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Carbocationic Polymerization in the Presence of Sterically Hindered Bases. I. α-Methylstyrene Polymerization in the Presence of Sterically Hindered Bases*

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ABSTRACT

The effect of the sterically hindered base 2,6-di-tert-butylpyridine (DtBP) on the polymerization of α-methylstyrene (αMeSt initiated by "H_2O"/BCl_3 in a wide temperature range) has been investigated. αMeSt polymerizations carried out under identical conditions except in the presence of DtBP give much lower yield, much higher molecular weight, and noticeably narrower distributions than those obtained in the absence of this hindered base. The possibility of DtBP acting as an inhibitor is ruled out. Yields, molecular weights, and molecular weight distributions virtually do not change by changing DtBP concentration from 1.0×10^{-1} to 1.0×10^{-3} M. Differences in conversion levels do not explain the observed phenomena. PαMeSt samples obtained in the presence of trace amount of DtBP were of much higher molecular weight than those prepared in the absence of hindered pyridine, even at the same conversion level. These findings are explained by proposing that DtBP is a

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specific proton scavenger able to trap protons emerging during chain transfer to monomer, and that other elementary events remain unaffected by the presence of this hindered base.

INTRODUCTION

In a series of pioneering publications [1-3], Brown showed that DtBP exhibits extraordinary specificity toward protons. These reports intrigued us and we decided to elucidate the effect of sterically hindered bases on select carbocationic polymerization systems. Specifically, we investigated the possibility of intercepting protons proposed to arise during chain transfer to monomer by DtBP. This article concerns preliminary investigations on the effect of DtBP on αMeSt polymerizations induced by the "H_2O"/BCl_3 initiating system.

EXPERIMENTAL

Polymerizations were carried out under N_2 atmosphere in a stainless steel enclosure. GPC measurements were carried out using five μ-styragel columns (10^6, 10^5, 10^4, 10^3, 500 Å) and a Waters R401 differential refractometer at 25°C. Sample concentrations were 0.1-0.2 wt% in THF and flow rate was 2.0 mL/min. The column set was calibrated with polystyrene standard (Water Inc.).

RESULTS AND DISCUSSION

The polymerization of αMeSt by the "H_2O"/BCl_3 initiating system in CH_2Cl_2 diluent in the -20 to -60°C range is profoundly affected by DtBP. Table 1 and Fig. 1 show representative data. Conversions obtained in the absence of DtBP were invariably 100%. Polymerizations were extremely rapid and complete conversions were reached a few seconds after BCl_3 addition. In contrast, under identical conditions, except in the presence of 2.5×10^{-2} M DtBP, much reduced conversions were obtained, i.e., 3.4% at -20°C to 58.3% at -60°C. As to molecular weights, $\overline{M}_n$ and $\overline{M}_w$ were much lower in the absence than in the presence of DtBP over the whole temperature range. Molecular weights increase by decreasing temperature (see Fig. 1), a phenomenon routinely observed in carbocationic polymerizations. While the molecular weights obtained in the presence of DtBP are about an order higher than those obtained in the absence of this hindered pyridine, the slopes of the Arrhenius lines in Fig. 1 are within experimental variation. Similarity in ΔH values (ΔH_a, control

TABLE 1. The Effect of DtBP on α-Methylstyrene Polymerization ($[M] = 0.62$ $\underline{M}$, $[BCl_3] = 1 \times 10^{-2}$ $\underline{M}$, CH_2Cl_2 solvent; in the experiments with *, $[DtBP] = 2.6 \times 10^{-2}$ $\underline{M}$ was used)

Sample	T (°C)	Conversion (%)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	Yield/$\overline{M}_n$ (mol)	No. of chain[a] transfers per kinetic chain
1	-20	100	2.0×10^3	5.2×10^3	2.7	9.1×10^{-4}	162
1*	"	8.4	2.9×10^4	4.8×10^4	1.6	5.6×10^{-6}	
2	-30	100	4.0×10^3	1.4×10^4	3.5	4.3×10^{-4}	82
2*	"	12.0	4.4×10^4	7.1×10^4	1.6	5.2×10^{-6}	
3	-40	100	6.8×10^3	2.5×10^4	3.7	2.8×10^{-4}	40
3*	"	22.5	6.2×10^4	1.1×10^5	1.8	7.0×10^{-6}	
4	-50	100	1.1×10^4	4.1×10^4	3.9	1.7×10^{-4}	27
4*	"	42.0	1.3×10^5	2.1×10^5	1.6	6.2×10^{-6}	
5	-60	100	2.1×10^4	7.8×10^4	3.6	9.0×10^{-5}	15
5*	"	58.3	1.9×10^4	3.1×10^5	1.6	6.0×10^{-6}	

[a] Comparison between yield/$\overline{M}_n$ values in the absence and presence of DtBP.

