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## DEVELOPMENT OF AN ADVANCED PROCESS FOR MANUFACTURING POLYACETAL RESIN†

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### ABSTRACT

An advanced process for manufacturing polyacetal resin has been developed. First, a new technology for the production of highly concentrated aqueous formaldehyde was developed by oxidizing methylal. Whereas the oxidation of methanol yields 1 mol water per mole formaldehyde, methylal oxidation produces only 1 mol water for every 3 mol formaldehyde. Thus, the output from methylal oxidation is more than 70% formaldehyde, compared with 55% from methanol oxidation. Second, a new extraction distillation process for formaldehyde purification was developed in order to get highly purified formaldehyde directly from formalin. By using highly purified formaldehyde, an end-capped polymer was obtained in the presence of acetic anhydride as a chain transfer or end-capping agent during polymerization. Third, the relatively high formaldehyde concentration enhances the formation of trioxane. Purified trioxane is copolymerized with ethylene oxide in the presence of an end-capping agent to get 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. Fourth, the world's first acetal block copolymer was commercialized by the polymerization of formaldehyde in the presence of a lubricant functional polymer having an active hydrogen atom. This acetal block copolymer exhibits super lubrication properties.

†Dedicated to Professor Otto Vogl in honor of his 65th birthday.

## 1. INTRODUCTION

In 1972, Asahi Chemical started to produce acetal homopolymer by utilizing the world's third type of polyacetal technology, the others being those of Du Pont (homopolymer) and Celanese (copolymer). Polyacetal resin is a mechanically well-balanced engineering plastic. Its use is growing steadily in the automobile and electronics industries. In Japan, demand for polyacetal resin is the largest among all the engineering plastics. Its demand in 1989 was about 130 thousand tons.

There are two types of polyacetal resin. 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 Fig. 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  $CH_3COO-$ .

For the copolymer, trioxane is produced from aqueous formaldehyde and copolymerized with ethylene oxide. The thermally unstable end group  $-(CH_2O)_nH$  of the newly obtained copolymer is then unzipped into a stable  $-CH_2CH_2OH$  end group.

## 2. BACKGROUND

Since its starting raw material is methanol, which is very cheap, polyacetal resin has a very promising future.

Asahi Chemical, already has a process for making acetal homopolymer. However, convinced of the further potential of the polyacetal resin in addition to the acetal homopolymer, we decided to develop the copolymer.

The homopolymer is superior to the copolymer in mechanical properties, while

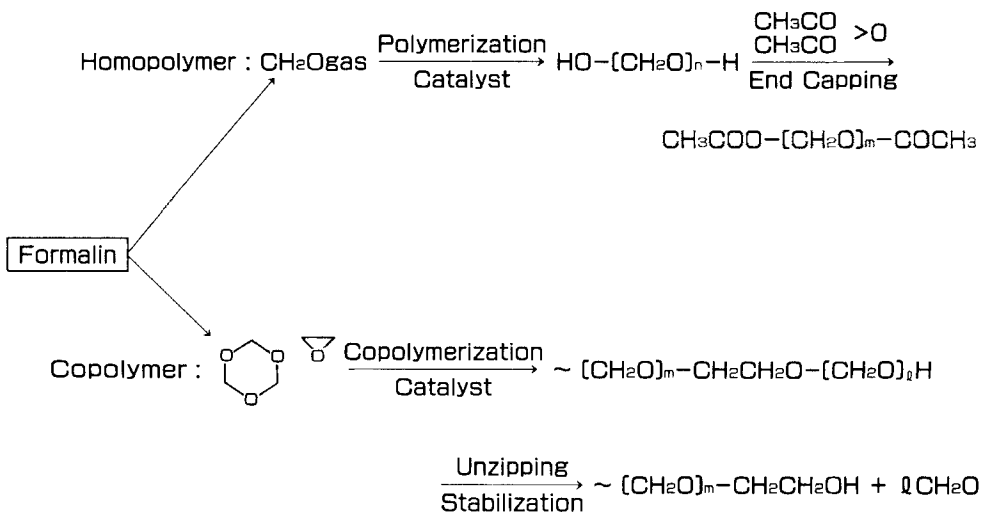


FIG. 1. Conventional method for the production of polyacetal resin.

the copolymer is superior to the homopolymer in processability. Production of both types of polymers provides us with the ability to serve market segment needs for both polymers. This is the first time this process has been utilized.

Production of the acetal block copolymer, provides us with a functional polymer. The acetal block copolymer shows excellent lubrication properties.

