Ultrahigh Molecular Weight Polyoxymethylene from Aqueous Formaldehyde Solution

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Ultrahigh molecular weight polyoxymethylene with a weight average molecular weight over 1000000 was obtained from an aqueous formaldehyde solution. The molecular weight of this polymer is much higher than the reported highest molecular weight value of 46000 obtained by the condensation polymerization of formaldehyde in aqueous solution.

The acetal homopolymer can be obtained by the homopolymerization of gaseous formaldehyde. In this case, for the polymerization of gaseous formaldehyde, the anionic or organometallic polymerization of formaldehyde is available, and purified formaldehyde is necessary for the production of the high molecular weight polymer.[1] As formaldehyde and water form an azeotropic mixture, thus purification of the formaldehyde by distillation was reported to be impossible.[2] For the purification of formaldehyde, only a very complicated method, such as the hemiformal method, was used for the commercial production of purified formaldehyde.[3] Obtaining a high molecular weight polyoxymethylene directly from aqueous formaldehyde solution without using purified gaseous formaldehyde is desired.

The synthesis of a high molecular weight polymer was attempted only from aqueous formaldehyde just below its equilibrium temperature between the liquid phase and solid polymer phase.[4] Reports about the polymerization of formaldehyde in aqueous solution are quite limited. Brown et al.[5] of the Du Pont group reported the polymerization of formaldehyde in aqueous solution and methanolic solution just below its equilibrium temperature. The maximum molecular weight of polyoxymethylene obtained by the condensation polymerization of formaldehyde in aqueous solution or methanolic solution was 46000.

The acetal homopolymer is produced by the polymerization of gaseous formaldehyde by a chain reaction, while the acetal copolymer is produced by the copolymerization of trioxane with ethylene oxide by a ring-opening polymerization. Trioxane is produced by the trimerization of aqueous formaldehyde. Recently, we observed a curious phenomenon such that the heat transfer coefficient of the condenser in the distillation tower in the trioxane production section gradually decreased with time during a 6-month operation. We found a polymeric film consisting of an ultrahigh molecular weight polyoxymethylene[6] on the surface of the inner tube of the condenser. We observed this phenomenon several times during our plant operation.

For the production of trioxane, 70 wt% aqueous formaldehyde produced by methylal oxidation[7] was supplied as a raw material. The 70 wt% aqueous formaldehyde was contacted with solid acid (solid acid: sulfonated crosslinked polystyrene beads; solid acid/feed formalin: 0.5 L • h/kg) in a fixed bed to form a formaldehyde - trioxane equilibrium mixture.

At the bottom of the distillation tower, 70 wt% aqueous formaldehyde was contacted with the solid acid to form a formaldehyde - trioxane equilibrium mixture. The mixtures consisting of water, formaldehyde, methanol and trioxane were distilled to the top of the distillation tower, and the vapors consisting of water, formaldehyde, methanol and trioxane were condensed in the condenser made of a stainless tube. Benzene was fed to the top of the condenser in the liquid state to contact the vapors. The stainless tube in the condenser was cooled with 45 °C hot water from the outside of the tube, and the temperature of the condensate from the distillate was controlled at 60 °C. The condensate flowed down from the top of the condenser to the bottom along the inner side of the tube. The benzene phase, which extracts the trioxane, was fed to the trioxane purification section. The water phase, which contained unreacted formaldehyde and methanol (weight ratio of water, formaldehyde and methanol; 55.6: 38.0: 6.4) was fed to the distillation tower again. After a 6-month plant operation, a polymeric film was observed on the inner wall surface of the tube in the condenser.

For characterization of the polymeric film, a 270 MHz ^{1}H-NMR measurement was done using a JEOL GX-270 FT-NMR at 55 °C. 1,1,1,3,3,3-Hexafluoroisopropanol-d_2 was used as the solvent. The reduced viscosity of the polymer was measured using a 1,1,2,2-tetrachloroethane-*p*-chlorophenol mixed solvent (1/1 weight ratio) at 60 °C. The gel permeation chromatography (GPC) measurement was done at 35 °C using an HLC-8120 GPC made by Showa Denko. It was calibrated using standard polymethyl methacrylate, and 1,1,1,3,3,3-hexafluoroisopropanol was used as the solvent. Scanning electron microscope (SEM) measurements were done using a Hitachi S-2400.

After a 6-month plant operation, a thin polymeric film was found all over the inner wall surface of the stainless tube of the condenser. The ^{1}H-NMR spectrum of this sample showed only one strong signal at 5.00 ppm, which was assigned to the oxymethylene proton. The reduced viscosity of this sample was 12.8, which was much higher than the highest molecular weight commercially available acetal homopolymer, Tenac 3010, whose reduced viscosity was 3.0.

Figure 1 shows the GPC curve of the polymer together with Tenac 3010, which was obtained by the chain reaction of formaldehyde and the highest molecular weight commercial polymer. The thin film polymer has Mn = 408000 and Mw = 1600000, while Tenac 3010 has Mn = 103000 and Mw = 241000. As far as the authors know, Mn = 408000 is the highest Mn for the polyacetal resin ever reported as a reliable value.

