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**Effect of Hexamethyl Phosphoric Acid
Triamide on the Polymerization of
Epichlorohydrin-Methyl Methacrylate
Initiated with Alkylaluminum**

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ABSTRACT

The effect of hexamethyl phosphoric acid triamide on the rate of polymerization of AlEt_3 -initiated polymerization of epichlorohydrin and methyl methacrylate was examined.

Benzene was used as solvent and the experiments covered AlEt_3 /hexamethyl phosphoric acid triamide ratios from 1:0 to 1:2. Rate of polymerization increased to a maximum at AlEt_3 /hexamethyl phosphoric acid triamide ratio of 1:0.2 and then decreased.

The reaction of hexamethyl phosphoric acid triamide with AlEt_3 appears to modify the catalytic nature and copolymerization of epichlorohydrin with methyl methacrylate as demonstrated by enhanced methyl methacrylate reactivity in the presence of hexamethyl phosphoric acid triamide.

INTRODUCTION

Copolymerizations of cyclic ethers with vinyl monomers were expected to be difficult because of their differences in structure. However, some attempts have been made. For example, reports of block copolymerization of cyclic ethers with living polystyrene [1, 2], copolymerization of ethylene oxide or propylene oxide with acrylonitrile [3], and epichlorohydrin with acrylonitrile [4] or vinyl toluene [5] were published.

In an anionic polymerization system it is probable that various additives may react or coordinate with a catalyst such as butyllithium to form different active species [6, 7]. The rate of polymerization, the stereochemistry, and the copolymerization characteristics reflect this mechanism. This was generally found to be true. Dimethylsulfoxide, dimethylformamide, and hexamethyl phosphoric acid triamide are capable of complexes with organomagnesium compounds and of affecting anionic polymerization of acrylonitrile in a different manner [8], and diethylzinc-dimethylsulfoxide catalyst can initiate the polymerization of propylene oxide [9].

This paper reports the investigation of the effect of hexamethyl phosphoric acid triamide (HMPA) as extended to the copolymerization of epichlorohydrin (ECH) with methyl methacrylate (MMA) catalyzed by organoaluminum compound.

EXPERIMENTAL

Materials

All reagents were commercially supplied and purified by conventional methods: benzene was distilled over sodium benzophenone and ECH over calcium hydride. MMA was distilled under reduced pressure. The distillations were carried out under a purified nitrogen atmosphere. HMPA was dried over calcium hydride, vacuum-distilled. AlEt_3 was distilled under reduced pressure.

Polymerization Procedure

Benzene solutions of AlEt_3 and of HMPA were mixed in an ampoule at -78°C to give an appropriate molar ratio of AlEt_3 to HMPA. The monomer was then added to the ampoule. The evacuated and sealed ampoule was kept at a given temperature. After a given time of reaction, the polymerization mixture was poured into isopropanol containing a small amount of hydrochloric acid. The precipitated

polymer was collected by filtration and washed with isopropanol and dried under high vacuum.

Polymer Characterization

Polymer composition was determined by chlorine analysis of the polymer (Schöniger's method). The polymer compositions calculated from the chlorine content agreed with those from C-H analyses. NMR spectra were run on several polymer samples in CDCl_3 solution to determine polymer composition. These spectra were complicated and it was difficult to distinguish individual protons. Polymer viscosities were measured by an Ostwald viscometer in benzene at 30°C .

NMR Spectra of AlEt_3 Complex

The NMR spectrum of an equimolar mixture of AlEt_3 and HMPA in benzene was measured at 80°C on a 100-Mc NMR spectrometer with the benzene solvent as the internal standard.

RESULTS

Mixtures of ECH and MMA (molar ratio, 57.5:42.5) in benzene (about 5 ml) were polymerized at 80°C for 20 hr by adding them to AlEt_3 solutions in benzene which had been reacted with HMPA. The results are given in Table 1 and Fig. 1.

