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Vinyl Polymerization Catalyzed by AIEt$_3$-Hexamethyl Phosphoric Acid Triamide Complex

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Vinyl Polymerization Catalyzed by $AlEt_3$-Hexamethyl Phosphoric Acid Triamide Complex

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ABSTRACT

The polymerization of methyl methacrylate and acrylonitrile is shown to occur by an anionic mechanism initiated by a 1:1 complex between triethyl aluminum and hexamethyl phosphoric acid triamide at a relatively high temperature. This complex can also initiate the radical polymerization of vinyl monomers at relatively low temperatures. A tentative initiation mechanism is presented.

INTRODUCTION

The activating effect of Lewis bases on the anionic polymerization of polar vinyl monomers has recently been studied on the basis of the results obtained from different systems of organometallic compounds. In the anionic polymerization of methyl methacrylate (MMA) with triethyl aluminum ($AlEt_3$), coordination of Lewis bases such as α,α'-dipyridyl was found to increase the anionic character of the alkyl group in the triethyl aluminum [1].

The reactivity of organomagnesium coordination complexes is dependent on the type and nature of the ligand, and these complexes show different catalytic activity for the polymerization of acrylonitrile (AN) [2, 3].

Copolymerization of polar vinyl monomers catalyzed by these complexes also reflects this mechanism. For example, the copolymerization of styrene with α-methylstyrene with n-butyllithium demonstrated the enhanced α-methylstyrene reactivity in the presence of hexamethyl phosphoric acid triamide (HMPA) [4].

In this paper the effect of HMPA on the polymerization of MMA and AN and the copolymerization of MMA with AN catalyzed by $AlEt_3$ is investigated.

EXPERIMENTAL

Materials

All the vinyl monomers and solvent used were purified by conventional methods. AN, vinyl acetate, and benzene were distilled under a purified nitrogen atmosphere. MMA and HMPA were distilled under reduced pressure. Vinyl chloride was used without further purification. $AlEt_3$ was purified by distillation under reduced pressure and was stored as a normal solution in benzene.

Polymerization Procedure

All the procedures were carried out under a purified nitrogen atmosphere. Benzene solutions of $AlEt_3$ and of HMPA were mixed in an ampule at -78°C to give an appropriate molar ratio of $AlEt_3$ to HMPA. The monomer was then added to the ampule. The evacuated and sealed ampule was kept at a given temperature. After a given time of reaction, the polymerization mixture was poured into methanol containing a small amount of hydrochloric acid (or, for polymerization of vinyl acetate, into petroleum ether). The precipitated polymer was collected by filtration and washed and dried under high vacuum.

NMR Spectra of $AlEt_3$ Complex

The NMR spectrum of a mixture of $AlEt_3$ and HMPA in benzene was measured at various temperatures on a 100-Mc NMR spectrometer with benzene as the internal standard.

RESULTS AND DISCUSSION

Table 1 shows the results of the polymerization of MMA and AN obtained with the $AlEt_3$-HMPA catalyst system at various HMPA/$AlEt_3$ molar ratios. The yields of polymer for a standard time interval were compared. $AlEt_3$ alone did not show any catalytic activity for the polymerization of MMA and gave small amounts of poly(AN).

TABLE 1. Polymerization of Methyl Methacrylate and Acrylonitrile Catalyzed by $AlEt_3$ and HMPA[a]

Expt. No.	Vinyl monomer	HMPA/$AlEt_3$ molar ratio	Yield (%)	$[\eta]$[b]
1	MMA	0.0	0	-
2	MMA	0.1	6	0.20
3	MMA	0.5	12	0.50
4	MMA	1.0	35	3.00
5	MMA	5.0	35	2.95
6	MMA	10.0	39	2.80
7	AN	0.0	6	-
8	AN	0.5	10	-
9	AN	1.0	43	3.55
10	AN	2.0	46	3.60
11	AN	5.0	60	-

[a] Vinyl monomer 5 ml, benzene 5 ml, $AlEt_3$ 1 mole % on monomer, polymerized at 80°C for 20 hr.

[b] In benzene at 30°C for poly(MMA) and in N,N-dimethylformamide at 30°C for poly(AN).

At a constant $AlEt_3$ content, the addition of HMPA increased the yields of poly(MMA) and poly(AN). The molar ratio of HMPA/$AlEt_3$ was then increased up to 5 or 10 and it was found that the yields of polymer increased suddenly around HMPA/$AlEt_3$ equal to 1 and thereafter remained almost steady.

