Complete End-Capping during the Copolymerization of Trioxane and Ethylene Oxide

Hajime Nagahara, Katsuhiko Hamanaka, Kohichi Yoshida, Kenji Kagawa, Toshiyuki lwaisako, and Junzo Masamoto *#
Technical Research Laboratory, Asahi Chemical Industry Co., Ltd., Samejima, Fuji 416-8501

(Received September 8, 1999; CL-990772)

Complete end-capping during the copolymerization of trioxane and ethylene oxide in the bulk polymerization state using boron trifluoride dibutyl ether as the initiator and methylal as the chain transfer agent was accomplished. By using highly purified trioxane as the starting material and by completely deactivating the catalyst residue, an almost completely end-capped polymer (degree of stability was over 99.5%) was obtained.

Acetal resin is a term used to describe high molecular weight polymers and the copolymers of formaldehyde. First commercialized as a homopolymer in 1960 by Du Pont, acetal resins are engineering thermoplastics which have found broad use in traditional metal applications.[1]

Shortly thereafter, Celanese researchers developed an acetal resin based on the copolymerization of trioxane and cyclic ethers, such as ethylene oxide.[2]

In 1972, Asahi Chemical started to produce the acetal homopolymer utilizing the world's third type of polyacetal technology.[3] Asahi Chemical also industrialized the acetal copolymer in 1985.

At present, the annual demand of polyacetal resin in the world is about 400000 ton. One of the biggest problems for polyacetals is end-stabilizing.

It is well-known that polymerized polyacetals have an unstable end-group. In the acetal copolymer, the polymerized polymer has a thermally unstable fraction, $-CH_2CH_2O-(CH_2O)_nH$ of nearly 10 wt%,[4] and this thermally unstable fraction $-(CH_2O)_nH$ was unzipped to stable oxyethylene unit, $-CH_2CH_2OH$, following the stabilizing section by the melt hydrolysis process. This end-group stabilizing process is the prevalent common knowledge for acetal copolymer in polymer chemistry and the chemical industry.[5]

Here we tried to obtain the polymer polymerized for the acetal copolymer with no substantial unstable fraction. We then tried the complete end-capping during the copolymerization of trioxane and ethylene oxide using methylal as the chain transfer agent or end-capping agent.

Trioxane was purified by distillation according to the method described in our patents,[6] and the water content in the purified trioxane was below 1 ppm. Commercially available ethylene oxide was used without further purification. Methylal was purified by immersion in 4A zeolite for the elimination of trace water and methanol. $BF_3·OBu_2$ was distilled under reduced pressure and then was diluted 50 times with cyclohexane.

Polymerization was done in the bulk state. For the polymerization on a small scale, we used a 100-mL glass ampoule. We sometimes used a 2-L table kneader. We also sometimes used a 5-inch kneader for the continuous polymerization experiment.

Into molten trioxane, methylal was mixed and gaseous ethylene was absorbed, and into this mixture the cyclohexane solution of $BF_3·OBu_2$ was injected.

For the case ampoule polymerization, the obtained polymer was pulverized in a mortar and immersed in hexane with tributyl amine. For the table kneader polymerization, the obtained polymers were immersed in water containing 1 wt% triethyl amine. For the 5-inch kneader polymerization, the polymerized polymer was crushed, and deactivated in 1 wt% aqueous triethylamine for 120 min. After the deactivation of the catalyst residue, the polymer was vacuum dried or dried in a nitrogen atmosphere.

The degree of stability of the as-polymerized polymer was calculated based on the polymer residue (wt%) at 222 °C after 50 min of heating in a vacuum. The ^1H-NMR spectrum of the polymer was measured using a 500 MHz NMR spectrometer (Bruker ARX-500). The polymer was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol-d_2 and measured at 50 °C.