TABLE 1. Effect of Hexamethyl Phosphoric Acid Triamide^a

Expt No.	AlEt_3 (mole %) ^b	HMPA (mole %) ^b	Polymer yield (%)	$[\eta]$	MMA units in polymer (mole %)
1	2	2	50	1.2	90
2	2	4	50	1.4	92
3	2	-	30	0.4	15

^aECH, 3.17 moles/liter; MMA, 2.35 moles/liter; total volume, 10 ml; polymerization at 80°C for 20 hr.

^bOn monomer mixture.

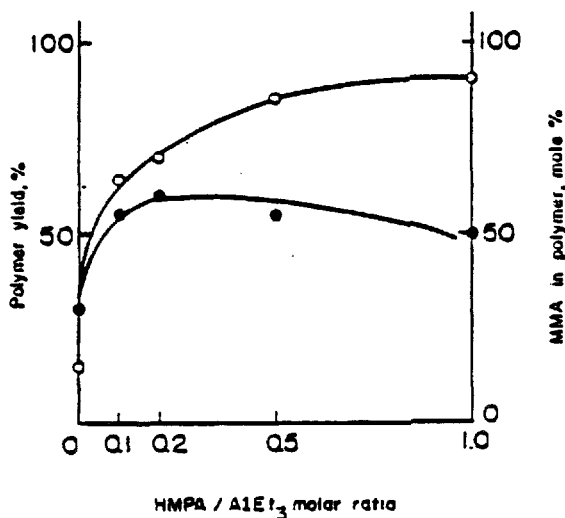


FIG. 1. Plots of various HMPA/AlEt₃ molar ratios vs polymer yield (●) and vs polymer compositions (○). AlEt₃, 0.11 mole/liter; ECH, 3.71 mole/liter; MMA, 2.35 mole/liter; total volume, 10 ml; polymerization at 80°C for 20 hr.

Polyepichlorohydrin produced under the same conditions contained a small isopropanol-soluble portion. The product copolymerized from an initial monomer ratio of about 57.5:42.5 was a white solid which was completely soluble in common organic solvents such as benzene, acetone, and chloroform. Table 1 shows the effects upon the rates of polymerization, $[\eta]$, and polymer compositions of the addition of HMPA.

It was found that addition of HMPA increased the rate of polymerization and raised the molecular weight. Furthermore, MMA was preferentially polymerized in the presence of HMPA.

The effects of the ratio of HMPA/AlEt₃ on the acceleration of the overall polymerization rate and polymer compositions were investigated (Fig. 1).

The rate of polymerization in benzene increased to a maximum at a ratio of about 0.2:1. Beyond that the rate decreased continuously. However, the MMA units of the polymers increased when the ratio of HMPA/AlEt₃ increased.

The yield of polymer with both catalysts increased linearly with polymerization time as shown in Fig. 2. The intrinsic viscosity of the polymer obtained with AlEt₃/HMPA catalyst at 80°C during 10 hr

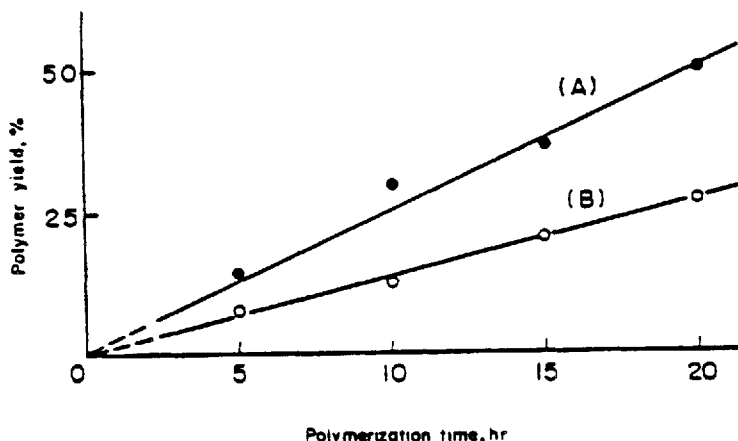


FIG. 2. Effect of polymerization time on yield. (A) $\text{AlEt}_3/\text{HMPA} = 1/1$. (B) AlEt_3 , AlEt_3 , 0.11 mole/liter; ECH, 3.17 mole/liter; MMA, 2.35 mole/liter, total volume, 10 ml; polymerization at 80°C .

from the same monomer mixture as in Fig. 1 was 1.2, indicating a relatively high molecular weight.

