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Carbocationic Polymerization in the Presence of sterically Hindered Bases. VI. The Polymerization of Methylstyrene with the “H_2O”/$SnCl_4$ Initiating System

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ABSTRACT

The polymerization of α-methylstyrene has been investigated using the "H_2O"/$SnCl_4$ initiating system in the presence of 2,6-di-tert-butylpyridine (DtBP) in CH_2Cl_2 solvent at -60° C. In the absence of DtBP and at low DtBP concentrations conversions are about 100%, but with increasing amounts of DtBP conversions drop to 3-5%. Polydispersity decreases with increasing [DtBP]. The $\overline{M}_n$ versus [DtBP] plot shows a maximum; thus $\overline{M}_n$ increases from ~70,000 to ~120,000 by increasing [DtBP] from 6×10^{-7} to 4.8×10^{-4} M and decreases to ~10,000 on further increasing DtBP. The effect of DtBP on this polymerization system can be explained by assuming nonprotic initiation, termination only by DtBP, depressed chain transfer to monomer, and complex formation between the propagating carbocation and DtBP.

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INTRODUCTION AND RESULTS OF A SCOUTING STUDY

Parts IV and V of this series of publications [1, 2] describe detailed investigations concerning the effect of DtBP on polymerizations in the "H_2O"/$AlCl_3$/isobutylene and "H_2O"/BCl_3/α-methylstyrene systems. The data presented in these and the other papers of this series can be explained by the hypothesis that DtBP competes for the proton with the monomer and thus suppresses chain transfer. In this context it was of interest to investigate the polymerization of α-methylstyrene (αMeSt) induced by another conventional Friedel-Crafts acid system "H_2O"/$SnCl_4$. A brief series of scouting experiments showed that αMeSt can be readily polymerized in the presence of DtBP with "H_2O"/$SnCl_4$; that is, initiation probably occurs by a concerted nonprotic process, and that the $\overline{M}_n$'s and MWD's are, respectively, higher and narrower than those obtained in the absence of this hindered pyridine. Encouraged by these results, it was decided to undertake a detailed investigation of the "H_2O"/$SnCl_4$/αMeSt system, and this paper summarizes the results of these studies.

EXPERIMENTAL

Purification of αMeSt and solvents has been described [2]. $SnCl_4$ (Ultrapure, Alfa) was purified according to Overberger et al. [3]. The flask containing $SnCl_4$ over P_2O_5 was connected to the vacuum unit and after stirring for 4 h it was degassed by several freeze-thaw cycles. The $SnCl_4$ was then distilled into precalibrated vials equipped with break seals. Throughout this purification $SnCl_4$ was protected from light. DtBP (99%, Chemical Samples) was used as received.

RESULTS AND DISCUSSION

Conversion-Time Studies and the Role of Water

Figure 1 shows conversion time plots for αMeSt polymerization with "H_2O"/$SnCl_4$ in the presence of DtBP. In the absence and low concentrations of DtBP, 100% conversions were rapidly obtained and the rate could not be followed. This phenomenon has also been observed with "H_2O"/BCl_3 [2]. At $[SnCl_4] = 2.05 \times 10^{-3}$ $\underline{M}$, increasing the concentration of DtBP from 1×10^{-3} to 2×10^{-3} $\underline{M}$ reduces the limiting conversion to ~5%. A further increase in DtBP concentration does not further reduce conversions and rates of polymerization.

Figure 2 is a plot of limiting conversion ξ_∞ against the logarithm of DtBP concentration at $[SnCl_4] = 1.42 \times 10^{-3}$ $\underline{M}$. Evidently the

