

Effect of Perchloric Acid on the Molecular Weight and Yield of Poly-THF

KAZUO MATSUDA, YOSHIAKI TANAKA, and TAKEYO SAKAI,
*Industrial Research Laboratories, Kao Soap Co., Ltd., 1334
Minatoyakushubata, Wakayama-shi, 640 Japan*

Synopsis

Polytetramethylene glycol (molecular weight range 1000-8000) was prepared by the polymerization of tetrahydrofuran (THF) using a binary catalyst system of fuming sulfuric acid and perchloric acid. When 28% fuming sulfuric acid alone was used as the catalyst, the average molecular weight of polymer was low, the maximum value being 1000-1100. By the combination of fuming sulfuric acid with a small amount of perchloric acid, the average molecular weight of the polymer was increased to about 8000. Furthermore, the molecular weight was readily controlled in the range of 1000 to 8000 by varying the amount of the binary catalyst.

INTRODUCTION

This paper describes the polymerization of tetrahydrofuran (THF) by a binary catalyst system of fuming sulfuric acid and perchloric acid, which produces poly-THF (P-THF) having hydroxyl groups at both ends of polymer molecule. The THF polymerization by cationic catalysts such as Lewis acid¹ and organoaluminum compounds² has long been known. Polyethers thus obtained are liquid or wax according to their molecular weights. At the present time, polymers of molecular weight of 600 to 3000 having hydroxyl endgroups are important in the preparation of polyurethanes and polyesters.

The industrial production of polytetramethylene glycol (PTMG) of the above medium molecular weights consists of the THF polymerization by the catalysts of acetic anhydride-perchloric acid or by fluorosulfonic acid.³ Poly-THF prepared by acetic anhydride-perchloric acid system has acetate endgroups. The hydrolysis of the PTMG diacetate requires severe conditions, which usually cause a considerable loss of the polymer. In the polymerization of THF by fluorosulfonic acid, on the other hand, poly-THF having hydroxyl endgroups can be obtained by the ready hydrolysis under acidic condition. But the production of hydrofluoric acid in the hydrolysis of the polymerization system is undesirable because of corrosion of the plant equipment.

In a previous paper, we reported the polymerization of THF by using fuming sulfuric acid (SO₃ 15-43%) as the catalyst which produces colorless P-THF having hydroxyl endgroup, i.e., PTMG, by the aftertreatment with water.⁴ However, the polymerization of THF by fuming sulfuric acid system

produces PTMG of average molecular weight below 1200. In the present study, the combination of fuming sulfuric acid with a small amount of perchloric acid is used as the catalyst which is effective in increasing the PTMG molecular weight up to 8000.

EXPERIMENTAL

Materials

THF was a commercial reagent of purity above 99.5%, which was purified by distillation before use. The maximum water content was 0.03 wt-%. Fuming sulfuric acid having 28 wt-% SO_3 was an Extra Pure Grade reagent of JIS (Japan Industrial Standards). Perchloric acid (70 wt-%) was a Guaranteed Grade reagent of JIS. $\text{Ca}(\text{OH})_2$ and benzene were JIS-Extra Pure Grade reagents.

Polymerization Procedure

A typical method is as follows. In a 500-ml, four-necked flask provided with a stirrer, a thermometer, a reflux condenser, and a dropping funnel, 100 g THF was charged under nitrogen atmosphere. With stirring and cooling, a required amount of 70% aqueous perchloric acid was added; next, the required amount of fuming sulfuric acid was added through a dropping funnel. In order to avoid overheating due to the violent exothermic reaction, sufficient stirring and cooling were necessary. Then, the reaction mixture was kept at a definite temperature for a definite time to complete the polymerization. After polymerization, 200 g water was added, and excess THF monomer was distilled out from the reaction mixture by heating. Finally, the residue was heated at about 90–100°C for an additional 2 hr under stirring in order to ensure the hydrolysis of the terminal endgroups. As the reaction mixture was allowed to cool, it separated into two layers. The upper oil layer was separated from the lower aqueous layer and was treated with excess aqueous $\text{Ca}(\text{OH})_2$. Then, about 100 g benzene was added to the oil layer, and the water contained in the oil layer was removed by distillation with an entrainer of benzene. After cooling, precipitated CaSO_4 and excess $\text{Ca}(\text{OH})_2$ were removed by filtration. The purified PTMG was obtained by removing benzene by reduced pressure distillation from the filtrate.

Analysis

The purity of PTMG was determined by hydroxyl number, acid number, carbonyl value, iodine value, and saponification value of the JIS methods. The average molecular weight (\bar{M}_n) of PTMG was calculated from the hydroxyl number. Color of PTMG was determined by A.P.H.A. (ASTM D1209-62). Total chlorine content was determined by the Volhard method after the decomposition of PTMG by oxygen-hydrogen combustion.