The compositions of the polymers polymerized with AlEt_3 -HMPA catalyst and AlEt_3 catalyst at a constant ECH/HMPA ratio (57.5/42.5) are presented in Fig. 3.

With AlEt_3 catalyst alone, the MMA content in the polymers increased gradually with increasing conversion. Because ECH is more reactive than MMA and is incorporated into the polymer more rapidly, it is supposed that ECH is therefore consumed first and MMA takes a significant part in polymerization only after the bulk of the ECH has been consumed. However, with AlEt_3 -HMPA catalyst, MMA is more reactive than ECH and incorporates into the polymer more rapidly.

In order to specify the nature of our catalyst system, this copolymerization with various monomer feeds was conducted with AlEt_3 in the presence and absence of HMPA, with the results given in Fig. 4. The apparent reactivity of MMA was surprisingly increased by the addition of HMPA.

DISCUSSION

The above results show that the addition of HMPA considerably modifies the catalytic nature of AlEt_3 to enhance the reactivity of MMA.

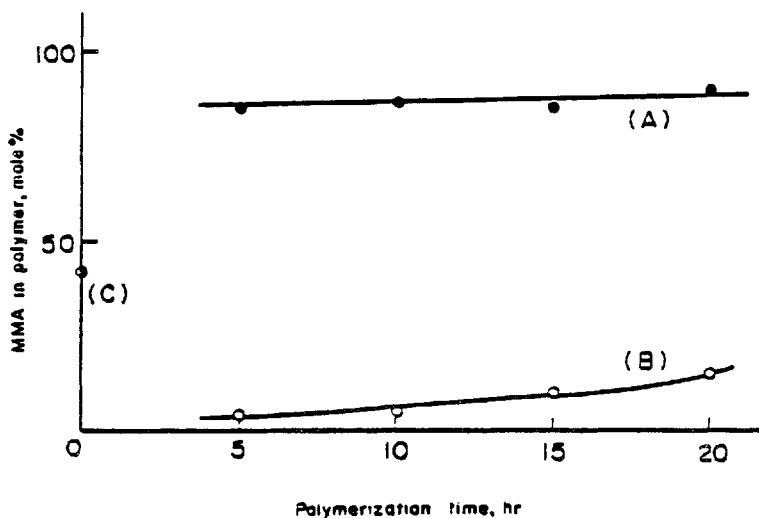


FIG. 3. Time-composition curve. Experimental conditions as in Fig. 2. Polymerized with (A) $\text{AlEt}_3/\text{HMPA} = 1/1$. (B) AlEt_3 . (C) Initial monomer feed.

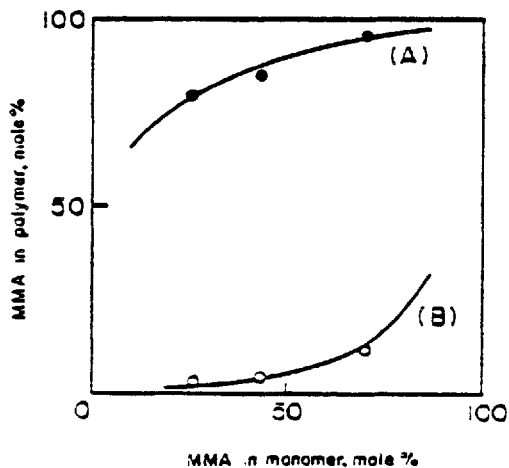


FIG. 4. Copolymerization of ECH with MMA. (A) $\text{AlEt}_3/\text{HMPA} = 1/1$. (B) AlEt_3 . AlEt_3 , 0.11 mole/liter; total monomer, 5.52 mole/liter; total volume, 10 ml; polymerization at 80°C for 5 hr.