There are two important points to be considered in the development of this process. First: Polyacetal production requires much energy, and the conversion cost from formalin to polyacetal is high. The main reason why polyacetal resin needs so much energy is the high energy requirement to get purified monomer; that is, 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.

Our targets in developing this advanced process were as follows.

1. A monomer process using highly concentrated aqueous formaldehyde solution. We changed the formalin manufacturing process from a methanol oxidation process to a methylal oxidation process. The concentration of formaldehyde was increased from 55% in the methanol process to 70% in the methylal process. This new process reduced the energy requirement for production of purified formaldehyde and trioxane, and also reduced plant construction costs of the trioxane synthesis section.
2. The use of highly purified formaldehyde and end capping during polymerization, using acetic anhydride as a chain transfer or end capping agent. We can get an end capped polymer with a stable acetyl group by a chain transfer reaction.
3. We use highly purified trioxane for the production of high quality acetal copolymer. From this highly purified trioxane we can get an end-capped polymer with a stable methoxyl group by a chain transfer reaction using methylal as the chain transfer agent or molecular weight regulator during polymerization.
4. We use highly purified formaldehyde and the chain transfer reaction to make acetal block copolymer. We use a functional polymer, which has good lubrication properties and an active hydrogen atom, as a chain transfer agent.

### 3. DETAILS

An example of Asahi Chemical's polyacetal process is given in Fig. 2. The starting raw material is methanol. Methylal is manufactured from methanol and the unreacted dilute aqueous formaldehyde solution that occurs as a by-product in the trioxane synthesis step. Methylal is then oxidized, and 3 mol formaldehyde and 1 mol water are formed. Thus, 70 wt% aqueous formaldehyde solution is obtained.

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

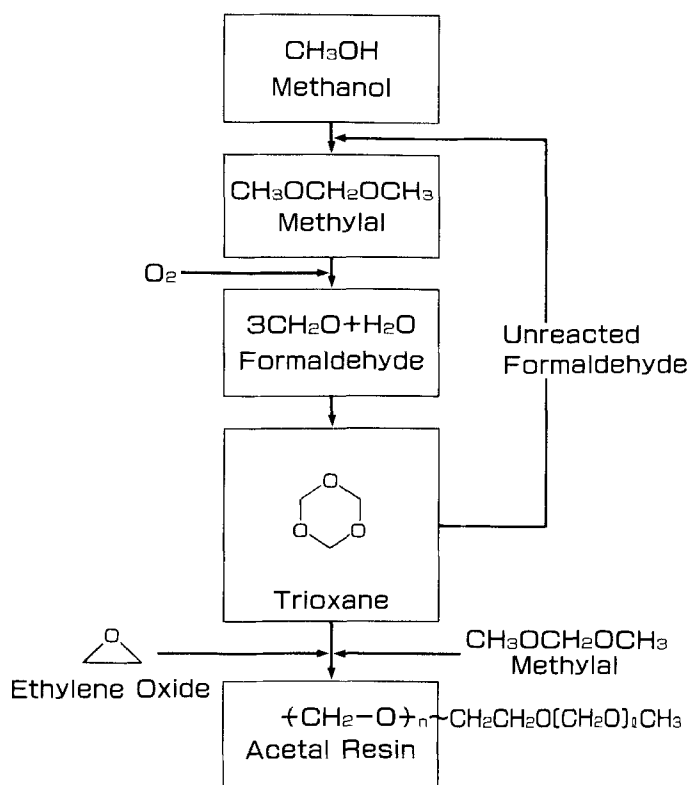
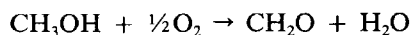


FIG. 2. Asahi Chemical's acetal copolymer process.

the presence of a chain transfer agent. We use methylal as the chain transfer or end capping agent. Thus, we can get the end-capped polymer with a stable methoxyl group.

### 3.1. New Formaldehyde Process [1]

Formaldehyde is conventionally produced by methanol oxidation. In the methanol oxidation, 1 mol  $\text{CH}_2\text{O}$  is formed with 1 mol  $\text{H}_2\text{O}$ , as shown in the following equation.

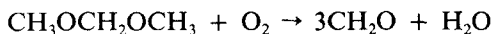


The maximum formaldehyde concentration industrially achievable today is 55%.

This methanol oxidation process is used industrially, but it has two problems.

1. Much energy is required to volatilize the water; half of the formalin is water.
2. Formaldehyde is volatilized with water, and the recovery of volatilized formaldehyde is very complicated.