First, the effect of the methylal feed on the reduced viscosity was investigated (Methylal feed was changed from 1.0×10^{-3} mol/mol-trioxane to 4.5×10^{-3} mol/mol-trioxane.). With the increase in methylal feed, the reduced viscosity of the polymer decreased (Reduced viscosity was changed from 2.8 to 1.1.). It was obvious that methylal acted as the chain transfer agent. The typical ^1H-NMR spectrum of the polymer obtained by the copolymerization of trioxane with ethylene oxide in the presence of methylal is shown in Figure 1. The clear signal of the methoxy end group at 3.50 ppm, which came from the chain transfer reaction of methylal, was observed. The ratio of the methoxy signal (3.50 ppm) to the oxymethylene signal (5.00

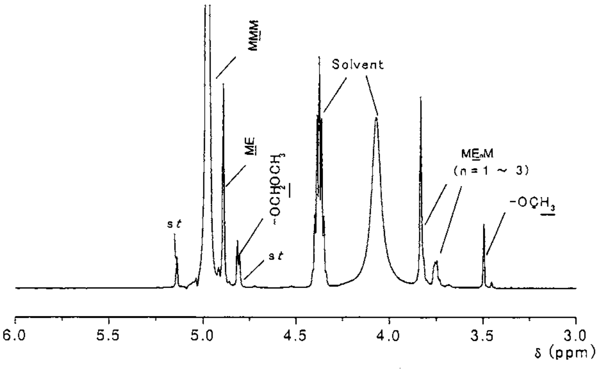

Figure 1. Typical ^1H-NMR spectrum of the copolymer from trioxane and ethylene oxide obtained using methylal as the chain transfer agent. Ethylene oxide concentration: 4.5 mol% of trioxane, methylal: 3×10^{-3} mol/mol-trioxane, $BF_3 \cdot OBu_2$: 0.7×10^{-4} mol/mol-trioxane, polymerization temperature: 70 °C.
Fairly good agreement was observed between the methoxy group found (2.5×10^{-3} mol/$-OCH_2$ unit) and methoxy group calculated (2.3×10^{-3} mol/$-OCH_2$ unit). M denotes oxymethylene, and E denotes oxyethylene.

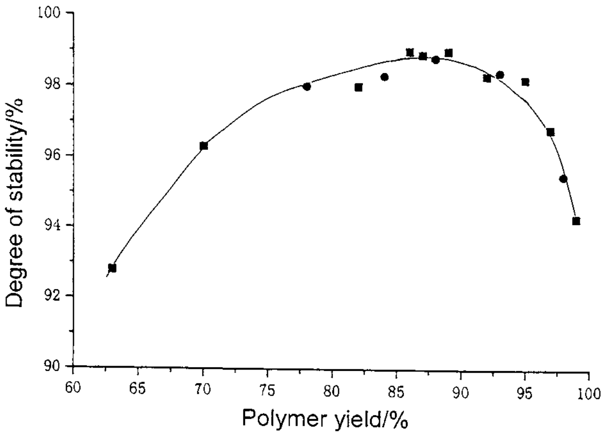

Figure 2. Effect of the polymer yield on the degree of stability of polymer. The degree of polymer stability is defined as "polymer residue (wt%) at 222 °C after 50 min of heating in a vacuum". ■:polymerization in glass ampoule, ●:polymerization in 2 L table kneader. Ethylene oxide concentration: 4.5 mol% of trioxane, methylal: 1.0 - 4.5 x 10^{-3} mol/mol-trioxane, $BF_3 \cdot OBu_2$: 0.7 - 1.4 x 10^{-4} mol/mol-trioxane, polymerization temperature: 70 °C.

ppm) showed that almost all of the methylal fed to the polymerization system became attached to the polymer end-group. Fairly good agreement was observed between the methoxy group found (2.5 x 10^{-3} mol/-OCH_2 unit) and methoxy group calculated (2.3 x 10^{-3} mol/-OCH_2 unit). Thus, both end-groups of the polymer were capped by the methoxy group. However, by using high purity trioxane, the maximum degree of stability was limited to around 99.0%. However, the value of 99.0% was indeed a high value, considering the 10 wt% unstable fraction data reported by Burg et al.[5] of the Hoechst group.

In Figure 2, the effect of polymer yield on the degree of polymer stability was plotted. At first, the degree of stability increased with the increase in the polymer yield, then the degree of stability showed a maximum value at the polymer yield from 85 to 92%, and then gradually decreased with increasing polymer yield.

In the case of low polymer yield, an insufficient acetal exchange reaction might be postulated, assuming that the comonomer distribution might not be random, thus the degree of polymer stability might be low. However, the increase in the polymer yield that decreased the degree of stability was thought to be very unusual.

