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New Polyacetal Process from Formaldehyde Polymerization in the Presence of a Chain Transfer Agent

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A new polyacetal process from formaldehyde polymerization in the presence of a chain-transfer agent was developed. For the acetal homopolymer, highly purified formaldehyde is polymerized in the presence of acetic anhydride. Thus, an end-capped polymer can be obtained during polymerization. This concept gave us a very simple process for manufacturing the acetal homopolymer, compared to the conventional process. If trifunctional or tetrafunctional alcoholic compounds are used as chain-transfer agents, branched poly(oxymethylene) is obtained; the melt viscosity of this branched poly(oxymethylene) shows a higher pressure dependence than the linear poly(oxymethylene). If a functional polymer is used as the chain-transfer agent, which has an active hydrogen, the acetal block copolymer, which shows characteristic properties, can be obtained.

There are two types of acetal resins. One is the acetal homopolymer; the other is the acetal copolymer. Conventional methods for producing both types of polymers are shown in Fig. 1.

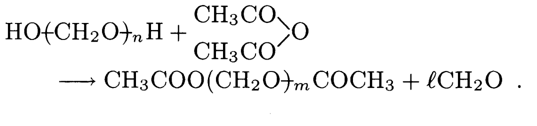
For the homopolymer, purified formaldehyde gas is first produced; formaldehyde is then polymerized into poly(oxymethylene). The unstable $-OH$ end group of the newly obtained acetal homopolymer is end-capped using acetic anhydride into a stable end group of CH_3COO-. For the copolymer, 1,3,5-trioxane is produced from formalin and copolymerized with ethylene oxide. The thermally unstable end group, $-CH_2CH_2O(CH_2O)_{\ell}H$, of the newly obtained copolymer is then unzipped into a stable $-CH_2CH_2OH$ end group.

At present, Du Pont and Asahi Chemical are the only producers of the acetal homopolymer, which is obtained from the polymerization of formaldehyde. Although details concerning the production of the acetal homopolymer have never been made public, the general processing steps can be outlined as monomer purification, polymerization, end-capping and finishing.

Conventionally, formaldehyde contains some impurities, such as water; when water acts as a chain-transfer agent, the polymer end groups are thermally unstable hydroxyl groups:

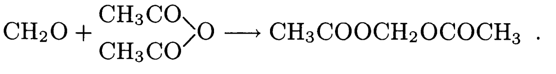
$$nCH_2O \xrightarrow{H_2O} HO(CH_2O)_nH \quad . \tag{1}$$

In this case, the polymer end groups are acetylated by acetic anhydride at elevated temperature from 403—433 K:



$$HO(CH_2O)_nH + \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O \longrightarrow CH_3COO(CH_2O)_mCOCH_3 + \ell CH_2O \quad . \tag{2}$$

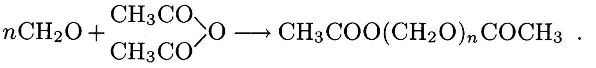
However, about 10% of the polymer is lost during acetylation due to unzipping from the unstable polymer end group, and methylene diacetate is formed as a byproduct from a side reaction:



$$CH_2O + \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O \longrightarrow CH_3COOCH_2OCOCH_3 \quad . \tag{3}$$

Ten percent of the polymer loss leads to a by-product of methylene diacetate, nearly 50% (by weight) of the final product; this is a significant amount of the by-product.

Masamoto of Asahi Chemical[1)] 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 (thus, polymer loss and by-product formation can be minimized during stabilization):



$$nCH_2O + \begin{matrix} CH_3CO \\ CH_3CO \end{matrix}\!\!>\!O \longrightarrow CH_3COO(CH_2O)_nCOCH_3 \quad . \tag{4}$$

We confirmed this not only on the laboratory scale, but also on the commercial plant scale.

This paper mainly concerns a new process for manufacturing the acetal homopolymer. Additionally, we invented new functional polyacetals which are obtained from formaldehyde polymerization in the presence of the chain-transfer agents.

Experimental

The laboratory-scale polymerization apparatus is shown in Fig. 2. Highly purified formaldehyde, in which no water and methanol was detectable by gas chromatography, was fed to a hexane solution using dimethyldioctadecylammonium acetate as the initiator in the presence of the chain-transfer agent. Gaseous formaldehyde was continuously fed to the hexane polymer slurry, which was intensively stirred. A hexane solution containing the initiator and a small amount of a chain-transfer agent was continuously fed to the polymerization reactor, and the polymer slurry was continuously withdrawn; thus, the polymer content in the slurry was adjusted to about 20 wt%. The polymerization temperature was maintained at 323 K using a controlling thermal jacket.

The withdrawn polymer slurry was first filtered and washed with methanol and acetone, and then dried under a nitrogen atmosphere.