In the methylal oxidation, only 1 mol water forms for every 3 mol formaldehyde:



Hence, a significantly increased formaldehyde concentration can be attained. Methylal is manufactured from methanol and the dilute aqueous formaldehyde solution which is produced as a by-product in trioxane synthesis.

Merits of the methylal process are as follows:

1. The energy requirement for evaporation of water is low because the water content in formalin is low.
2. Since the formaldehyde concentration is high, the yield of synthesized trioxane is also high.
3. The recovery step for the diluted aqueous formaldehyde solution can be omitted.

### 3.1.1. Methylal Synthesis

It is generally known that methylal can be obtained by heating methanol and aqueous formaldehyde solution in the presence of an acid catalyst such as sulfuric acid, but there is no established technology for the commercial production of methylal.

Our methylal-oxidation formaldehyde process development activities sought to establish a commercially feasible process for methylal synthesis.

From the basic experimental results we developed the industrial methylal synthesis technology.

Methylal is synthesized in a quaternary reaction system involving formaldehyde, methanol, methylal, and water. Productivity was found to be determined by their reaction equilibrium. We therefore adopted a reaction distillation system. There are two main points for this industrial methylal synthesis process.

The first point is the development of a solid acid catalyst. A well-known catalyst like sulfuric acid has the problem of corrosion. We developed a solid acid catalyst with a high selectivity, nearly 100%, and a long-life catalytic activity.

The second point is the development of the reaction distillation system. We achieved nearly 100% conversion of formaldehyde and methanol into methylal. We also devised a technique for breaking the methylal-to-methanol ratio of 93 to 7 in the azeotropic mixture.

As a result of these refinements, 99% pure methylal was obtained from the top of the distillation column, and wastewater was taken out from the bottom.

Thus, we established the world's first technology for the commercial production of methylal.

### 3.1.2. Methylal Oxidation

We found that the use of a conventional methanol oxidation catalyst for methylal oxidation resulted in a short catalyst life.

We then developed the industrial methylal oxidation technology [2]. The main point was development of a catalyst. We developed a catalyst, composed of iron, molybdenum, and a third component which can withstand long-term use for over a year of methylal oxidation. High conversion of over 98%, high selectivity of over 94%, and long continuous operation have been attained.

As a result of our methylal oxidation technology, we increased oxidation capacity over 70% compared to methanol oxidation in the same oxidation reactor.

Asahi Chemical completed the world's first development and commercialization of a new process for manufacturing formaldehyde. This highly concentrated aqueous formaldehyde solution is the feed for the acetal homopolymer and copolymer plants of Asahi Chemical, whose combined capacity is 35,000 T/Y.

### 3.2. Acetal Homopolymer

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. Third, the process yields a high quality product which shows excellent thermal stability.

We will now discuss formaldehyde purification technology and end capping during polymerization in more detail.

#### 3.2.1. Formaldehyde Purification

Conventional formaldehyde purification technology employs the hemiacetal method. We recently invented an extraction distillation process as a new purification technology [3].

It is well known that the vapor-liquid equilibrium of aqueous formaldehyde solution has an azeotropic point as shown in Fig. 3. Therefore, it was believed to be impossible to purify formaldehyde by the distillation method.

Thompson et al. of the Du Pont group [4] and Illicet et al. of Italian chemists [5] studied the physical chemistry of aqueous formaldehyde. Based on their re-

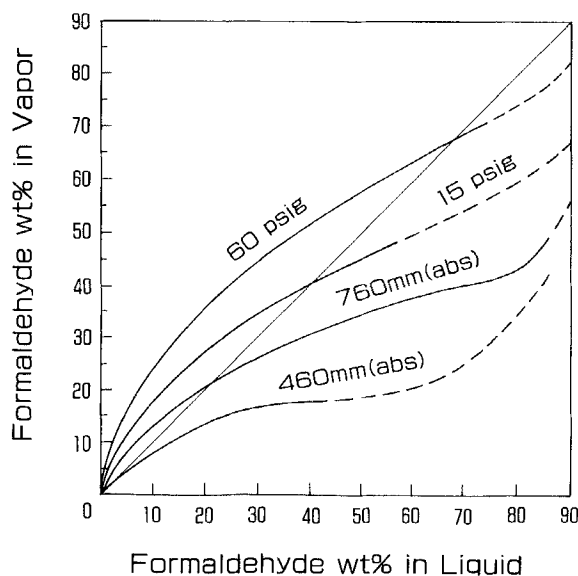


FIG. 3. Vapor-liquid equilibrium of aqueous formaldehyde solution.

search, we investigated the vapor-liquid equilibrium of aqueous formaldehyde, and we concluded that the vapor pressure of formaldehyde is determined by the free formaldehyde concentration (mol/L) and that the vapor pressure of water is decided by the molar ratio of free water. Based on these considerations, we calculated the vapor-liquid equilibrium of formaldehyde and water in the presence of an inert solvent, and we found that there is no azeotropic point in some special conditions. That is, formaldehyde always has a higher volatility than water. This calculation was experimentally confirmed.

