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Carbocationic Polymerization in the Presence of Sterically Hindered Bases. V. The Polymerization of α-Methylstyrene by the "H_2O"/BCl_3 Initiating System

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ABSTRACT

The influence of 2,6-di-tert-butylpyridine (DtBP) on the polymerization of α-methylstyrene (αMeSt) induced by the "H_2O"/BCl_3 initiating system in the -20 to -60°C range has been studied in detail. Adventitious H_2O ("H_2O") is the initiating cationogen and initiation most likely proceeds by a concerted route in the absence of free protons or the acid $H^{\oplus}BCl_3OH^{\ominus}$. Polymerizations are extremely rapid and kinetic termination is absent (conversions are 100%) in the absence of DtBP. In the presence of DtBP, polymerizations are still very fast; however, conversions are reduced. Significantly, conversions increase with decreasing temperatures, which suggests the operational presence of terminative proton entrapment. Molecular weights increase with decreasing temperatures in the presence and absence of DtBP and the slopes of the linear Arrhenius plots ($\ln \overline{M}_w$ versus 1/T) are parallel; the molecular weights obtained in the presence of DtBP are close to a factor of 10 higher than those produced in the absence of this hindered pyridine. The virtual identity of the slopes of Arrhenius plots indicates close

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similarity between the nature and rate of molecular-weight-determining events in the absence and presence of DtBP, i.e., $k_p/k_{tr,M}$ and $k_p/k_{tr,G^{\ominus}}$. DtBP profoundly affects molecular weight dispersity: $\overline{M}_w/\overline{M}_n$ = 3.0-4.0 in the absence of DtBP whereas $\overline{M}_w/\overline{M}_n$ = 1.5-1.8 in the presence of DtBP. The number of polymer molecules formed (yield/$\overline{M}_n$) in the absence of DtBP decreases with decreasing temperatures while those formed in the presence of DtBP remain constant. According to Mayo, ($1/\overline{DP}_n$ versus $1/[M]$) plots chain transfer to monomer in the presence of DtBP is very low ($k_{tr,M}/k_p = 6.4 \times 10^{-4}$ and 2.8×10^{-4} at -30 and -50°C) but not zero. Conceivably two kinds of chain transfer to monomer reactions may exist (direct and indirect) and only one (i.e., the indirect one) may be trappable by DtBP. The effect of [DtBP] on the percent conversion and $\overline{M}_n$ was investigated: Above a fairly well defined [DtBP], neither conversions nor $\overline{M}_n$'s were affected by [DtBP]. With increasing [DtBP] molecular weight dispersions rapidly decrease and $\overline{M}_w/\overline{M}_n$'s seem to level off at ~ 1.5 at relatively high [DtBP]. Changing the polarity of the solvent characteristically affects the mechanism of αMeSt polymerization in the presence and absence of DtBP. While increasing the solvent polarity in the absence of DtBP results in a strong increase in $\overline{M}_w/\overline{M}_n$ (from ~1.5 to ~4.0), in the presence of DtBP $\overline{M}_w/\overline{M}_n$ remains virtually unchanged at ~1.5.

INTRODUCTION

Preliminary experiments with the "H_2O"/BCl_3/αMeSt/CH_2Cl_2 system have shown that DtBP dramatically affects conversion, molecular weights, and molecular weight distributions (MWD) [1, 2], and that at least some of the effects could only be explained by proton trapping. Thus it was decided to investigate in depth the influence of hindered bases in general and DtBP in particular on the polymerization of αMeSt induced by a variety of initiating systems under various conditions. This paper concerns a detailed description of rate, molecular weight, and MWD phenomena observed during the polymerization of αMeSt by the "H_2O"/BCl_3 initiating system in CH_2Cl_2 solvent in the presence and absence of DtBP, and an attempt to outline a mechanism that explains the observations.

EXPERIMENTAL

Materials

α-Methylstyrene (αMeSt) was washed successively with dilute NaOH and distilled water. It was refluxed over CaH_2 and freshly distilled before use. Boron trichloride (99.9% C.P. grade, Linde Division, Union Carbide Co.) was used as received. Initially 2,6-di-tert-butylpyridine (DtBP) (ICN Inc., 99% purity) was dried with CaH_2 and distilled under reduced pressure; later experience showed that distillation over CaH_2 was unnecessary so that DtBP was used as received.

Polymerization

Polymerizations were carried out under nitrogen atmosphere ($<$ 100 ppm moisture level) in culture tubes in a stainless steel enclosure [1]. CH_2Cl_2, αMeSt, and DtBP were pipetted into the culture tubes, capped, and cooled to the desired temperatures. Reactions were started by addition of a solution of BCl_3 in CH_2Cl_2. Polymerizations were stopped by the addition of a few milliliters of prechilled methanol. Volatile products were evaporated and the polymer was dried to constant weight at 50°C in a vacuum oven.