As the chain-transfer agent for the acetal homopolymer, acetic anhydride was used, and for the branched poly(oxy-

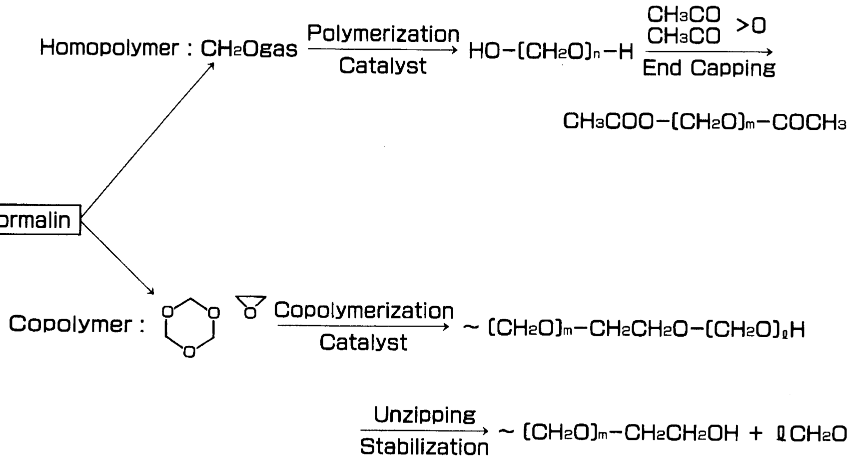


Fig. 1. Conventional method for production of acetal resin.

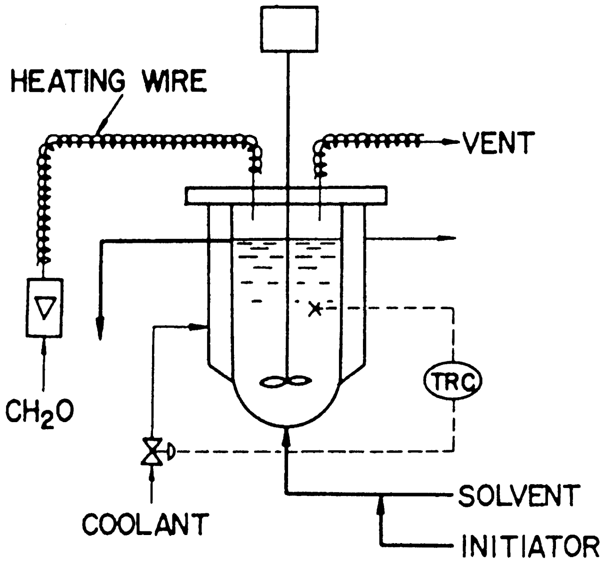


Fig. 2. Polymerization apparatus.

methylene), trifunctional or tetrafunctional alcoholic compounds were used. We used the addition polymerization product of propylene oxide to glycerol, having a number-average molecular weight of 300, as the trifunctional alcoholic compound, and the addition polymerization product of propylene oxide to 3,3′-oxy-bis[1,2-propanediol], having a number-average molecular weight of 1500 as the tetrafunctional alcoholic compound.

For the ethylene propylene rubber (EPR) grafted with poly(oxymethylene), EPR with hydroxyl groups in the main chain was used as the chain-transfer agent. Modified EPR was synthesized as follows. EPR having a number-average molecular weight of 60000 containing 30 wt% propylene was reacted in as extruder at 493 K with 2-hydroxyethyl methacrylate (HEMA) in the presence of peroxide, and then washed with hot methanol.

For the acetal block copolymer, polypropylene glycol monooctadecylether, having a number-average molecular weight of 2000, was used as the chain-transfer agent. An elementary analysis of the acetal block copolymer is given as follows: C: 41.6%, H: 6.9%.

The carbon content of ordinary poly(oxymethylene) was 40%, while the acetal block copolymer showed a slightly higher content of carbon, which is attributed to the block parts.

The proton NMR spectra of the various species of polymer were measured in 1,1,1,3,3,3-hexafluoro-2-propanol-d_2 at 323 K using a JEOL GX-270.

Results and Discussion

1. Acetal Homopolymer. Figure 3 shows the infrared spectrum of the polymer obtained by polymerization of formaldehyde in the presence of a small amount of acetic anhydride as the chain-transfer agent.