Figure 4 shows the vapor-liquid equilibrium of formaldehyde and water in the presence of polyethylene glycol dimethyl ether [PEGDME]. When the weight ratio of PEGDME/Formalin is 20, there is no azeotropic point [3].

According to our calculations, when formalin is diluted by an inert solvent, the ratio of free formaldehyde,  $\text{CH}_2\text{O}$ , to associated formaldehyde,  $\text{HO}(\text{CH}_2\text{O})_n\text{H}$ ,

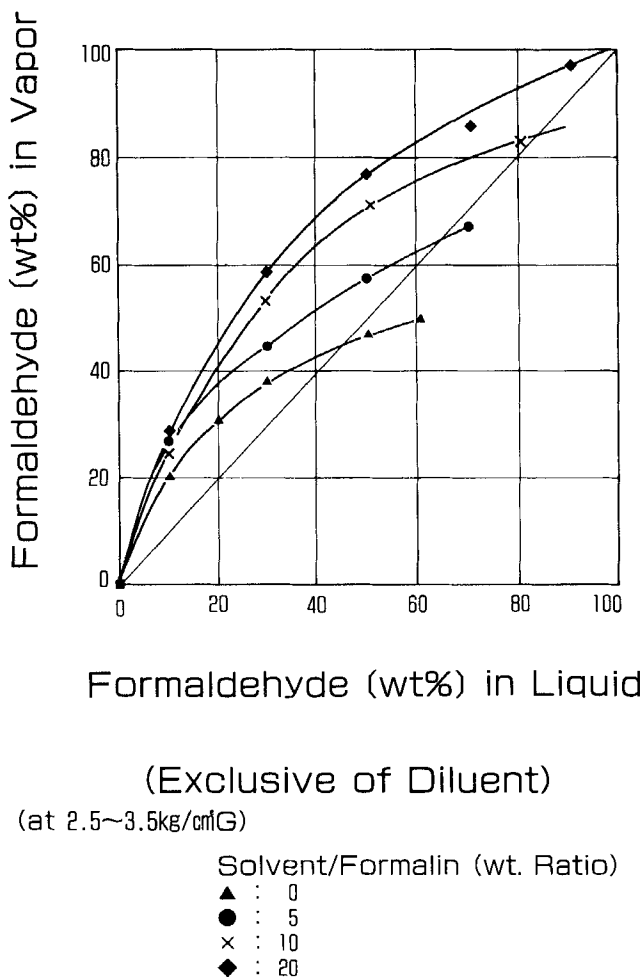


FIG. 4. Vapor-liquid equilibrium of formaldehyde and water in the presence of polyethylene glycol dimethyl ether.



is remarkably increased. From this discovery, we can see that aqueous formaldehyde can be purified by a distillation technique; that is by an extraction distillation technique.

Figure 5 shows the principle of formaldehyde purification by the distillation method [3]. Aqueous formaldehyde is fed to the middle (A) of the tower (1), and polyethylene glycol dimethyl ether, used as the extracting agent, is fed to the top (C) of the tower. Vapor is generated at the bottom of the tower by using a reboiler (2). From the top (B) of the tower, purified formaldehyde gas is obtained, and from the bottom (D), polyethylene glycol dimethyl ether containing dilute aqueous formaldehyde is withdrawn. Polyethylene glycol dimethyl ether and dilute aqueous formaldehyde are separated, and polyethylene glycol dimethyl ether is recycled as the extracting agent.

### 3.2.2. End Capping during Polymerization

Conventionally, formaldehyde contains impurities such as water and, as shown in Fig. 6, when water acts as a chain transfer agent, the polymer end groups are the thermally unstable  $-OH$  groups. In this case the polymer end groups are acetylated by acetic anhydride.

However, about 10% of the polymer is lost during acetylation, and methylene diacetate is formed as a by-product by a side reaction. The Asahi Chemical Process uses highly purified formaldehyde and acetic anhydride as a chain transfer or end capping agent to cap the polymer ends [6]. Thus, polymer loss and by-product formation can be minimized during stabilization.

