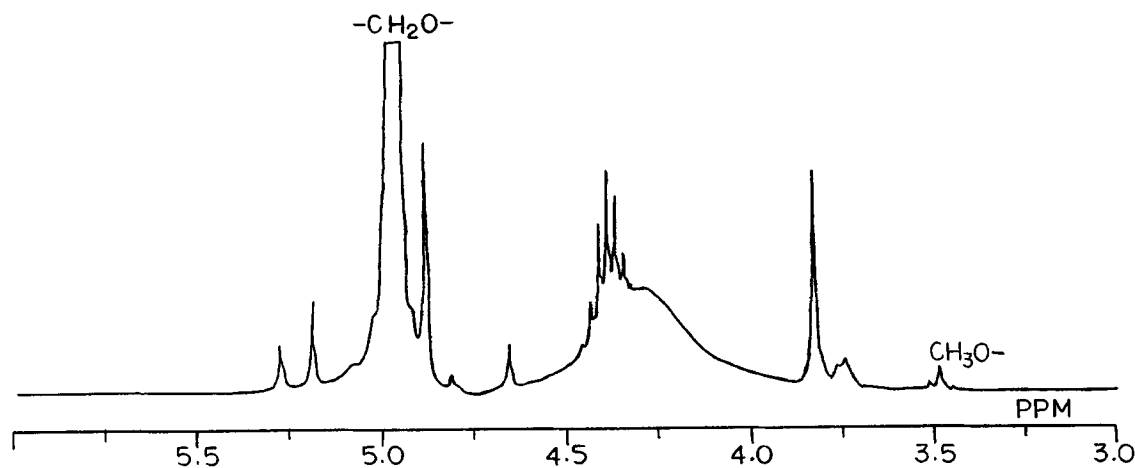


Figure 15 Proton NMR pattern of end-capped trioxane ethylene oxide copolymer by methylal.

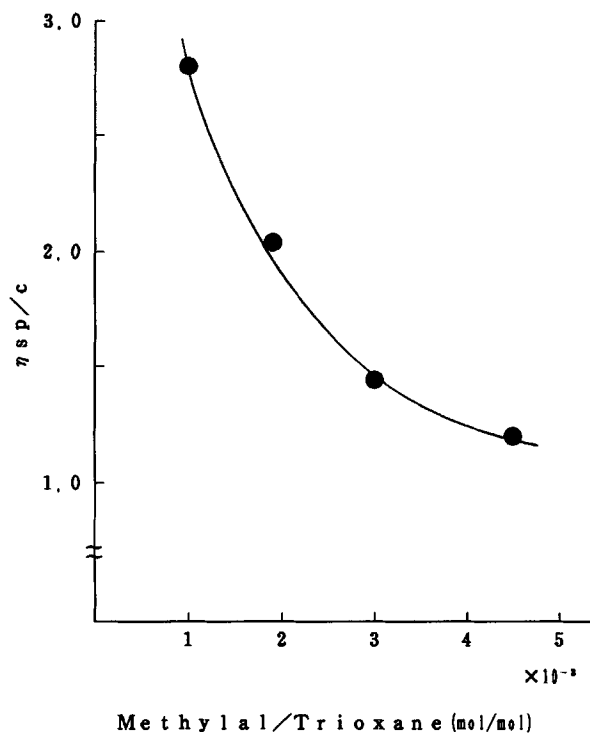
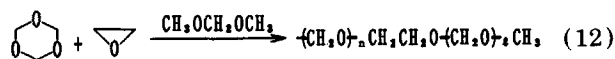


Figure 16 Effects of methylal on the reduced viscosity of the polymer.

Figure 15 shows proton NMR pattern of the obtained polymer. The proton of the $-\text{OCH}_3$ end group was observed at 3.5 ppm, and the proton of $-\text{OCH}_2-$ unit, at 5.0 ppm.

Figure 16 shows the effects of methylal on the reduced viscosity of polymer obtained. With the increase of methylal, the reduced viscosity decreases due to a chain-transfer reaction of methylal. A polymer with both end groups capped with stable methoxyl groups was obtained [eq. (12)]:



This was confirmed by the fact that the polymer obtained shows only a very small amount of unstable portion, less than 0.5 wt %, when the polymer is treated at 230°C for 60 min under reduced pressure. Therefore, polymer loss during polymer stabilization can be minimized and high-quality products can be obtained.

As for the polymerization reactor at present, twin screw-type reactors are prevalent,³⁵⁻⁴² the so-called reactive processing. The design of an effective polymerization reactor is the most important point in the copolymerization section. This design was based on the polymerization mechanism.

Based on findings concerning the copolymerization mechanism, Asahi designed an effective polymerization reactor.

The polymerization behavior of trioxane is as follows: In the early stage, reactants are nonviscous liquids; then they become viscous, forming a slurry, and then powdery.

With respect to polymerization behavior, Asahi designed an effective self-cleaning-type polymerization reactor that is compact and has a high polymerization capacity. Polymerization with a low concentration of catalyst yields a high-quality polymer.

CONCLUSIONS

Asahi developed an advanced process for manufacturing acetal homopolymer and copolymer. End-capping during polymerization of formaldehyde for acetal homopolymer or trioxane for acetal copolymer results in a simple process and high-quality products.

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