Absorption of the acetyl group 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 a qua-

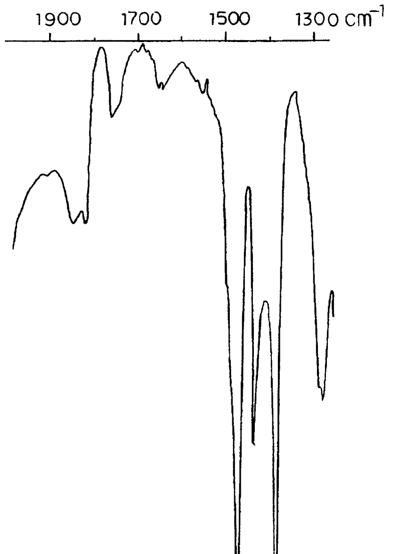


Fig. 3. Infrared spectrum of the polymer. η sp/c : 3.0.

ternary ammonium salt as the initiator can be written as follows:

Initiation

$$\mathrm{CH_3COO^{\ominus\oplus}NR_4 + CH_2O \longrightarrow CH_3COOCH_2O^{\ominus\oplus}NR_4}\ . \tag{5}$$

Propagation

$$\mathrm{CH_3COO(CH_2O)_n{}^{\ominus\oplus}NR_4 + CH_2O \longrightarrow CH_3COO(CH_2O)_{n+1}{}^{\ominus\oplus}NR_4}\ . \tag{6}$$

Chain transfer

$$\mathrm{CH_3COO(CH_2O)_n{}^{\ominus\oplus}NR_4 + \begin{array}{l}\mathrm{CH_3COO}\diagdown\\ \mathrm{CH_3COO}\diagup\end{array}\!O \longrightarrow CH_3COO(CH_2O)_nCOCH_3 + CH_3COO^{\ominus\oplus}NR_4}. \tag{7}$$

Figure 4 shows the effects of acetic anhydride on the reduced viscosity (η sp/c) of the obtained polymer. The reduced viscosity was measured in a *p*-chlorophenol/1,1,2,2-tetrachloroethane mixed solvent at 333 K.

Acetic anhydride was dissolved in the feed hexane solvent in which the acetic anhydride content was varied from 400—1200 ppm.

Nearly 100% of the acetic anhydride in the feed solvent was confirmed to be consumed during the polymerization. In the withdrawn polymer slurry, acetic anhydride could not be detected using gas chromatography.

The acetyl group of the polymer chain end was detected in the infrared spectrum at 1755 cm^{-1}; the main chain oxymethylene unit was also detected in the infrared spectrum at 1470 cm^{-1}.

In Fig. 5, the ratio of extinction of the carbonyl band (EC=O) at 1755 cm^{-1} and a reference band ($\mathrm{ECH_2}$) at 1470 cm^{-1}, which represents the ratio of the acetyl group of the polymer end chain to the polymer main-chain oxymethylene unit, is plotted versus the fed acetic anhydride formaldehyde ratio. A good linear relationship was observed.

Figure 6 shows the proton NMR spectrum of the polymer (η sp/c=1.7). The proton of the acetyl group was found at 2.1 ppm and the proton of the oxymethylene unit was found at 5.0 ppm. In this proton NMR spectrum, the $\mathrm{-OCH_2-}$ unit mole fraction is 99.8% and that of the $\mathrm{CH_3COO-}$ group is 0.2%, which is approximately in good accordance with the ratio of the fed acetic anhydride to formaldehyde.

The obtained polymer thus showed a negligible polymer loss during the following acetylation step, and also showed a negligible generation of the methylene diacetate by-product.

End-capping during polymerization was confirmed not only in laboratory-scale experiments, but also at our acetal homopolymer plant. The loss of the polymer in the following acetylation step is negligible, and the generation of the methylene diacetate by-products is also negligible. Thus, an advanced process for manufacturing the acetal homopolymer has been developed. End-capping during the polymerization of formaldehyde for the acetal homopolymer involves a simple process,

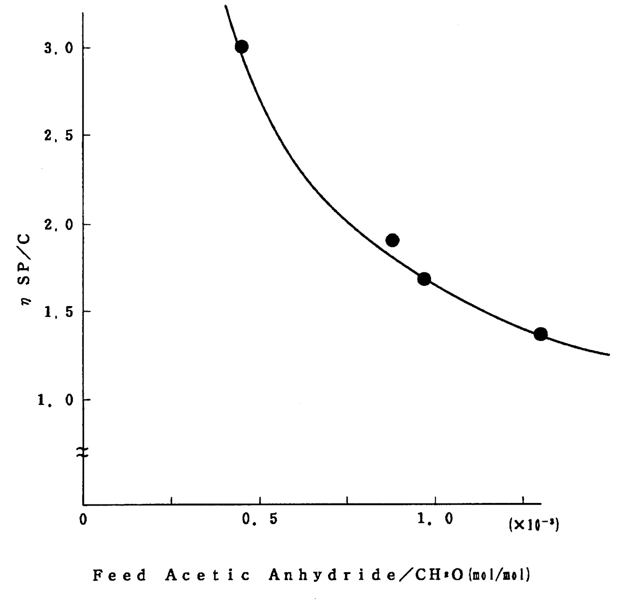


Fig. 4. Effects of feed acetic anhydride on the reduced viscosity of the polymer.