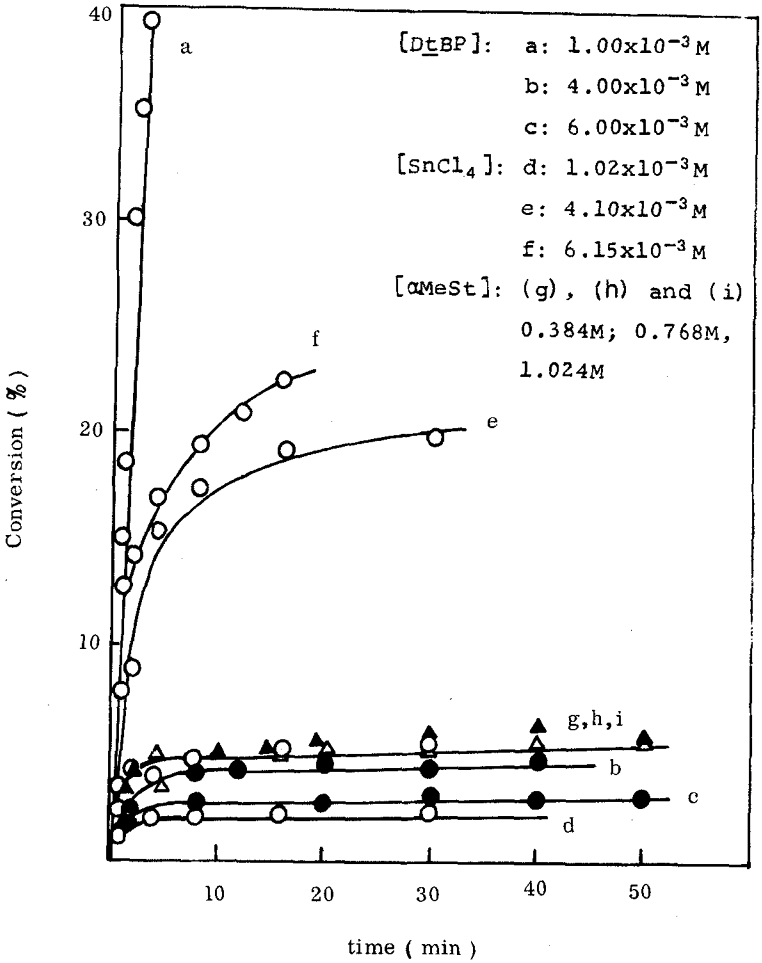

FIG. 1. αMeSt conversion versus time plots with CH_2Cl_2 diluent at -60°C under various conditions. (a), (b), and (c): [$SnCl_4$] = 2.05 × 10^{-3} M, [αMeSt] = 0.768 M. (d), (e), and (f): [DtBP] = 2.00 × 10^{-3} M, [αMeSt] = 0.768 M. (g), (h), and (i): [$SnCl_4$] = 2.05 × 10^{-3} M, [DtBP] = 2.00 × 10^{-3} M.

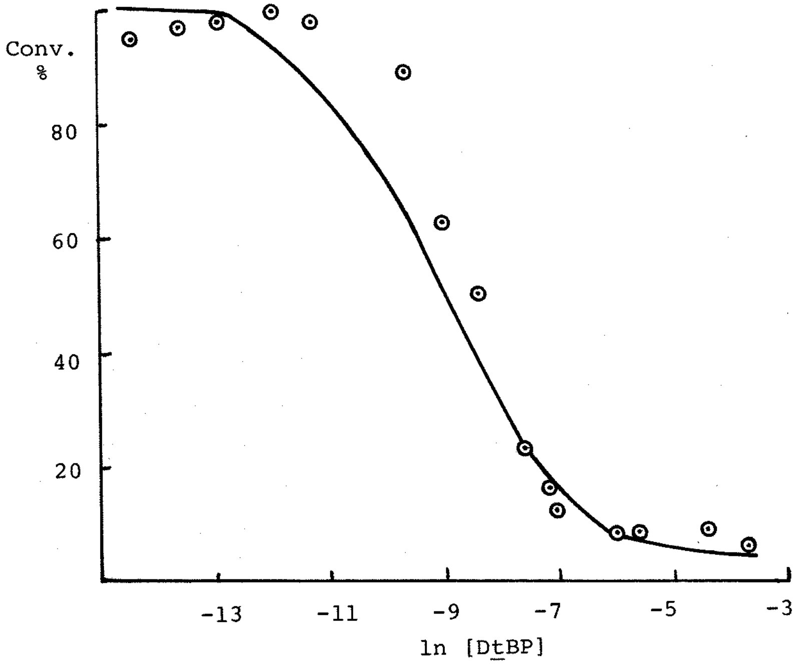

FIG. 2. Limiting αMeSt conversion as a function of the logarithm of DtBP concentration. ([αMeSt] = 0.512 M; [$SnCl_4$] = 1.42 × 10^{-3} M; CH_2Cl_2 solvent, -60°C.) The circles are experimental points; the line has been calculated as described in Ref. 5.

conversion sharply decreases with increasing amounts of DtBP. The position of the sharp change is affected by the concentrations of $SnCl_4$ and "H_2O" which together determine the amount of carbenium ions. The fact that polymerizations could not be completely stopped, even in the cases when the amount of the DtBP was comparable to that of the monomer, suggests that some kind of free-protonless initiation by "H_2O" may occur, probably via a concerted mechanism.