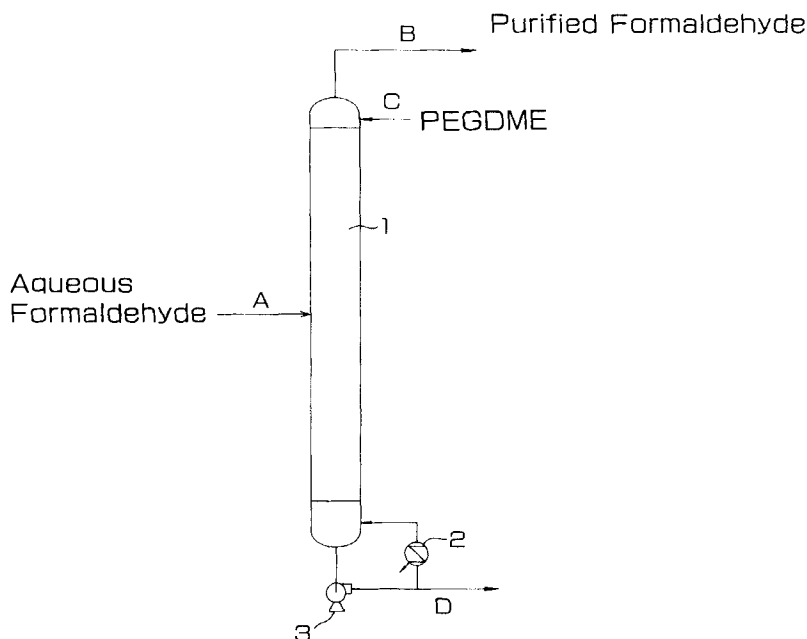
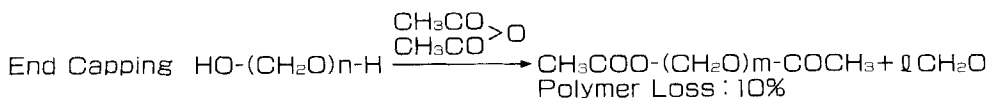
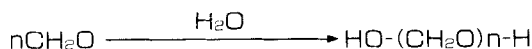


FIG. 5. Principle of purification of formaldehyde by distillation.

**Conventional :** Formaldehyde Contains Impurities



**Asahi Chemical :** End Capping during Polymerization



Polymer Loss, Byproduct → Minimal

FIG. 6. End capping during polymerization (homopolymer).

**3.3. Acetal Copolymer**

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

1. Trioxane synthesis and purification.
2. Polymerization. That is, using highly purified trioxane and end capping during polymerization. Design of the polymerization reactor is one of the features. This design is deduced from the copolymerization mechanism of trioxane and ethylene oxide.
3. High quality product.

**3.3.1. Trioxane**

The reaction from formaldehyde to trioxane is as follows:



The key points of the 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, but we developed a new reaction system employing a noncorrosive solid acid [7]. Thus, we 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 formaldehyde concentration on trioxane formation is shown in Fig. 7. Since the reaction is based on an equilibrium, a high concentration of formaldehyde solution

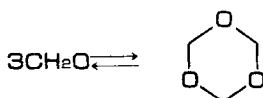
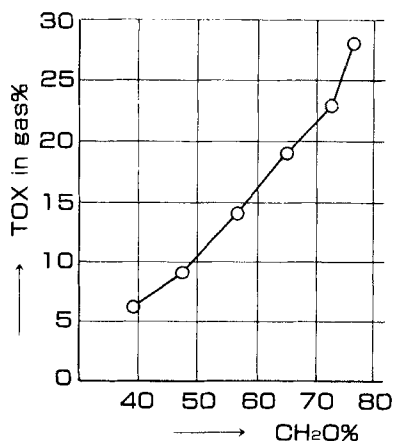


FIG. 7. Effect of formaldehyde concentration on trioxane formation.

favors this reaction. The trioxane thus produced is distilled and extracted by a water-insoluble organic solvent, such as benzene, and fed to the purification section.

We developed a new process to obtain highly purified trioxane by a distillation technique [8]. From this process, purified trioxane containing less than several parts per million impurities, such as water and formic acid, can be obtained. This purified trioxane is fed to the copolymerization section.

### 3.3.2. Copolymerization

In the conventional technique, the polymerization grade trioxane used includes some impurities such as water, methanol, formic acid, etc.