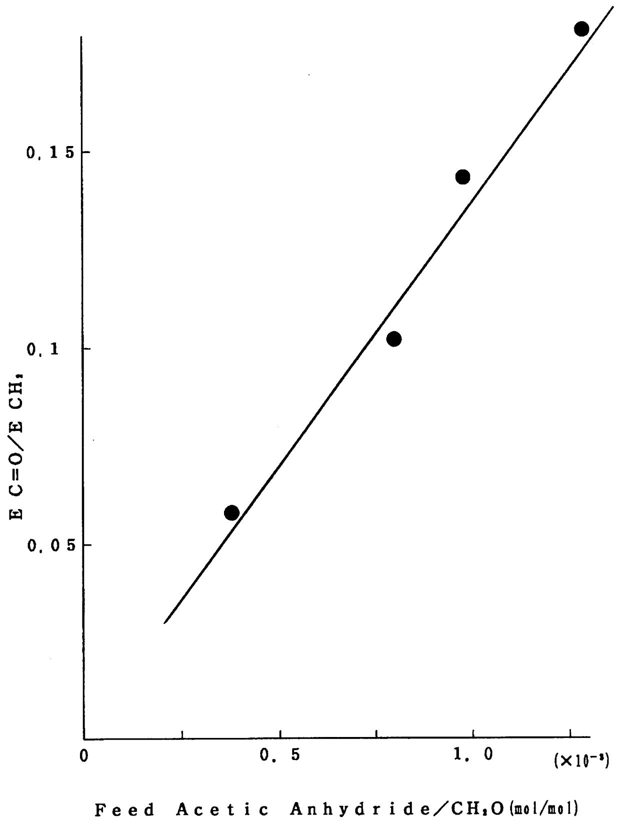


Fig. 5. Relationship between feed acetic anhydride and the ratio of extinction of the carbonyl band (EC=O) and reference band ($\mathrm{ECH_2}$).

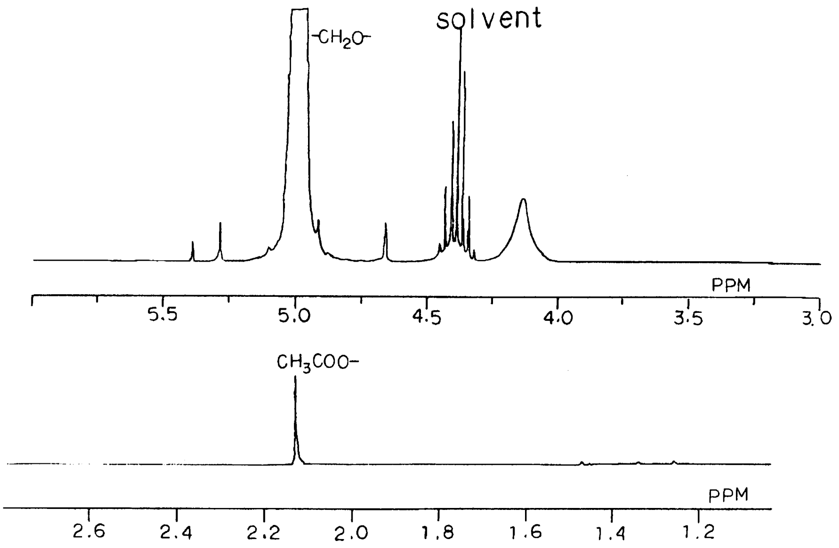


Fig. 6. Proton NMR spectrum of polymer.

and produces high-quality products.

2. Branched Poly(oxymethylene). Polyacetal has many desirable properties—toughness, stiffness, creep resistance, solvent resistance, and impermeability—which were thought to make it a good candidate for use in blow-molded aerosol containers. However, the standard linear poly(oxymethylene) was found to be unsuitable for use in extrusion blow-molding. However, the branched poly(oxymethylene) does have a higher viscosity at lower shear rates than does the linear one, but has a lower viscosity at high shear rates.[2,3] Various branching agents have different effectivenesses, which is tentatively explained by considering the effects of the branch point clusters on the molecular-weight distribution.[4]

We obtained long-branched poly(oxymethylene) by the anionic polymerization of formaldehyde in the presence of trifunctional or tetrafunctional alcoholic compounds as the chain-transfer agents (the end groups of the branched poly(oxymethylene) were acetylated by acetic anhydride):