We then assumed that deactivation of the catalyst might be insufficient. In the case of the high polymerization yield, permeation of the base to acid catalyst residue might be difficult, thus, some of the catalyst residue might be activated and decomposed the polymer.

To clarify this point more clearly, we tried to complete the deactivation of the catalyst residue. Figure 3 shows the effect of the polymer particle size on the degree of polymer stability. With the decrease in the polymer particle size, the degree of stability increased to the extent of over 99.5%.

Thus the deactivation of the catalyst residue was the main factor for obtaining the high degree of stability if the monomeric trioxane was highly purified. The completely deactivated polymer showed a thermally unstable fraction below 0.5%.

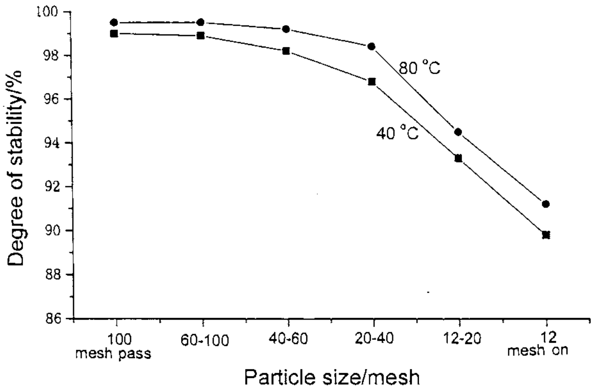

Figure 3. Effect of the particle size on the degree of stability of the polymer. The degree of polymer stability is defined as "polymer residue (wt%) at 222 °C after 50 min of heating in a vacuum". ■: deactivated at 40 °C, ●: deactivated at 80 °C. Ethylene oxide concentration: 4.5 mol% of trioxane, methylal: 3 x 10^{-3} mol/mol-trioxane, $BF_3 \cdot OBu_2$: 0.7 x 10^{-4} mol/mol-trioxane, polymerization temperature: 70 °C. Initial polymer was obtained during continuous polymerization using 5 inch kneader. 100 mesh: 148 μm, 60 mesh: 250 μm, 40 mesh: 420 μm, 20 mesh: 840 μm, 12 mesh: 1400 μm.

This value might be remarkable, considering the fact that the conventional polymerized acetal copolymer usually contained nearly 10 wt% of the thermally unstable fraction.

As a conclusion, complete end-capping during the copolymerization of trioxane in the presence of methylal was accomplished by using highly purified trioxane and complete deactivation of the catalyst residue. Complete end-capping during the polymerization will change the common knowledge about the acetal copolymer (trioxane-ethylene oxide copolymer) currently written in textbooks.

References and Notes

Present Address: Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

1 a) C. E. Schweitzer, R. N. MacDonald, and J. O. Punderson, *J. Appl. Polym. Sci.*, **1**, 158 (1959). b) T. A. Koch and P. E. Lindvig, *J. Appl. Polym. Sci.*, **1**, 164 (1959).

2 a) C. Walling, F. Brown, and K. Bartz, U.S. Patetnt 3027352 (1962), assigned to Celanese.

3 a) Y. Kobayashi, I. Suzuki, and S. Ishida, *Hydrocarbon Process.*, **51(11)**, 111 (1972). b) K. Matsuzaki and J. Masamoto, *Ind. Eng. Chem. Res.*, **37**, 1729 (1998).

4 K. Burg, H. Schlaf, and H. Cherdon, *Makromol. Chem.*, **145**, 247 (1971).

5 a) G. Sextro, in "Ulmann's Encyclopedia of Industrial Chemistry," VCH Publishers, Inc., (1992), Vol. A21, p 591. b) J.-P. Vairon and N. Spassky, in "Cationic Polymerization," ed by K. Matyjaszewski, Marcel Dekker, Inc., New York (1996), p. 683.

6 a) K. Hamanaka, T. Iwaisako, J. Masamoto, and K. Yoshida, U.S. Patent 4332644 (1982), assigned to Asahi Chemical. b) J. Masamoto, WO 98-13362, assigned to Asahi Chemical.