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Cationic Polymerization of Tetrahydrofuran with Fuming Sulfuric Acid Initiator: Effects of Superacid Salts and Aromatic Compounds on $\bar{M}_n$ and Yield of the Polymer

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ABSTRACT

Bulk polymerization of tetrahydrofuran was studied to find a facile method for the preparation of polytetramethyleneglycol having molecular weight more than 1000 initiated by fuming sulfuric acid as a main component at -5 to 0°C. Superacid salts, being soluble in tetrahydrofuran, showed excellent activity for increasing the molecular weight. The polymerization initiated by fuming sulfuric acid in combination with sodium trifluoromethane sulfonate was examined under several conditions. It was also found that a mixture of fuming sulfuric acid and an aromatic compound such as benzenesulfonic acid, benzene, and xylene, contributed to an increase in the molecular weight of polymer.

INTRODUCTION

Many initiators have been reported to be effective for the ring-opening polymerization of tetrahydrofuran (THF) [1-4]. Particularly,

fluorosulfuric acid [5] and the acetic anhydride-perchloric acid binary system [6] have been adopted as initiators to obtain polytetramethyleneglycol (PTMG) as an important raw material for the polyurethane industry. These initiators, however, have some drawbacks, as described in a previous paper [7].

Fuming sulfuric acid is known to be an initiator of the polymerization of THF [4]. This compound was re-evaluated in a previous report [8] as a commercially favorable initiator for obtaining PTMG under limited polymerization conditions, but it was difficult to obtain PTMG having molecular weight ($\overline{M}_n$) over 1200.

In order to increase $\overline{M}_n$ of the PTMG, initiators for the reactions, for example, fuming sulfuric acid combined with a small amount of perchloric acid [7], metal fluoride [9], or metal oxide [9], were investigated.

This paper deals with the effects of addition of a small amount of superacid salts [10-13] or aromatic compounds [14] to fuming sulfuric acid initiator on $\overline{M}_n$ and yield of PTMG.

EXPERIMENTAL

THF, fuming sulfuric acid, calcium hydroxide, 70% perchloric acid solution, and sodium trifluoromethane sulfonate (CF_3SO_3Na) were similar to those previously used [7, 15]. Perchlorates and aromatic compounds were reagent-grade chemicals and used without further purification. The methods of determining color number and $\overline{M}_n$ of the polymer and the polymerization procedure were the same as reported previously [7]. Superacid salts were dissolved in THF and aromatic compounds were mixed with fuming sulfuric acid before use.

RESULTS AND DISCUSSION

Effect of Superacid Salts

Effect of Some Perchlorates. As shown in Table 1, the combination of fuming sulfuric acid with magnesium perchlorate or with ferric perchlorate, which were soluble in THF, gave an increased molecular weight PTMG.

On the other hand, potassium perchlorate and ammonium perchlorate, which were almost insoluble in THF, did not increase $\overline{M}_n$. The solubility of perchlorate in THF was, therefore, an important factor

TABLE 1. Effect of Some Perchlorates in Fuming Sulfuric Acid-Initiated Polymerization of THF[a]

Perchlorate		PTMG		
Type	Wt (g)	Yield (%)	$\overline{M}_n$	Color[c]
-	-	50.9	993	10-15
$LiClO_4 \cdot 3H_2O$[b]	0.7	50.6	1370	15-20
$NaClO_4 \cdot H_2O$	3.8	70.7	2200	10-15
$Ba(ClO_4)_2 \cdot 3H_2O$	5.2	72.2	1870	10-15
$Mg(ClO_4)_2$	3.0	68.4	5620	25-30
$Fe(ClO_4)_3 \cdot XH_2O$	3.1	69.2	6980	Light brown

[a]Conditions: THF, 100 g; 28% fuming sulfuric acid, 21 g; -5°C, 18 hr.
[b]Solution polymerization (dichloroethane 30 g).
[c]APHA (ASTM Method D 1209-62).

in producing an increase in $\overline{M}_n$. The amount of magnesium perchlorate greatly affected the molecular weight, though it had little effect on polymer yield. The results are shown in Fig. 1. Perchloric acid and perchlorates promote the formation of trisulfate anion in pyrosulfuric acid as shown in Eqs. (1) and (2) [16], where M denotes a metal.

$$HClO_4 + 2\ H_2S_2O_7 \rightleftharpoons H_2ClO_4^+ + HS_3O_{10}^- + H_2SO_4 \quad (1)$$

$$MClO_4 + 2\ H_2S_2O_7 \rightleftharpoons M^+ + HClO_4 + HS_3O_{10}^- + H_2SO_4 \quad (2)$$

The contribution of the trisulfate anion to producing an increase in molecular weight has already been described [9]. The resulting polymer was colored when a large amount of perchloric acid or its salts was used. The coloration was similar to that of the polymer obtained by sulfuric acid-perchloric acid and sulfuric acid-perchlorate [17] binary initiators.