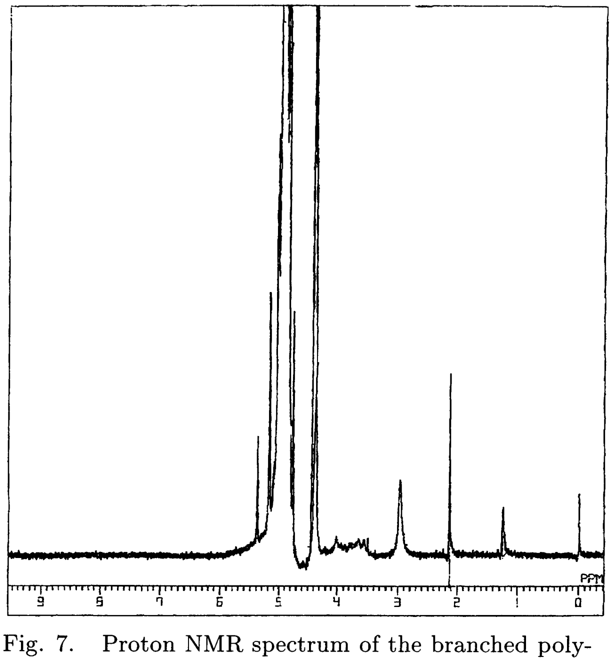


Fig. 7. Proton NMR spectrum of the branched poly(oxymethylene) using trifunctional alcoholic compound as the chain transfer agent.

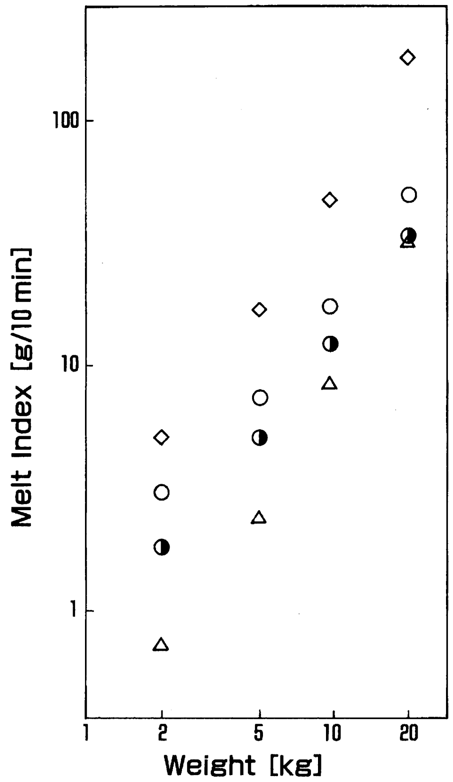


Fig. 8. The relation between melt index and weight at 463 K. ○ Linear polymer, △ Triol chain transferred polymer, ◑ Linear polymer, ◇ Tetrol chain transferred polymer.

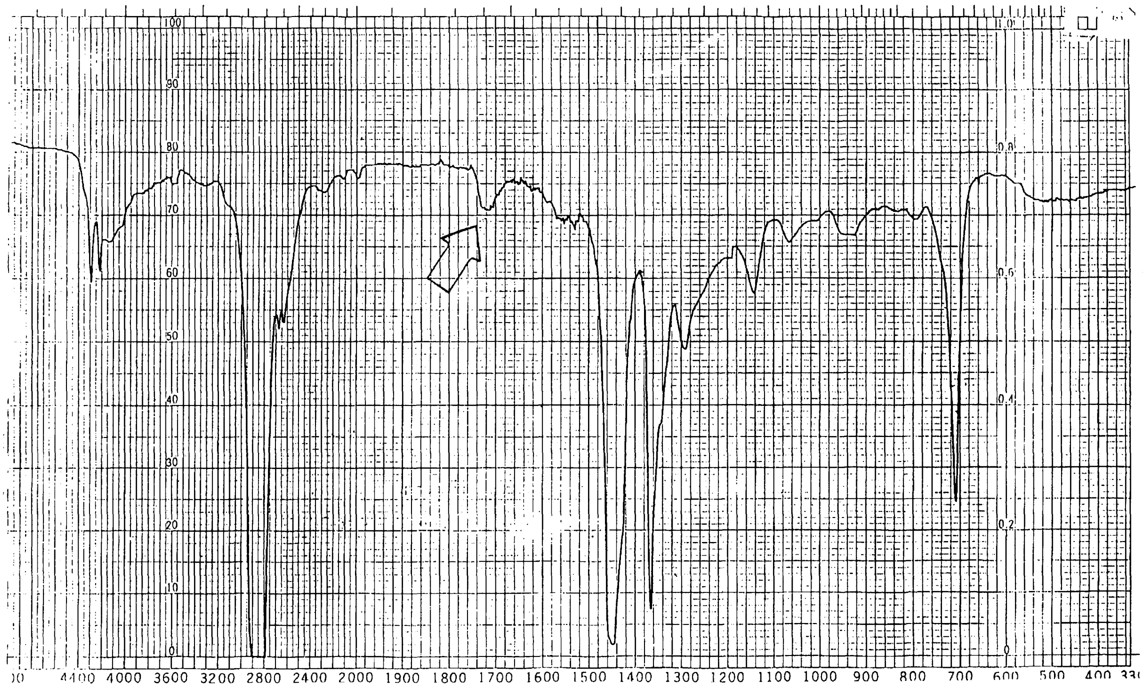
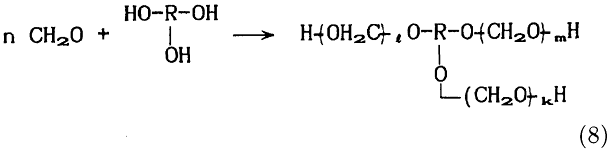