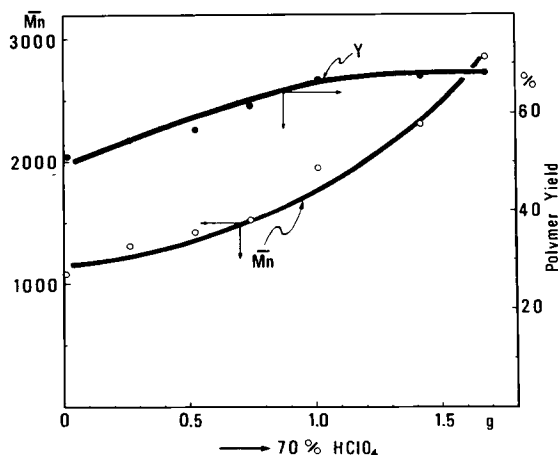


Fig. 1. Effect of amount of perchloric acid with a fixed amount of fuming sulfuric acid on \bar{M}_n and polymer yield. Conditions: 23 g 28% fuming sulfuric acid addition at $0^\circ \pm 2^\circ\text{C}$ during 1 hr; reaction at $0^\circ \pm 1^\circ\text{C}$ for 5 hr; THF, 100 g.

RESULTS AND DISCUSSION

Effect of Perchloric Acid on Molecular Weight and Yield of P-THF

With 23 g 28% fuming sulfuric acid per 100 g THF, the effect of the amount of 70% aqueous perchloric acid on the average molecular weight (\bar{M}_n) and the polymer yield (%) are shown in Figure 1. The \bar{M}_n was low when the amount of perchloric acid was small. As the amount of perchloric acid was increased, the \bar{M}_n and the polymer yield were increased.

Effect of Amount of Fuming Sulfuric Acid with a Fixed Amount of Perchloric Acid on \bar{M}_n and Polymer Yield

Figure 2 shows the results varying the amount of fuming sulfuric acid in combination with a fixed amount of perchloric acid. With stirring and cooling to keep the reaction temperature at $0^\circ \pm 2^\circ\text{C}$, 1.0 g 70% aqueous perchloric acid was added to 100 g THF, and then 18–35 g 28% fuming sulfuric acid was added during 1 hr. The reaction was carried at $0^\circ \pm 1^\circ\text{C}$ for 5 hr. As the amount of fuming sulfuric acid was increased, the average molecular weight and yield of the polymer were decreased. When fuming sulfuric acid alone was used as the catalyst, the average molecular weight was not decreased noticeably as the amount of the catalyst was increased. The findings in Figure 2 are quite characteristic for this polymerization system.

Effect of Amount of Catalyst with a Fixed Ratio of Fuming Sulfuric Acid and Perchloric Acid

As the average molecular weight and the polymer yield were found to be varied by the change in the amounts of fuming sulfuric acid and perchloric acid (Figs. 1 and 2), the polymerizations were carried out with various

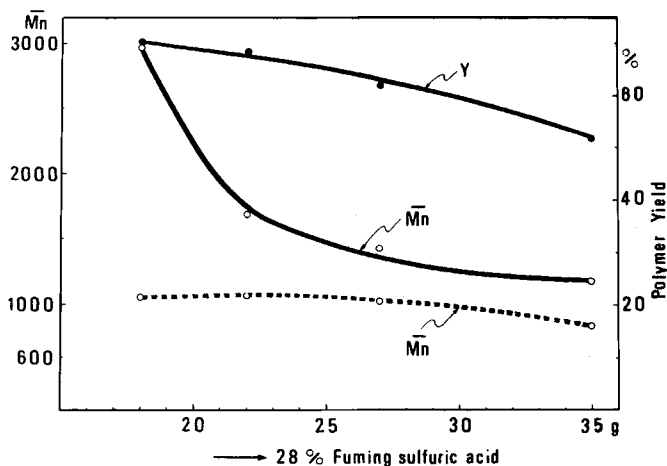


Fig. 2. Effect of amount of fuming sulfuric acid with a fixed amount of perchloric acid on \bar{M}_n and polymer yield: (—) 28% fuming sulfuric acid addition at $0^\circ \pm 2^\circ\text{C}$ during 1 hr, reaction at 0°C for 5 hr, 1.0 g 70% aqueous perchloric acid and 100 g THF; (- - -) same conditions as the above, but 70% aqueous perchloric acid was omitted.