Although it is not clear which anion, $HS_3O_{10}^-$ or ClO_4^-, contributed more to the increase the molecular weight, the contribution of perchloric acid formed in situ may not be neglected.

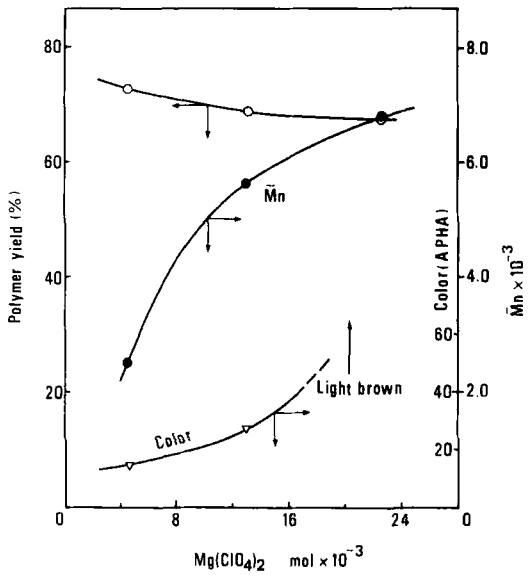


FIG. 1. Effect of the amount of magnesium perchlorate with a fixed amount of fuming sulfuric acid on $\overline{M}_n$ and yield of polymer. Conditions: THF, 100 g; 28% fuming sulfuric acid, 21 g; -5°C; 20 hr.

Effect of Sodium Trifluoromethane Sulfonate. With a fixed amount of 28% fuming sulfuric acid and THF, the effects of the amount of CF_3SO_3Na on $\overline{M}_n$ and yield of the polymer are shown in Fig. 2. As the CF_3SO_3Na content in fuming sulfuric acid was increased, $\overline{M}_n$ and yield of the polymer increased steadily, while as the amount of 70% perchloric acid solution increased, a maximum in the polymer yield was observed though $\overline{M}_n$ increased [18] (Fig. 2).

This phenomenon was also observed in the fuming sulfuric acid-benzene binary system as noted below. It was assumed that this was due to a decrease in the SO_3 content of fuming sulfuric acid. Perchloric acid as is commonly done, was used as the 60-70% aqueous solution, because anhydrous perchloric acid is an extremely dangerous material to handle. Therefore, the effect of water content in the polymerization system increased with increasing amount of aqueous perchloric acid (Fig. 2). With the use of super acid salts soluble in THF instead of aqueous perchloric acid, PTMG having

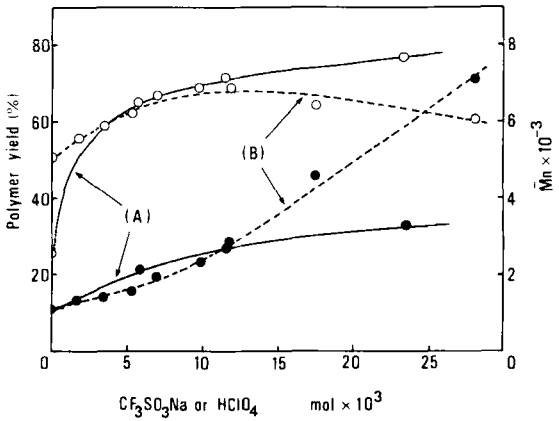


FIG. 2. Effect of the amount of CF_3SO_3Na or 70% $HClO_4$ solution with a fixed amount of fuming sulfuric acid on (•) $\bar{M}_n$ and (○) yield of polymer: (A) fuming sulfuric acid-CF_3SO_3 Na binary system, THF 100 g, 28% fuming sulfuric acid 15 g, 0°C, 5 hr; (B) fuming sulfuric acid-70% $HClO_4$ binary system, THF, 100 g, 28% fuming sulfuric acid 23 g, 0°C, 5 hr.

molecular weight up to 3000 was easily prepared in good yield in a short time without the influence of water, and the molecular weight of the polymer could be controlled by the quantity of the salt added. Addition of fuming sulfuric acid with CF_3SO_3Na led to the production of colorless polymer.