Fig. 9. Infrared spectrum of modified EPR.



$$n\ CH_2O + \underset{OH}{HO{-}\underset{|}{R}{-}OH} \longrightarrow H{(OH_2C)}_{\ell}\,O{-}\underset{O{-}(CH_2O)_kH}{R}{-}O{(CH_2O)}_mH \qquad (8)$$

Figure 7 shows the proton NMR spectrum of the branched poly(oxymethylene) using the addition polymerization product of propoylene oxide to glycerol as the trifunctional alcoholic compound. The proton of CH_3 of the 1-oxy-2-methyl-ethylene unit was clearly found at 1.2 ppm. Vague signals were observed from 3.5—4.0 ppm, which might be assigned to CH_2, CH of the 1-oxy-2-methyl-ethylene unit and the glycerol unit. The proton of the acetyl group of the polymer chain end was observed at 2.1 ppm, and the proton of the oxymethylene unit was found at 5.0 ppm. By acid hydrolysis of the obtained polymer, we confirmed that the added multifunctional alcoholic compounds, as chain-transfer agents, reacted quantitatively with the polymer chain.

We clarified that the melt viscosity of long-branched poly(oxymethylenes) has a higher pressure dependence than does linear poly(oxymethylene), as shown in Fig. 8. These long-branched polymers show that the melt viscosity has a high pressure dependence. Even though these polymers have a high molecular weight (M_n is over 60000) with high tenacity, these polymers show good flow properties under a high shear rate, as well as good injection moldability and blow moldability with high tenacity.

We also observed that ethylene propylene rubber (EPR) grafted with poly(oxymethylene) had improved the toughness.

EPR was reacted with 2-hydroxyethyl methacrylate (HEMA) in the presence of peroxide, and modified. The infrared spectrum of the modified EPR is shown in Fig. 9. The absorbance at 1720 cm^{-1}, which is attributed to the carbonyl group of HEMA, showed that HEMA reacted with EPR.

Formaldehyde was then polymerized in the presence of these modified EPRs used as the chain-transfer agent (Eq. 9).

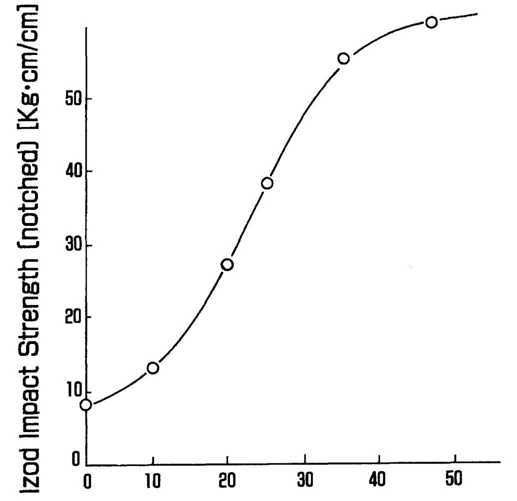


Fig. 10. Notched izod impact strength of poly(oxymethylen) grafted EPR.