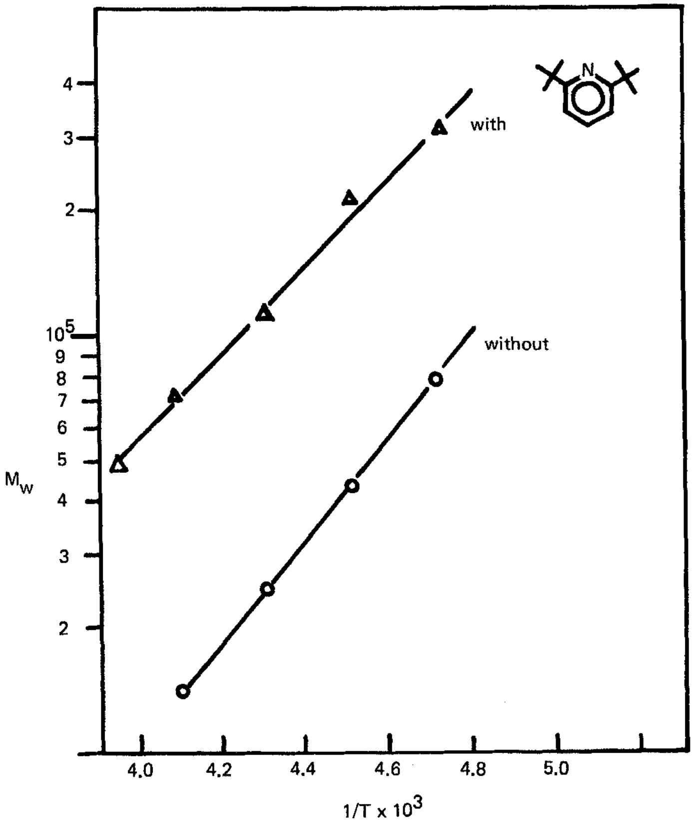

FIG. 1. Effect of temperature on $\overline{M}_w$ of PαMeSt in the presence and absence of DtBP. ([αMeSt] = 0.62 M, [BCl_3] = 1.0×10^{-2} M, DtBP = 2.6×10^{-2} M, CH_2Cl_2, 5 min.)

= -5.6 ± 0.5; ΔH_a, DtBP = 4.8 ± 0.5 kcal/mol) suggests that the overall molecular weight determining mechanisms are probably identical. Interestingly, DtBP also affects polymer polydispersity $\overline{M}_w/\overline{M}_n$. For example, $\overline{M}_w/\overline{M}_n$ = 1.5-1.8 in the presence of DtBP.

These results can be explained by assuming highly specific proton scavenging by DtBP during chain transfer to monomer. The low yields obtained in the presence of DtBP are due to proton trapping during the first chain transfer to monomer step. The kinetic chain cannot progress beyond the first chain transfer event because the chain carrier, a species akin to proton momentarily emerging during proton elimination, is immediately trapped by DtBP. The narrower

TABLE 2. The Effect of DtBP Concentration on α-Methylstyrene Polymerization ([αMeSt] = 0.62 M, [BCl_3] = 5×10^{-3} M, CH_2Cl_2, -60°C)

Sample	[DtBP] (M)	$\frac{[BCl_3]}{[DtBP]}$	Conversion (%)	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
1	1.0×10^{-1}	0.17	54.2	1.0×10^5	1.5×10^5	1.50
2	2.0×10^{-2}	9.14	53.3	8.7×10^4	1.4×10^5	1.48
3	3.8×10^{-2}	1.3	51.6	3.6×10^4	1.4×10^5	1.48
4	2.0×10^{-3}	2.5	52.6	1.3×10^5	1.8×10^5	1.42
5	1.0×10^{-3}	5	56.7	1.1×10^5	1.6×10^5	1.51
6	4.8×10^{-4}	10.6	100	6.8×10^4	1.2×10^5	1.74
7	2.0×10^{-4}	25.5	100	5.4×10^4	8.2×10^4	1.78
8	1.0×10^{-4}	51	100	3.8×10^4	6.9×10^4	1.84
9	0	-	100	1.2×10^4	4.2×10^4	3.4

MWD's and higher MW's are consequences of suppressed chain transfer to monomer.

According to the last two columns in Table 1, the number of molecules (yield/$\bar{M}_n$) obtained in the absence of DtBP decreases with decreasing temperature, indicating the "freezing out" of chain transfer. In contrast, the number of molecules obtained in the presence of DtBP remains largely unaffected (yield/$\bar{M}_n = 5\text{-}7 \times 10^{-6}$) over the whole temperature range. Dividing the number of molecules obtained in the presence and absence of DtBP and assuming that chain transfer to monomer is absent in the presence of DtBP gives the number of chain transfer per kinetic chain in the "control" run.

The possibility that decreased conversions obtained in the presence of DtBP may be due to inhibition can be discounted. A series of polymerizations has been carried out in which [DtBP] was varied from 1.0×10^{-1} M to zero. Table 2 shows representative data. Yields, molecular weights, and their distributions remain virtually unchanged in the presence of [DtBP] $> 1.0 \times 10^{-3}$ M. If DtBP were an inhibitor or retarder, these parameters would have been affected by increasing [DtBP] by more than two orders of magnitude.

The dramatic differences in yields, molecular weights, and molecular weight distributions have been obtained on polymers prepared at quite different conversion levels. Samples obtained in the absence of DtBP always gave complete conversions whereas those prepared in the presence of DtBP yielded much lower conversions. That differences in conversion levels do not explain the observed phenomena are indicated by independent experiments. Results of these studies are included in Table 2 and will be discussed in later papers.

Experimentation with hindered pyridines promises to be of great value of mechanistic studies in cationic polymerization and is being pursued with vigor.

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