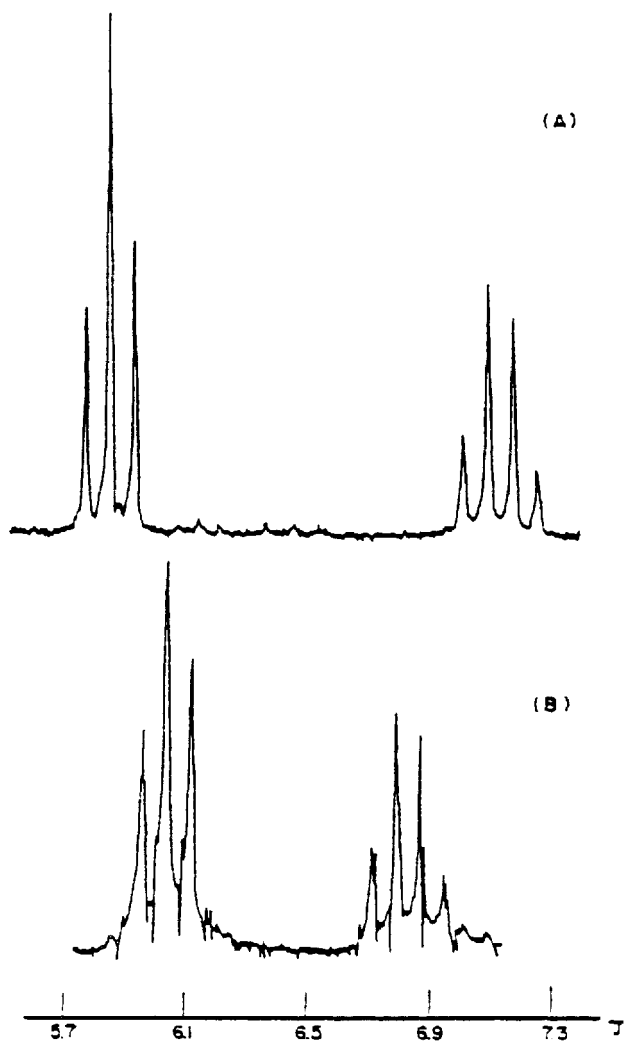


FIG. 5. NMR spectra of (A) $\text{AlEt}_3/\text{HMPA}$ (1/1) and (B) AlEt_3 . Solvent, C_6H_6 ; temperature, 80°C .

The increase of the rate of polymerization, the raising of molecular weight, and the high reactivity of MMA must be attributed to the presence of some particular active species other than the usual C—Al bond which exclusively initiates the polymerization of ECH as found in the absence of an additive. Since AlEt₃ alone cannot initiate the polymerization of MMA, any incorporation of MMA in a polymer chain in the absence of HMPA was expected only in the cross-propagation steps of a poly(ECH) anion.

In anionic polymerization with organometallic compounds, coordination of the Lewis base was observed to increase the anionic character of the alkyl group in the organometallic compound, and the active propagation end was found not to be a free anion nor a solvent separated ion-pair [10].

Figure 5 presents the NMR spectrum of AlEt₃ and AlEt₃/HMPA compounds at 80°C. The new complex formation between AlEt₃ with HMPA was identified from this spectrum [10].

The addition of HMPA appear to modify the catalytic site and to enhance the propagating site.

MMA polymerization with AlEt₃-Lewis base is said to be a coordination-type polymerization. The reactivity of the organometallic complex is dependent on the type and nature of the ligand. The presence of this active species, which differs in nature, seems to be responsible for the selective coordination of MMA.

Once initiation of MMA has occurred, the cross-propagation reaction, carbanion to opening epoxide, seems to be indistinct. A clear mechanism for this reaction cannot be offered at present. Studies of polymer characterization and mechanism details are now in progress.

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