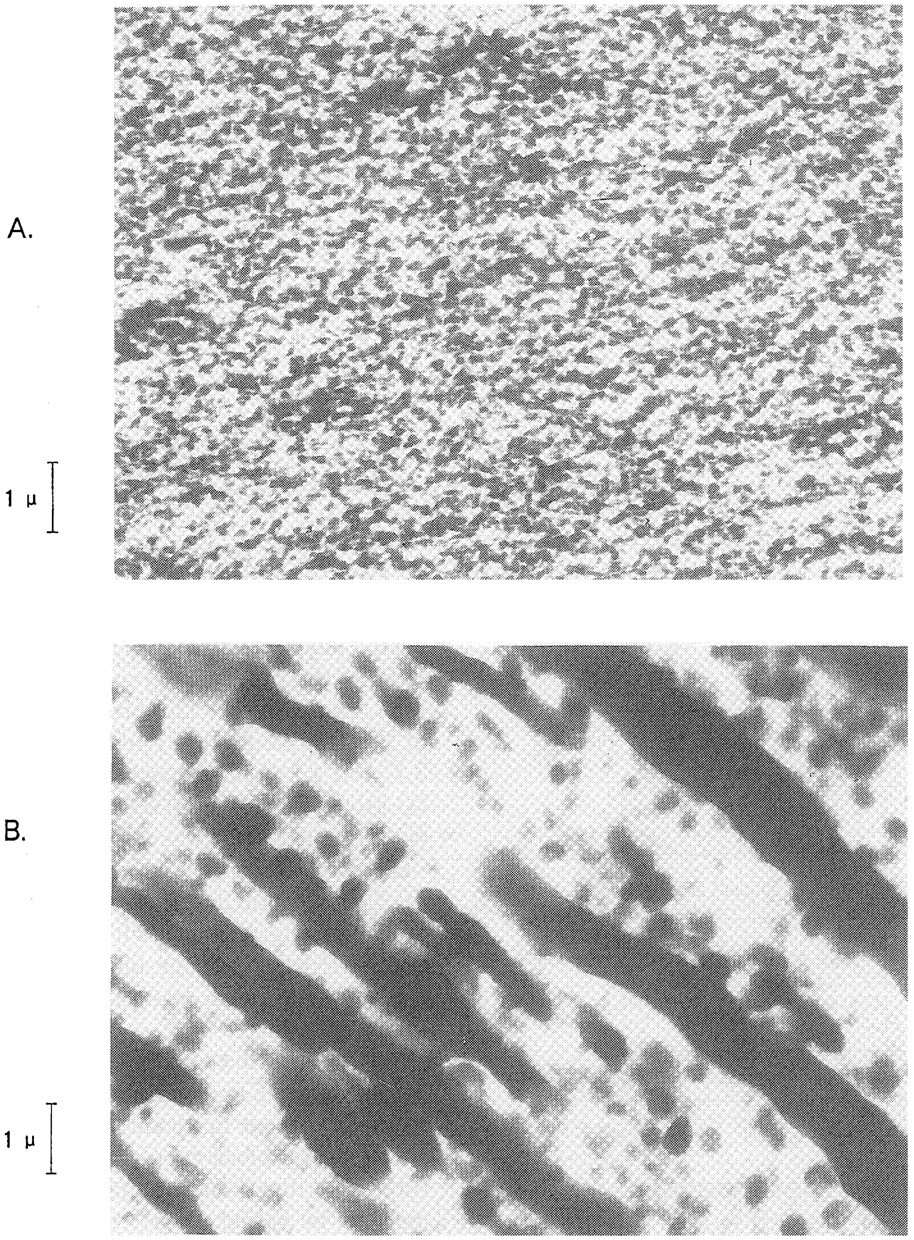
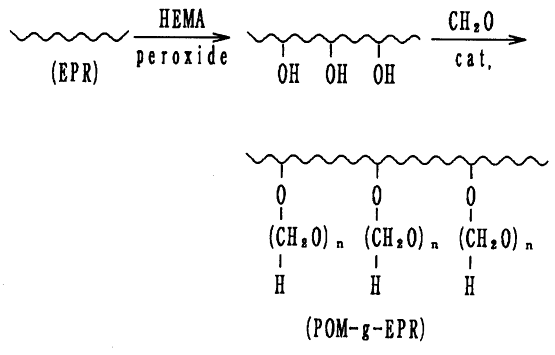


Fig. 11. TEM of material. Material A: poly(oxymethylene) grafted EPR, Material B: EPR blended poly(oxymethylene).



(9)

By acid hydrolysis of the obtained poly(oxymethylene)-grafted EPR, EPR was confirmed to attach to poly(oxymethylene).

These poly(oxymethylene)- grafted EPRs showed about a 5-times higher impact strength (notched Izod impact strength of 38 kg cm/cm) when compared to ordinary poly(oxymethylene), as shown in Fig. 10.

The results of the transmission election microscopy (TEM) of poly(oxymethylene)-grafted EPR are shown in Fig. 11. The particle size of EPR in poly(oxymethylene) grafted EPR (material A) was nearly 0.1 μm, while the particle size of EPR blended in poly(oxymethylene) (material B) was several microns; material B showed no improved toughness.