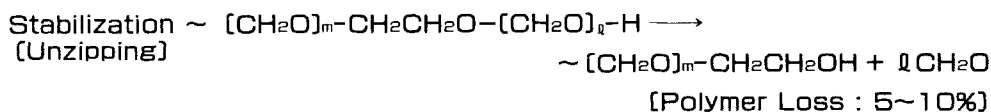
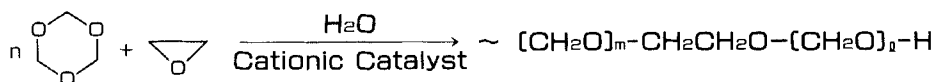
For example, as shown in Fig. 8, when the water acts as a chain transfer agent, the unstable polymer end group  $-(\text{CH}_2\text{O})_n\text{H}$  is generated. This unstable end group is unzipped by the stabilization technique, and a polymer with a stable  $-\text{CH}_2\text{CH}_2\text{OH}$  end group is obtained. In these cases, polymer losses during polymer stabilization are from 5 to 10%.

However, 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. A polymer with both end groups capped with stable methoxyl groups was obtained [9]. Therefore polymer loss during polymer stabilization can be minimized and high quality products can be obtained.

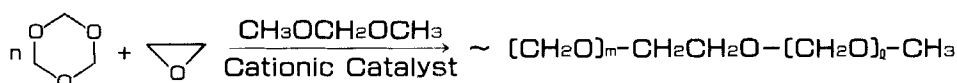
The design of an effective polymerization reactor is the most important factor in the copolymerization section. This design is based on the polymerization mechanism.

We have discovered the initiation mechanism for copolymerization of trioxane and ethylene oxide. The previously held theory concerning the mechanism for the

Conventional : Trioxane Contains Impurities



Asahi Chemical : End Capping during Polymerization



Polymer Loss during Stabilization  $\Rightarrow$  Minimal

FIG. 8. End capping during polymerization (copolymer).

copolymerization of trioxane and ethylene oxide is based on much experimental data. Trioxane is decomposed to form formaldehyde, the formaldehyde then reacts with ethylene oxide to produce dioxolane and trioxepane. These two chemicals then copolymerize with trioxane.

We carefully studied the initiation mechanism during bulk copolymerization of trioxane and ethylene oxide using boron trifluoride dibutyl ether as initiator, and isolated the new intermediates or novel compounds [8,9] 1,3,5,7-tetraoxacyclononane (TOCN) and 1,3,5,7,10-pentaoxacyclododecane (POCD) which disclosed the precise initiation mechanism as shown in Fig. 9. First, ethylene oxide reacts with

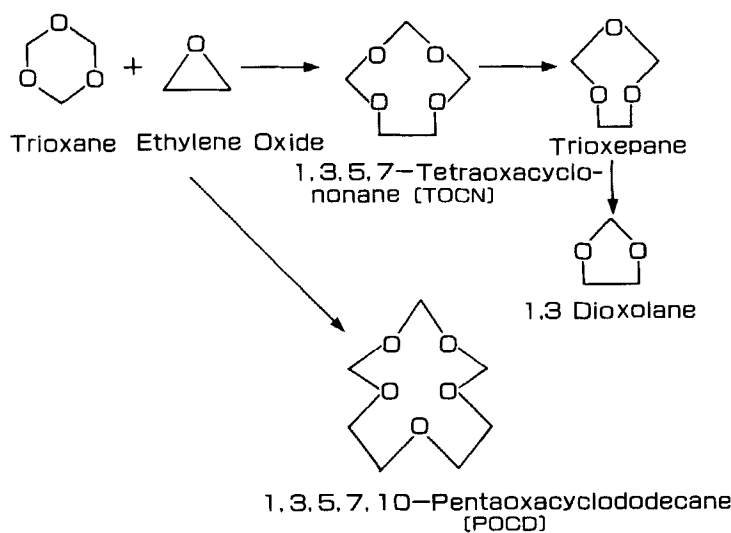


FIG. 9. Initiation mechanism of copolymerization.

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 in Fig. 10. At first, as the ethylene oxide concentration decreased, TOCN and POCD appeared. After the ethylene oxide 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.

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 the 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. Dioxolane is not observed in this time period.

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.