The presence of HMPA leads to a marked increase in the molecular weight of poly(MMA) and poly(AN), and high molecular weight polymers ($[\eta] \geq 3.00$) of MMA and AN were obtained with a molar ratio of HMPA/$AlEt_3$ of 1.

The molecular weight of poly(MMA) is a maximum at a 1/1 molar ratio. An increase in this ratio to 10 reduces the molecular weight of poly(MMA).

Because the experiments in the presence of HMPA were carried out at low concentrations of HMPA, its content in the reaction mixture did not change the polarity of the medium in the case of low molar ratios of HMPA/$AlEt_3$. A steady rate of polymerization was also observed at higher molar ratios. This means that the polarity of this medium does not increase the rate of polymerization of this catalyst system [1]. The cause of this phenomenon is that the participation of HMPA results in the formation of new catalytic sites.

In alkyl aluminum chemistry the electronegativity of aluminum ion of an alkyl aluminum can be estimated from the difference between the internal chemical shifts of the methyl and methylene protons, $\delta_{int.} = \delta_{CH_3} - \delta_{CH_2}$, in the NMR spectrum [5].

In Fig. 1, $-\delta_{int.}$ is shown as a function of the HMPA/$AlEt_3$ molar ratio. $-\delta_{int.}$ increased from an initial value for $AlEt_3$ in benzene of 80 (Hz) to a maximum value of 129 (Hz). This was attained when the ratio just exceeded 1.0. This implies that a strong 1:1 HMPA-$AlEt_3$ complex was formed. Once the reagent ratio just exceeds 1.0, it may be assumed that the 1:1 complex is the only form of $AlEt_3$ present in solution. This result of internal chemical shift reflects the rate of polymerization of MMA and of AN with the HMPA-$AlEt_3$ catalyst system at various molar ratios.

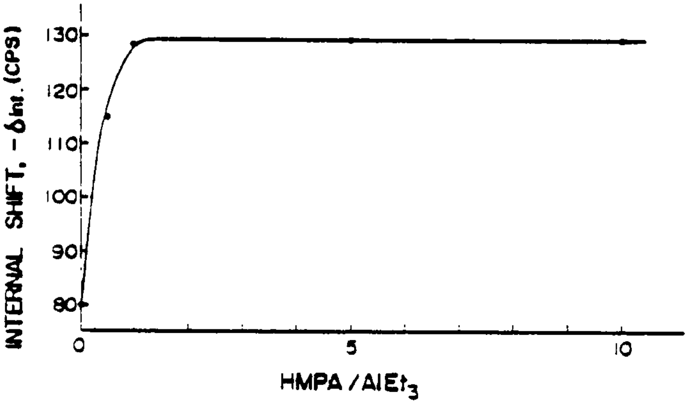

FIG. 1. Internal chemical shift of the aluminum ethyl protons: $\delta_{int.} = \delta_{CH_3} - \delta_{CH_2}$ in the 100 MHz NMR spectrum of HMPA-$AlEt_3$ mixtures in benzene at 80°C as a function of HMPA:$AlEt_3$ molar ratio.

The copolymerization of MMA with AN was investigated with the HMPA-$AlEt_3$ catalyst system (HMPA/$AlEt_3$ = 1) at various temperatures. For each experiment the monomer mixtures were polymerized in the range of 2 to 5% by weight. The monomer content of the copolymers was determined by IR spectroscopy using the calibration curve. Elemental analyses for carbon and nitrogen were also carried out on most of the copolymers but reproducibility was poor.

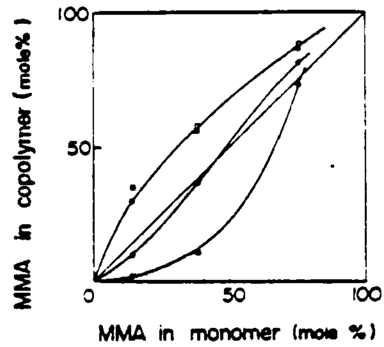

FIG. 2. Composition diagram for the copolymerization of MMA with AN at various temperatures: •, 80°C; ◑, 60°C; ◐, 30°C; and ○, 60°C with AIBN.

The surprising results are shown in Fig. 2. The copolymerization curve at 80°C was only a little different from that of typical anionic copolymerizations [6].

The MMA content in copolymers gradually increased as the temperature of copolymerization decreased, and the copolymerization at 30°C showed the composition curve of a radical mechanism [7].