Figure 2 shows an SEM of the thin film. A highly fibrous structure was observed, which is thought to be a lammelae crystal and may come from the high molecular weight macromolecular chain.

We first thought that no polymerization should occur on the inside of the tube, because the temperature of the

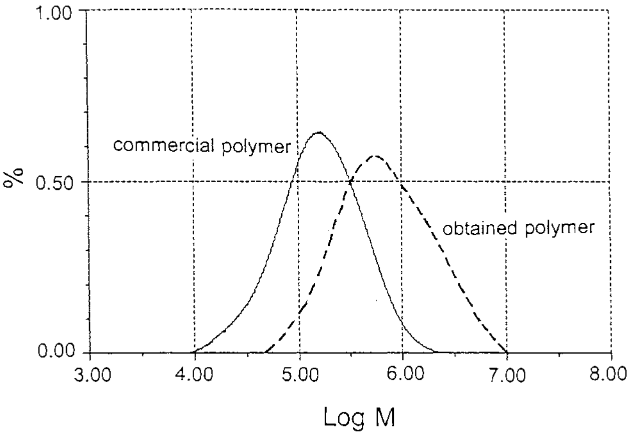

Figure 1. GPC comparison of the obtained polymer with the commercial acetal resin.

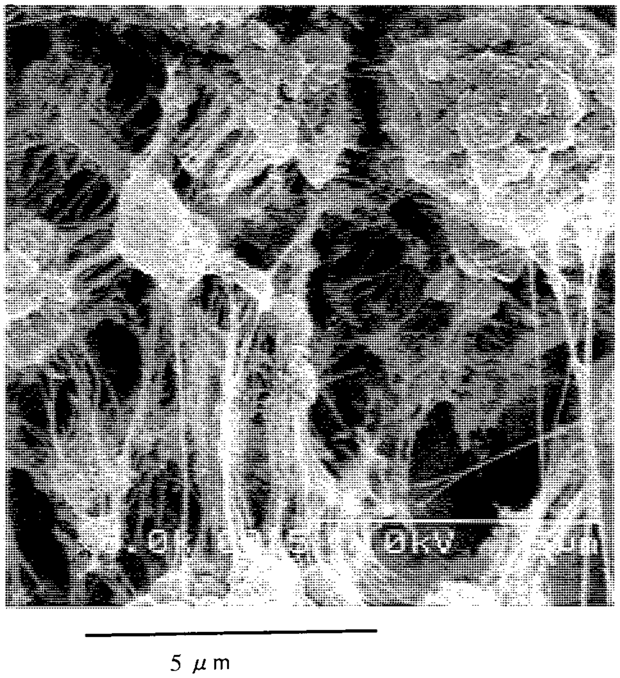

Figure 2. SEM of the obtained polymer.

condensate was higher than the equilibrium temperature of the aqueous formaldehyde solution. The equilibrium temperature of the aqueous formaldehyde solution (weight ratio of water, formaldehyde and methanol; 55.6: 38.0: 6.4) is supposed to be around 50 °C, based on the data that the equilibrium point of 38 wt% aqueous formaldehyde with no methanol is 65 °C,[8] and the addition of methanol decreases the temperature by 14 °C/6 wt%-methanol.[2]

Though the average temperature of the condensate was 60 °C, which is above the equilibrium temperature, the surface temperature of inside of the tube was thought to be equal to the temperature of the cooling water, which was 45 °C, thus lower than the equilibrium temperature. Therefore, if some kind of polymerization happened to occur on the inner surface of the tube wall, a long residence time might be possible between the wall surface and the polymer surface. This might be the starting point for the polymerization, thus, polymerization at the wall surface could be possible.

It is already known that there exists a reaction equilibrium between soluble polyoxymethylene glycol and monomeric liquid formaldehyde.[8] It is also known that there exists an equilibrium temperature between aqueous formaldehyde solution and solid polyoxymethylene, and below this equilibrium temperature, polyoxymethylene glycol with a polymerization degree over 5 could precipitate, which allows the nucleation of the polymerization.[8] Monomeric liquid formaldehyde may add to the active hydroxy end-group of the solid polyoxymethylene, and thus the molecular weight of the solid polyoxymethylene was thought to increase. The degree of polymerization may be given by the ratio of [addition of monomeric formaldehyde (mol/h)] to [nucleation (mol/h)].

In our polymerization system, on the surface of the stainless steel tube, the polymerization temperature was thought to be just below the equilibrium temperature, thus, the nucleation speed was very low. Though the addition of monomeric formaldehyde to the active site was slow, the ratio of the addition of monomeric formaldehyde to nucleation was very large, thus, the active site could not be buried and was always alive. These long active site lives produced the ultrahigh molecular weight polyoxymethylene with a weight average molecular weight over 1000000, which was much higher than the reported value of 46000 by Brown,[4] over the entire inner wall surface of the stainless tube during the 6-month operation.

We observed this formation phenomenon for a thin polymeric film and ultrahigh molecular weight polymer during every 6-month plant cycle.

References and Notes

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