Figure 12 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 a polymer is an interesting subject. A maximum reduced viscosity is observed around a polymer conversion of 50%. It then decreases

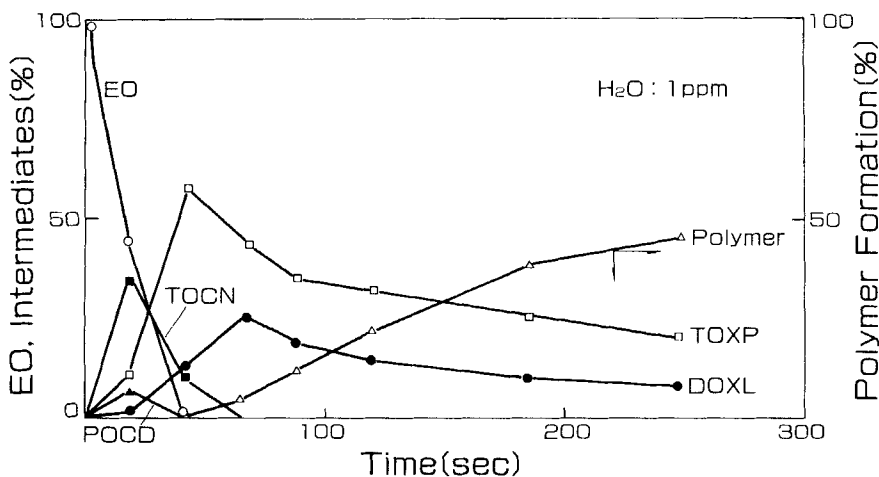


FIG. 10. Concentration profile of reactants and intermediates in TOX/EO copolymerization.

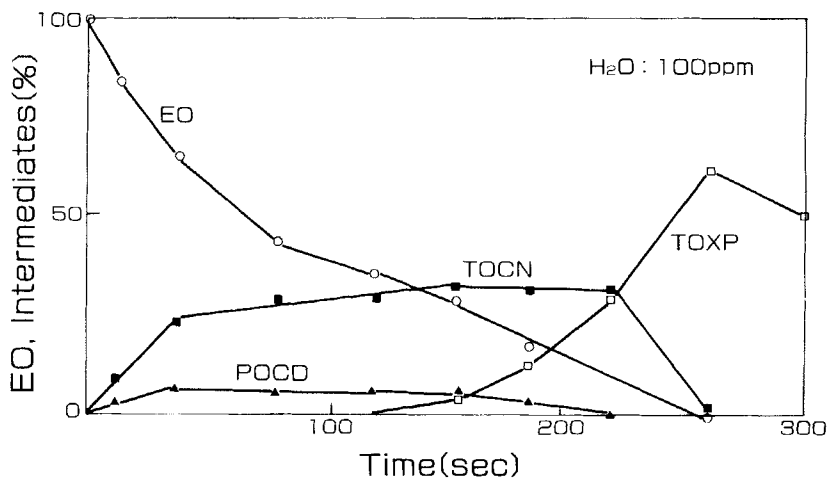


FIG. 11. Concentration profile of reactants and intermediates in TOX/EO copolymerization.

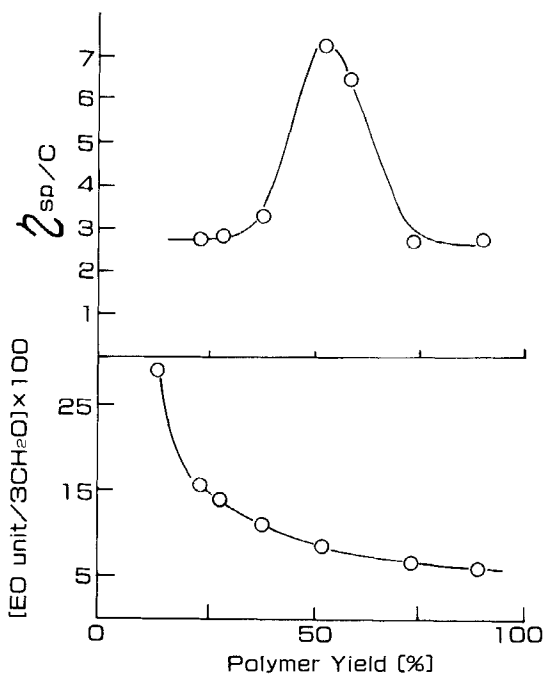


FIG. 12. Transacetalization during polymerization.

to a constant value with polymer conversion. This phenomena 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. Based on these findings concerning the copolymerization mechanism, we 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 they become powdery.

With respect to polymerization behavior, we 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.

### 3.3.3. Catalyst Deactivation and Products

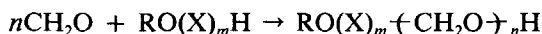
Catalyst deactivation after polymerization was found to be an important factor in obtaining a thermally stable acetal copolymer. We developed a technique for effectively deactivating the polymerization catalyst through the use of an alkaline base as a catalyst neutralizer and optimization of the polymer particle size.