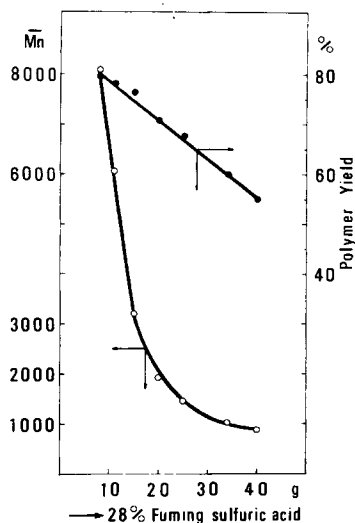


Fig. 3. Effect of amount of catalyst with a fixed ratio of fuming sulfuric acid and perchloric acid on \bar{M}_n and polymer yield: catalyst addition at $0^\circ \pm 2^\circ\text{C}$ during 1 hr; reaction at $0^\circ \pm 1^\circ\text{C}$ for 3 hr; ratio of 28% fuming sulfuric acid (g) per 70% aqueous perchloric acid (g) is 22.7 (constant); 100 g THF.

amounts of the mixed catalyst with a fixed ratio of 22.7 of 28% fuming sulfuric acid and 70% aqueous perchloric acid. The range of fuming sulfuric acid was 8 to 40 g per 100 g THF. The results are shown in Figure 3. As the amount of the catalyst was increased, the average molecular weight and the yield of polymer were decreased. The decrease in polymer yield may be ascribed to the increase in water-soluble (lower molecular weight) fraction. It is seen that the molecular weight is readily controlled in the range of 1000 to several thousand by varying the amount of the binary catalyst.

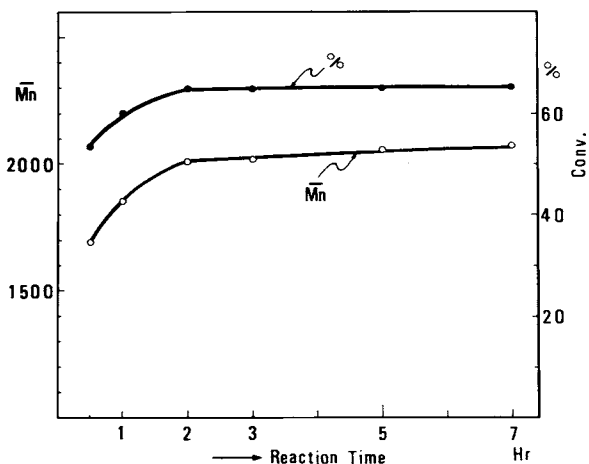


Fig. 4. Effect of reaction time on \bar{M}_n and conversion (at 0°C): 20 g 28% fuming sulfuric acid addition at $0^\circ \pm 2^\circ\text{C}$ during 1 hr; 1.3 g 70% aqueous perchloric acid and 100 g THF.

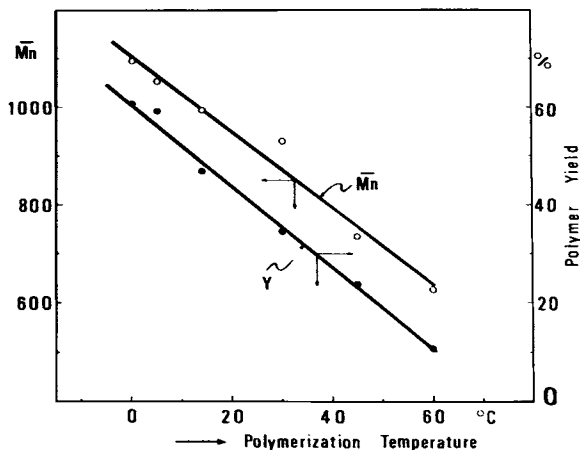


Fig. 5. Effect of polymerization temperature on \bar{M}_n and polymer yield: 34 g 28% fuming sulfuric acid addition during 1 hr; reaction for 10 hr; 1.5 g 70% aqueous perchloric acid and 100 g THF.

Effect of Reaction Time

Following a typical procedure, 1.3 g 70% aqueous perchloric acid per 100 g THF were mixed, and then 20 g 28% fuming sulfuric acid was added during 1 hr at a temperature of $0^\circ \pm 2^\circ\text{C}$. The reaction was continued at 0°C for various lengths of time (0.5 to 7 hr). Figure 4 shows that the overall velocity of polymerization was fairly fast, and, under these polymerization conditions, the polymerization equilibrium was attained in 3 hr.