In a separate set of experiments at -60°C we deliberately added water to charges (containing [$SnCl_4$] = 1.03 × 10^{-3} M, [DtBP] = 1.8 × 10^{-3} M; [αMeSt] = 0.924 M in CH_2Cl_2) so as to have [H_2O] between 4.44 × 10^{-7} to 4.44 × 10^{-6} M in excess of what was initially present in the form of impurities "H_2O." Limiting conversions were about 6-8%, which implies that the DtBP concentration in the system was sufficient to compensate the increased initiation efficiency caused by the added water.

According to our investigations, the ^1H NMR spectrum of DtBP remains unchanged upon the addition of excess $SnCl_4$ in dry CH_2Cl_2 solvent, i.e., DtBP and $SnCl_4$ do not interact under these conditions;

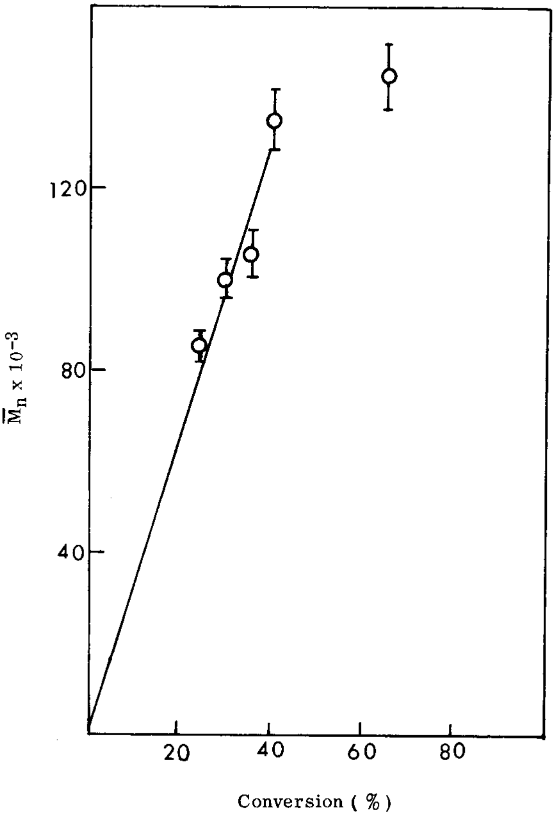

FIG. 3. Dependence of PαMeSt $\overline{M}_n$ on conversion during polymerization. ([αMeSt] = 0.924 M, [$SnCl_4$] = 3.51 × 10^{-3} M, [DtBP] = 1.2 × 10^{-3} M; CH_2Cl_2 solvent, -60°C.)

however, in the presence of moisture $DtBP^{\oplus}H$ is formed as indicated by the appearance of an absorption band at 3335 cm^{-1} in the IR spectrum characteristic of unbonded –NH– stretching vibrations in pyridine derivatives.

Mechanistic Aspects

Key features of the polymerization of αMeSt by the "H_2O"/$SnCl_4$ initiating system in the presence of DtBP are as follows: The rate approaches zero before monomer consumption is complete (Fig. 1). The conversion vs time curves are independent of the initial

TABLE 1. Effect of DtBP Concentration on α-Methylstyrene Polymerization (CH_2Cl_2, -60°, 30 min, total volume 30 mL)

[αMeSt] (M)	[$SnCl_4$] (M × 10^3)	[DtBP] (M × 10^3)	$\xi_\infty \times 10^2$ (%)	$\overline{M}_n \times 10^3$
0.924	1.03	0	100	10
"	"	0.0012	97	80
"	"	0.0600	89	110
"	"	0.1200	62	130
"	"	0.4800	23	110
"	"	1.2000	7	60
"	"	3.6000	8	40
"	"	12.0000	9	15
"	"	24.0000	6	9

monomer concentration but they strongly depend on the concentration of the initiator and DtBP. Conversion increases with the amount of $SnCl_4$ and is inversely proportional with the amount of DtBP. Also, the initial rate of polymerization increases with increasing $SnCl_4$ concentration (a similar observation was made by Villesange [4] with the "H_2O"/n-BuO·$TiCl_3$/αMeSt/CH_2Cl_2/-70°C system).

Figure 2 shows the dependence of the limiting conversion on the logarithm of [DtBP] and it indicates an inflection at medium [DtBP]. At low [DtBP] the limiting conversion is constant and high; at high [DtBP] the limiting conversion is low and constant. The polymerization is not completely inhibited even in the presence of large amounts of DtBP; the limiting conversion is finite and independent of [DtBP].

Molecular weights increase with increasing polymerization time, i.e., with increasing conversions (Fig. 3), and also tend to a limiting value. The dependence of the limiting molecular weights on DtBP concentration (data in Tables 1 and 2 plotted in Fig. 4) shows a maximum at medium [DtBP]. Also, the limiting molecular weights are constant at very low and very high DtBP concentrations. Polydispersities, as shown in Table 2, decrease with increasing [DtBP].