A thermally stable base polymer which has a stability of over 99% is obtained as follows:

1. Use of highly purified trioxane and end capping during polymerization.
2. A polymerization reactor system with a low catalyst concentration.
3. Complete deactivation of the catalyst residue.

### 3.4. Acetal Block Copolymer

Acetal block copolymer is obtained by the polymerization of formaldehyde in the presence of the lubricant functional polymer,  $\text{RO(X)}_m\text{H}$ , which has an active hydrogen atom.



The functional polymer block,  $\text{RO(X)}_m$ , is chemically bonded to the polyoxymethylene block.

Figure 13 shows the lubrication properties of the acetal block copolymer compared with other lubricant grade materials blended with lubricant oil or polytetrafluoroethylene-silicon oil. The acetal block copolymer shows excellent wear properties.

## 4. RESULTS

We have high quality, highly functional products. Several new products are under development. We obtained high quality products by complete end capping during polymerization.

Features of our products are as follows: (1) A high quality base polymer which includes high thermal stability, low deposition on the injection mold, and negligible

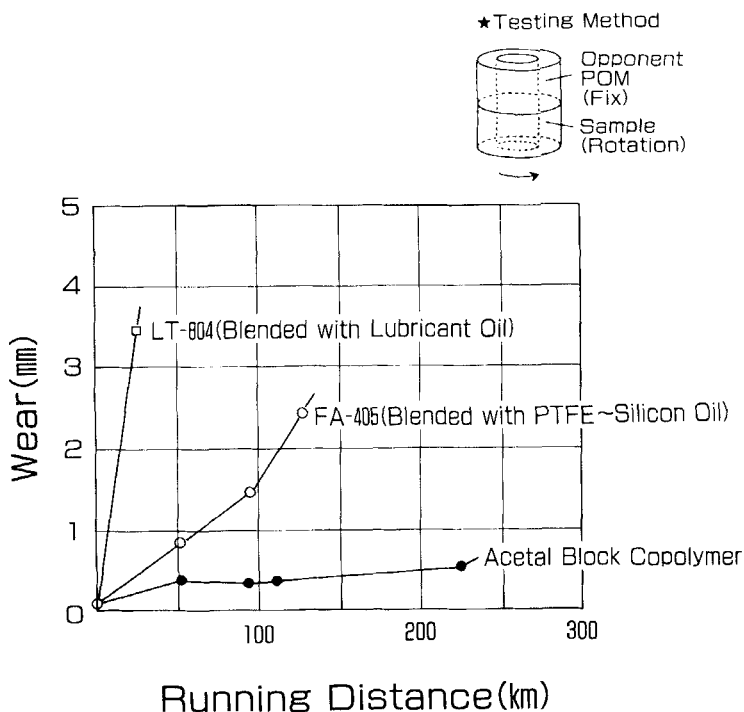


FIG. 13. Comparison of acetal block copolymer with other lubrication-grade materials.

decoloration of the polymer when the polymer remains in the injection machine for a long time. (2) Highly functional products can be obtained because of the excellent thermal stability of our base polymer and its compoundability with fillers.

Several products are now under development; for example, superdraw polyacetal fiber and polyacetal film.

Table 1 shows the technology for the worldwide manufacturing of polyacetal resin. There are 8 technologies from 6 companies for manufacturing polyacetal resin. Only Asahi Chemical has 3 technologies for manufacturing the acetal homopolymer, copolymer, and block copolymer.

TABLE 1. Technology for Worldwide Manufacturing of Polyacetal Resin

Technology	Homopolymer	Copolymer	Block copolymer
Du Pont	○		
Hoechst · Celanese		○	
Asahi Chemical	○	○	○
BASF		○	
Mitsubishi Gas Chemical		○	
Ube Industries		○	



The results of our inventions are summarized as follows:

1. World's first technology for the production of highly concentrated aqueous formaldehyde by methylal oxidation.
2. World's first technology for the production of acetal block copolymer.
3. Process innovation by end capping during polymerization. We can therefore minimize polymer loss during stabilization.
4. A drastic reduction in plant construction costs. For the copolymer case, plant construction costs have been reduced by one-third.
5. Reduction in energy consumption.
6. High quality products.

## 5. CONCLUSIONS

Asahi Chemical has completed development of an advanced process for manufacturing polyacetal resin, a new formaldehyde process, acetal homopolymer, acetal copolymer, and acetal block copolymer.

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