Effect of the Amount of Fuming Sulfuric Acid. The effects of the amount of 28% fuming sulfuric acid on the $\bar{M}_n$ and yield of the polymer in the presence and absence of CF_3SO_3Na [8] are shown in Figs. 3 and 4. The polymer yield increased linearly with decreasing amount of fuming sulfuric acid in the presence of CF_3SO_3Na, but in its absence maximum was observed at about 60% polymer yield (Fig. 3). As shown in Fig. 4, the molecular weight of the polymer increased in the presence of CF_3SO_3Na but not in the absence of CF_3SO_3Na.

Effect of the Amount of Initiator with a Fixed Ratio of Fuming Sulfuric Acid and CF_3SO_3Na. Figure 5 shows the effects of the amount of initiator for a given composition on $\bar{M}_n$ and yield of the polymer. Decreasing the amount of initiator led to an increase in both molecular weight and yield of the polymer similarly to the facts mentioned above.

The organic acid anhydride-superacid salt-sulfuric acid ternary

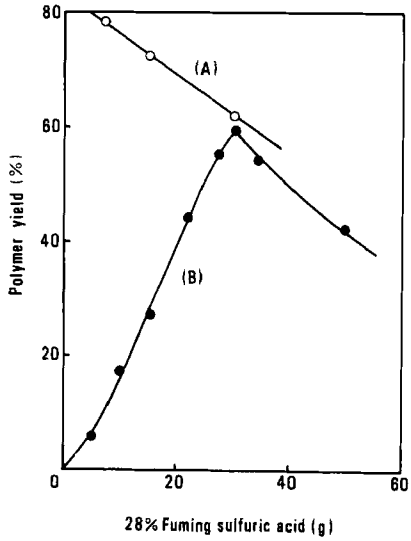


FIG. 3. Effect of the amount of fuming sulfuric acid with a fixed amount of CF_3SO_3Na on polymer yield: (A) THF 100 g, CF_3SO_3Na 2 g, 0°C, 5 hr; (B) THF 100 g, 0°C, 5 hr.

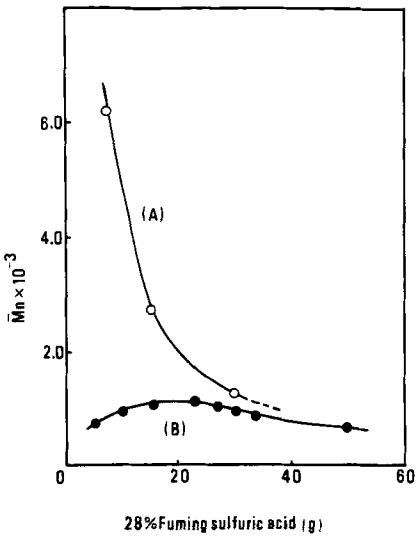


FIG. 4. Effect of the amount of fuming sulfuric acid with a fixed amount of CF_3SO_3Na on $\bar{M}_n$ of polymer: (A) THF 100 g, CF_3SO_3Na 2 g, 0°C, 5 hr; (B) THF 100 g, 0°C, 5 hr.

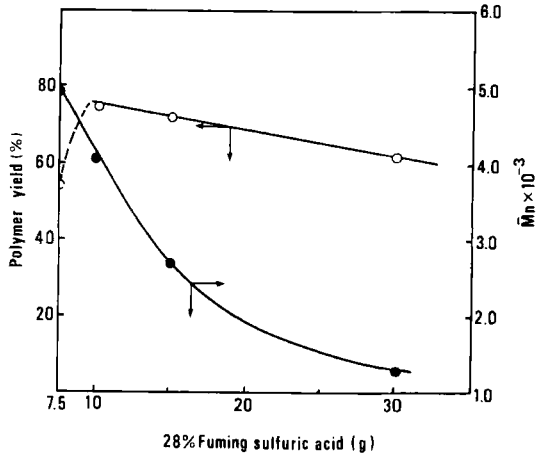


FIG. 5. Effect of the amount of initiator at a fixed ratio of fuming sulfuric acid and CF_3SO_3Na on (•) $\bar{M}_n$ and (○) yield of polymer. Conditions: THF, 100 g; 28% fuming sulfuric acid/CF_3SO_3Na=15/2 (w/w); 0°C, 5 hr.

system has been reported to be the initiator for THF polymerization [15]. The function of superacid salt in this ternary system is not similar to that in binary system as noted above.