Effect of Polymerization Temperature

The polymerization was carried out by using 1.5 g 70% aqueous perchloric acid and 34 g 28% fuming sulfuric acid per 100 g THF at various temperatures from 0° to 60°C . Figure 5 shows that as the temperature is increased,

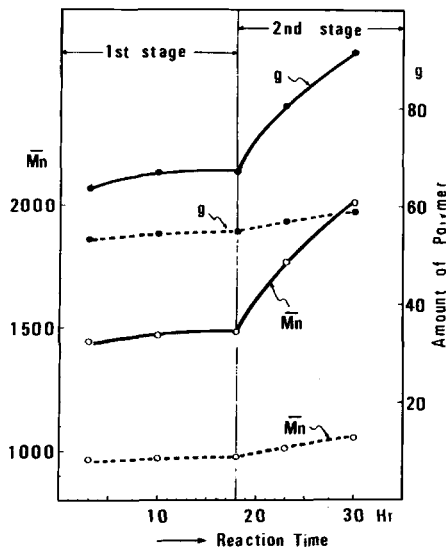


Fig. 6. Two-stage polymerization: (—) 27 g 28% fuming sulfuric acid addition at $0^{\circ} \pm 2^{\circ}\text{C}$ during $\frac{1}{4}$ hr; reaction at 0°C ; 1.2 g 70% aqueous perchloric acid and 100 g THF; after 18 hr, 100 g THF was added to the reaction system. (---) Same conditions as the above, but 70% aqueous perchloric acid was omitted.

both the average molecular weight and the yield of the polymer are decreased.

Two-Stage Polymerization

Following a typical procedure, 1.2 g 70% aqueous perchloric acid per 100 g THF were mixed, and 27 g 28% fuming sulfuric acid was added during $\frac{1}{4}$ hr at $0^{\circ} \pm 2^{\circ}\text{C}$, and the polymerization reaction was continued at 0°C for 18 hr. Then, an additional 100 g THF was added to the polymerization mixture of the first stage. Figure 6 shows that the molecular weight and the amount of polymer are increased with reaction time in the second stage, too. Under the same conditions with 28% fuming sulfuric acid alone as the catalyst, the increases in the average molecular weight and the amount of polymer in the second stage were not so noticeable as in the case of the binary catalyst system.

From the above results, the reactive species with fuming sulfuric acid alone as the catalyst is almost lost or very sluggish after the polymerization reached the equilibrium. But in the case of the binary catalyst system, a part of the propagating species remains reactive, and the reactive species continued to grow in the second stage.

Quality

Typical analytical data of purified PTMG are as follows: hydroxyl value, 58.5; acid number, 0.04, saponification value, 0.2; carbonyl value, 0.006%; iodine value, 0.08; water content, 0.02%; and color (A.P.H.A.), 20. Total chlo-

rine is nil. The infrared spectrum agreed with that of the PTMG prepared by using fluorosulfonic acid as the catalyst.

CONCLUSIONS

Poly-THF (molecular weight 1000 to several thousand) having hydroxyl groups at both ends was prepared by the polymerization of THF with a binary catalyst system of 28% fuming sulfuric acid and a small amount of perchloric acid. The polymerization was carried out in the range of 8–40 g of the mixed catalyst of 28% fuming sulfuric acid and 70% aqueous perchloric acid per 100 g THF, the weight ratio of the catalyst components being fixed at 22.7 at 0°C for 2 to 3 hr. Thus, the molecular weight is readily controlled in the range of 1000 to several thousand by varying the amount of the binary catalyst.

References

1. H. Meerwein, D. Delfs, and H. Morschel, *Angew. Chem.*, **72**, 927 (1960); J. Furukawa and T. Saegusa, *Polymerization of Aldehydes and Oxides*, Wiley, New York, 1963; P. Dreyfuss, *Ring-Opening Polymerization*, K. C. Frisch and S. L. Reegen, Eds., Marcel Dekker, New York, 1969, p. 111; T. Saegusa, H. Imai, and J. Furukawa, *Makromol. Chem.*, **79**, 221 (1964); H. Imai, T. Saegusa, and J. Furukawa, *Makromol. Chem.*, **81**, 92 (1965).
2. P. Dreyfuss and M. P. Dreyfuss, *Advan. Polym. Sci.*, **4**, 528 (1967); D. Sims, *Markromol. Chem.*, **98**, 235 (1966); R. C. Burrows and B. F. Crowe, *J. Appl. Polym. Sci.*, **6**, 465 (1962).
3. F. B. Hill and R. A. Schulze, U.S. Pat. 2,751,419 (1956).
4. K. Matsuda, Y. Tanaka, T. Sakai, and I. Iwasa, *ACS Meeting, Polym. Div. Prepr.*, Apr. 4, 1974, p. 468; K. Matsuda, *Chem. Technol.*, **4**(12), 744 (1974).

Received November 4, 1975

Revised December 4, 1975