A mechanistic scheme that explains these observations has been developed [5]. The scheme involves fast initiation (an assumption substantiated by Fig. 3 and by Sigwalt et al.'s data [6] obtained in the "H_2O"/$SnCl_4$/indane system) in the absence of protons, the formation of a complex between the growing chain ends and DtBP, termination only by DtBP, and reduced chain transfer to monomer. Details of the mechanism together with the kinetic analysis will be described separately [5].

TABLE 2. Effect of Monomer, Coinitiator, and DtBP Concentration on α-Methylstyrene Polymerization (polymerization time 30 min, -60° C, CH_2Cl_2, total volume 30 mL)

$[M]_0$ (mol × 10^3)	$[SnCl_4]$ (mol × 10^5)	[DtBP] (mol × 10^5)	$\xi_\infty \times 10^2$	$\overline{M}_n \times 10^{-3}$	$\overline{N}^a$ (mol × 10)	$\overline{M}_w/\overline{M}_n$
23.04	3.1	-	100	50	500	
"	3.1	5.8	3.5	64	15	1.77
"	6.2	5.8	5.6	90	16	1.72
"	12.3	5.8	20	108	50	1.83
"	18.5	5.8	23	125	50	1.66
"	6.2	2.9	39	130	82	1.82
"	6.2	8.7	5.2	85	17	1.69
"	6.2	11.4	4.7	83	16	1.68
"	6.2	14.5	4.0	60	18	1.64
"	6.2	17.3	3.0	50	16	1.59
7.68	6.2	5.8	5.3	40	13.2	1.40
11.52	6.2	5.8	5.3	64	12.0	1.46

[a] N = Number of moles of PαMeSt

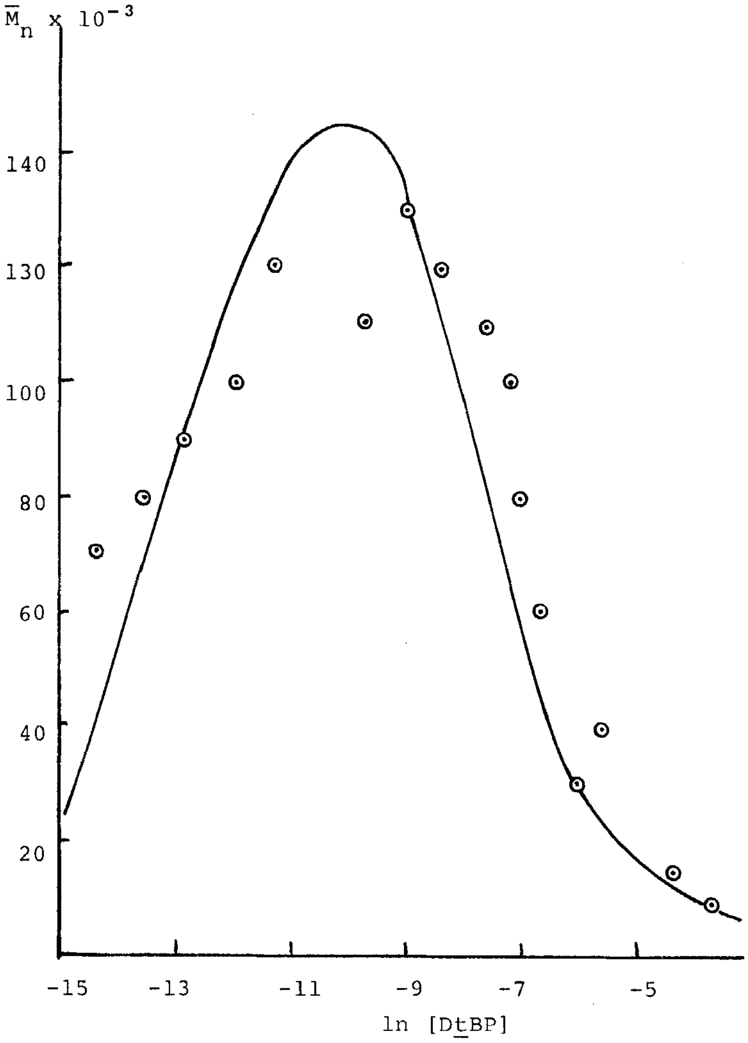

FIG. 4. PαMeSt $\overline{M}_n$ as a function of the logarithm of [DtBP]. ([$SnCl_4$] = 1.03 × 10^{-3} M, [αMeSt] = 0.924 M, CH_2Cl_2 diluent, -60°C.) The circles are experimental points; the line has been calculated as described in Ref. 5.

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