3. Acetal Block Copolymer. The acetal block copolymer was first commercialized by us in 1987. The acetal block copolymer is obtained by the polymerization of formaldehyde in the presence of a func-

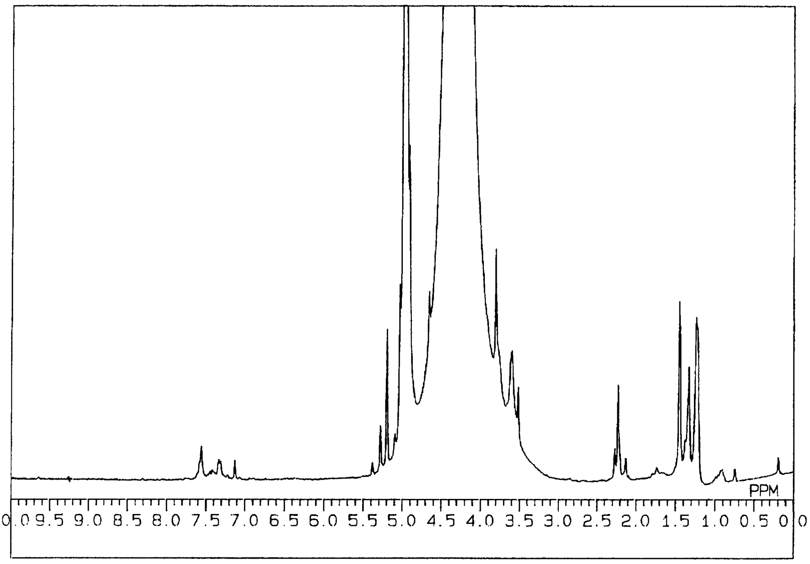


Fig. 12. Proton NMR pattern of acetal block copolymer.

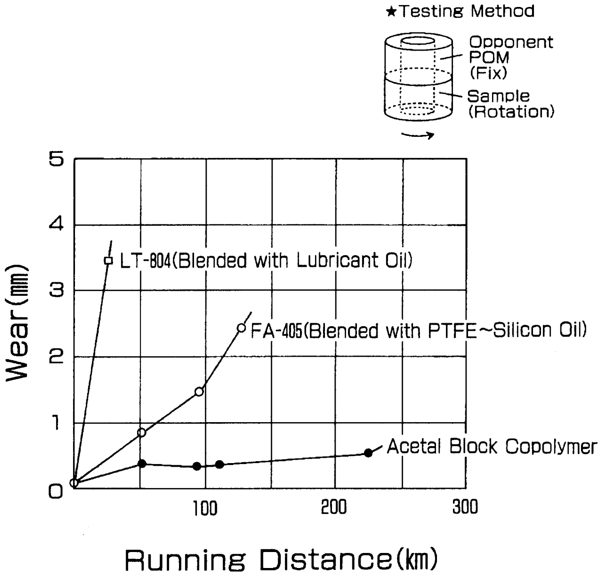


Fig. 13. Comparison of acetal block copolymer with other lubrication grade materials.

tional polymer, $\mathrm{R(X)}_m\mathrm{OH}$, which has an active hydrogen atom:[5)]

$$n\mathrm{CH_2O} + \mathrm{R(X)}_m\mathrm{OH} \longrightarrow \mathrm{R}(\mathrm{X}\!\!-\!\!)_m\mathrm{O}(\mathrm{CH_2O}\!\!-\!\!)_n\mathrm{H}\ . \tag{10}$$

Here, R is an octadecyl group, and X is an 1-oxy-2-methyl-ehylene group.

In this case, $\mathrm{R(X)}_m\mathrm{OH}$ is a lubricant functional polymer. This functional polymer block, $\mathrm{R(X)}_m\mathrm{O}$, is chemically bonded to the poly(oxymethylene) block. The hydroxyl end group of the acetal block copolymer was acetylated by acetic anhydride.

Figure 12 shows the proton NMR spectrum of the acetal block copolymer. The proton of the $\mathrm{CH_2}$ and $\mathrm{CH_3}$ of the octadecyl group was found at 1.2 and 0.9 ppm, respectively. The protons of $\mathrm{CH_2}$, CH, and $\mathrm{CH_3}$ of the 1-oxy-2-methyl ethylene unit were found at 3.6, 3.7, and 1.2 ppm, respectively. The proton of the acetyl group was found at 2.1 ppm, and the proton of the oxymethylene unit was found at 5.0 ppm.

Figure 13 shows the lubrication properties of the acetal block copolymer compared with other lubricant-grade materials blended with lubricant oil or poly(tetrafluoroethylene)–silicone oil. Wear of the acetal block copolymer is much less than that of other lubricant-grade materials.

At present, this acetal block copolymer is used for office automation and audio-video equipment parts, which require excellent lubricant properties.

The acetal block copolymer has a very promising future. The functional group of the acetal block copolymer can be varied. Thus, various types of acetal block copolymers can be synthesized.

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