Fuming sulfuric acid in combination with a small amount of superacid salt promotes the in situ formation of superacids, such as perchloric acid, trifluoromethanesulfonic acid, and trisulfuric acid, and these superacids contribute greatly to activation of the polymerization system by improving the stability of counteranions of the propagating species. Thus polymer (PTMG) having molecular weight over 1000 was obtained in a good yield.

Recovery and Recycling of CF_3SO_3Na

Sodium trifluoromethane sulfonate was recovered in 89.5% yield by the aftertreatment of waste acid. The polymerizations were carried out in the presence of new CF_3SO_3Na or recovered CF_3SO_3Na in order to recycle CF_3SO_3Na. As shown in Table 2, no difference was observed in $\bar{M}_n$ and yield of the polymer obtained with these two CF_3SO_3Na.

TABLE 2. Polymerization of THF Initiated by Fuming Sulfuric Acid in Combination with the New or Recovered CF_3SO_3Na Binary System[a]

	Polymer	
CF_3SO_3Na	Yield (%)	$\overline{M}_n$
Recovered	75.8	2700
New	73	2780

[a]Conditions: THF, 100 g; CF_3SO_3Na, 2 g; 28% fuming sulfuric acid, 15 g; -5°C; 5 hr.

TABLE 3. Effect of Benzene or Benzenesulfonic Acid on $\overline{M}_n$ and Yield of Polymer[a]

	Benzene		Benzenesulfonic acid	
Amount (10^2 mole)	Polymer yield (%)	$\overline{M}_n$	Polymer yield (%)	$\overline{M}_n$
-	50.3	739	50.3	739
1.0	52.3	836	58.6	993
2.0	54.8	1209	56.1	1088
2.6	52.2	1497	-	-
3.9	39.9	2230	52.8	1474
5.1	15.7	3425	47.8	1485

[a]Conditions: THF, 100 g; 28% fuming sulfuric acid, 34 g; -5°C; 18 hr.

Effects of Aromatic Sulfonic Acid

The molecular weight of polymer obtained could be increased by using a mixture of fuming sulfuric acid and benzenesulfonic acid as an initiator. A similar phenomenon was also observed by using a mixture of fuming sulfuric acid and benzene [14].

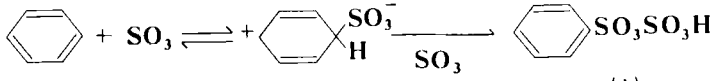
The yield of polymer, however, decreased considerably with increasing amount of benzene. The results are given in Table 3. The contents of SO_3 in the polymerization system would be decreased by

TABLE 4. Effect of Some Aromatic Compounds in the THF Polymerization Initiated by Fuming Sulfuric Acid[a]

	PTMG	
Aromatic hydrocarbon	Yield (%)	$\overline{M}_n$
-	50.3	739
Anthracene	54.2	1206
Naphthalene	52.1	1063
Anisole	61.4	1015
Xylene	54.2	881
Toluene	52.3	836
Benzene	52.3	836
Chlorobenzene	50.5	766
Fluorobenzene	47.0	775

[a]Conditions: THF, 100 g; 28% fuming sulfuric acid, 34 g; aromatic compound, 1.0×10^{-2} mole; -5°C; 18 hr.

the formation of benzene pyrosulfuric acid (I) in situ according to Eq. (3) [19], as described in a previous report [8].



(I) (3)

The mixture of fuming sulfuric acid and aromatic hydrocarbon, such as benzene, toluene, and xylene, may give a similar result to that of benzenesulfonic acid by controlling the SO_3 content in the fuming sulfuric acid.

The effects of some aromatic hydrocarbons are summarized in Table 4. The activity of the hydrocarbons in increasing the molecular weight seemed to be proportional to the S_E2 reaction rate with SO_3 [19], and, therefore, closely related to the quantity of aromatic pyrosulfonic acid formed and the stability of aromatic pyrosulfate anions as the counteranion of the propagating species.

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