Table 2 presents the results of the polymerization of vinyl acetate and vinyl chloride with HMPA-$AlEt_3$ catalyst. This catalyst has a weak activity toward vinyl acetate and vinyl chloride at 30 and 60°C. Thus it can be concluded that the HMPA-$AlEt_3$ catalyst system has two different catalytic active sites, one anionic and the other radical site. The catalytic nature was greatly dependent on the reaction temperature.

In Fig. 3 the chemical shifts of the methyl protons of HMPA in the NMR spectrum are shown as a function of HMPA/$AlEt_3$ ratio. Chemical shifts of the methyl protons increased in the presence of $AlEt_3$ from an initial absorption band. This means that the $-N(CH_3)_2$ group of HMPA strongly interacts with $AlEt_3$ and that the 1:1 complex, mentioned earlier, is complicated.

It has been reported that amide derivatives of titanium [8] and

TABLE 2. Polymerization of Vinyl Acetate and Vinyl Chloride with $AlEt_3$ and HMPA[a]

Expt. No.	Vinyl monomer	Yield (%)	$[\eta]$[c]
12	VAc	9.5	-
13	VAc[b]	5.5	0.76
14	VC	6.1	-
15	VC[b]	5.7	0.80

[a] Vinyl monomer 5 ml. benzene 5 ml, $AlEt_3$ 1 mole % on monomer, $HMPA/AlEt_3$ = 1/1 (mole), polymerized at 30°C for 30 hr.

[b] Polymerized at 60°C for 20 hr.

[c] In benzene at 30°C for poly(VAc) and in nitrobenzene at 30°C for poly(VC).

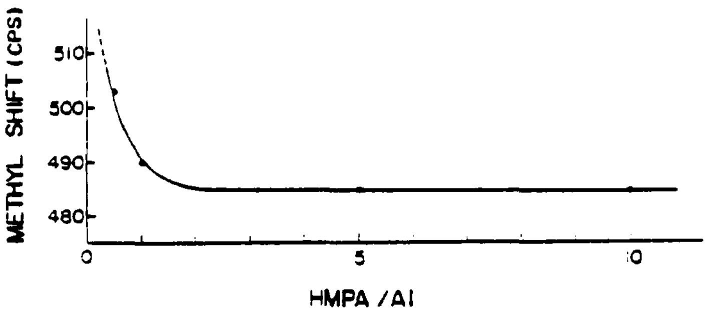

FIG. 3. Chemical shift of the HMPA methyl protons in the 100 MHz NMR spectrum of $HMPA\text{-}AlEt_3$ mixture in benzene at 30°C as a function of $HMPA{:}AlEt_3$ molar ratio.

aluminum [9] have been used as initiators for the polymerization of vinyl monomers, and that they may function either as ionic or as free radical initiators. The probable source of the free radicals was the decomposition reaction of the metal-amide derivatives. These metal-nitrogen bonds have an unusual chemical catalytic reactivity.

In the present studies it is likely that the interaction of the $-N(CH_3)_2$ group of HMPA with $AlEt_3$, i.e., the charge transfer reaction, leads to the radical polymerization of vinyl monomer. This type of radical has been found elsewhere by means of ESR [1].

However, a clear initiation mechanism for the radical polymerization cannot be offered at present.

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REFERENCES

[1] M. Ikeda, T. Hirano, and T. Tsuruta, Makromol. Chem., 150, 127 (1971).
[2] B. L. Erussalimskii, I. V. Kulevskaya, and V. V. Masurek, J. Polym. Sci., C, 16, 1355 (1967).
[3] B. Erussalimsky and I. Krassnoseslskaya, Makromol. Chem., 123, 80 (1969).
[4] W. Kampf, H. Weber, and K. P. Stocks, Angew. Makromol. Chem., 24, 177 (1972).
[5] P. T. Narasimhan and M. T. Rogers, J. Amer. Chem. Soc., 82, 5983 (1960).
[6] Y. Landler, J. Polym. Sci., 8, 63 (1952).
[7] F. M. Lewis, F. R. Mayo, and W. F. Hulse, J. Amer. Chem. Soc., 67, 1701 (1945).
[8] E. Perry, Makromol. Chem., 65, 145 (1963).
[9] S. Murahashi, T. Niki, T. Kobokata, H. Yuki, and K. Hatada, Kobunshi Kagaku, 24, 198 (1967).

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