The series of experiments in which $[H_2O]$ was varied was carried out by mixing suitable amounts of "wet" and "dry" CH_2Cl_2. The "wet" CH_2Cl_2 was prepared by adding 0.2 μL H_2O to 100 mL driest CH_2Cl_2 and shaking for 12 h at room temperature.

Measurements

$\overline{M}_n$'s were determined by the use of a Hewlett-Packard osmometer (Model 503) with an S-08 membrane and toluene at 37°C. $\overline{M}_w$'s were determined by a SOFICA light-scattering photometer at 4358 Å using toluene at 25°C. The refractive index increment of PαMeSt in toluene is 0.137 cm^3/g at 4358 Å. Measurements were made between 30 and 150° angles at four different concentrations per sample. Intrinsic viscosities were determined by the use of a low shear capillary Ubbelohde viscometer in toluene at 31°C. Measurements in the concentrations range from 0.1 to 1.0% were extrapolated to infinite dilution by means of linear η_{sp}/c against c plots.

GPC measurements were carried out using five μ-Styragel columns (10^6, 10^5, 10^4, 10^3, 500 Å), a Waters R401 differential refractometer at 25°C, and a Waters 440 (254 nm) UV absorbance detector. Sample concentrations were from 0.1 to 0.2 wt% in tetrahydrofuran and the flow rate was 2.0 mL/min. Since PαMeSt with narrow MWD could not be obtained in a wide range of molecular weights, the column set was calibrated by polystyrene standards (Waters Inc.)

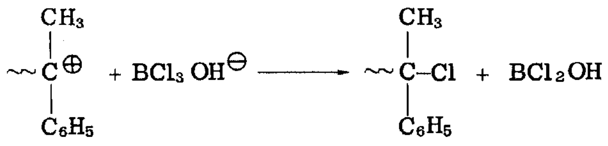
To ascertain the accuracy of our molecular weight data (and to reinforce the conclusions derived from them), a series of samples has been analyzed simultaneously by GPC and absolute (colligative) techniques, i.e., osmometry and light scattering. Results are compiled in Table 1. The agreement between $\overline{M}_n$ and $\overline{M}_w$ data obtained by GPC on the one hand and $\overline{M}_n$ (osmometry) and $\overline{M}_w$ (light scattering, LS) on the other hand is satisfactory. Molecular weights obtained by GPC are somewhat lower than those generated by the absolute methods. The difference may be at least partly due to the fact that the GPC calibration was carried out with standard PSt samples (see Experimental) and not with PαMeSt samples.

RESULTS AND DISCUSSION

1. Kinetic Studies and the Effect of Reaction Conditions on the Polymerization of αMeSt in the Absence and Presence of DtBP

A. Initiation in the "H_2O"/BCl_3/αMeSt System in the Presence of DtBP: The Role of H_2O

Stopping experiments carried out under super-dry high-vacuum conditions have shown that H_2O is the true cationogen (initiating species) in the "H_2O"/BCl_3/i-C_4H_8 system [3] (the quotation marks "H_2O" indicate that the source of moisture is impurities) and that limited isobutylene conversions are due to termination by chlorination of the propagating carbocation [4]. In contrast, the role of H_2O has not yet been elucidated by stopping experiments for the "H_2O"/BCl_3/αMeSt system. Results of repeated experiments carried out in open systems in a dry box under a nitrogen atmosphere have shown (see Sections I-B, I-C, and I-D) that polymerizations rapidly reach 100% in these systems, i.e., termination is absent, over a broad temperature range. Termination by chlorination is absent in these αMeSt polymerizations because even if chlorination did occur:



$$\sim\sim\overset{CH_3}{\underset{C_6H_5}{C^{\oplus}}} + BCl_3OH^{\ominus} \longrightarrow \sim\sim\overset{CH_3}{\underset{C_6H_5}{C}}\text{–}Cl + BCl_2OH$$

TABLE 1. Characterizations of PαMeSt Obtained at Different Conversions ([αMeSt] = 0.62 $\underline{M}$, [BCl_3] = 5.0 × 10^{-3} $\underline{M}$, -55°C, CH_2Cl_2)

Sample	[DtBP] ($\underline{M}$)	Conversion (%)	$\overline{M}_n \times 10^{-4}$	$\overline{M}_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$ (GPC)	$\overline{M}_n \times 10^{-4}$ (osmometry)	$\overline{M}_w \times 10^{-4}$ (LS)	$\overline{M}_w/\overline{M}_n$	$[\eta]^a$ (dL/g)
1	7.7×10^{-3}	41	16.5	25.8	1.57	19.2	28.4	1.48	0.79
2	2.5×10^{-4}	68	13.8	22.2	1.61	16.5	24.8	1.50	0.71
3	"	84	11.9	18.9	1.59	14.6	22.1	1.51	0.65
4	"	100	8.9	14.7	1.65	10.6	19.4	1.8	0.59
5	0	100	1.8	6.3	3.5	(1.5~3)	6.4	>3	0.24

[a] $[\eta_{sp}/c]_{c \to 0}$, toluene, 31°C.

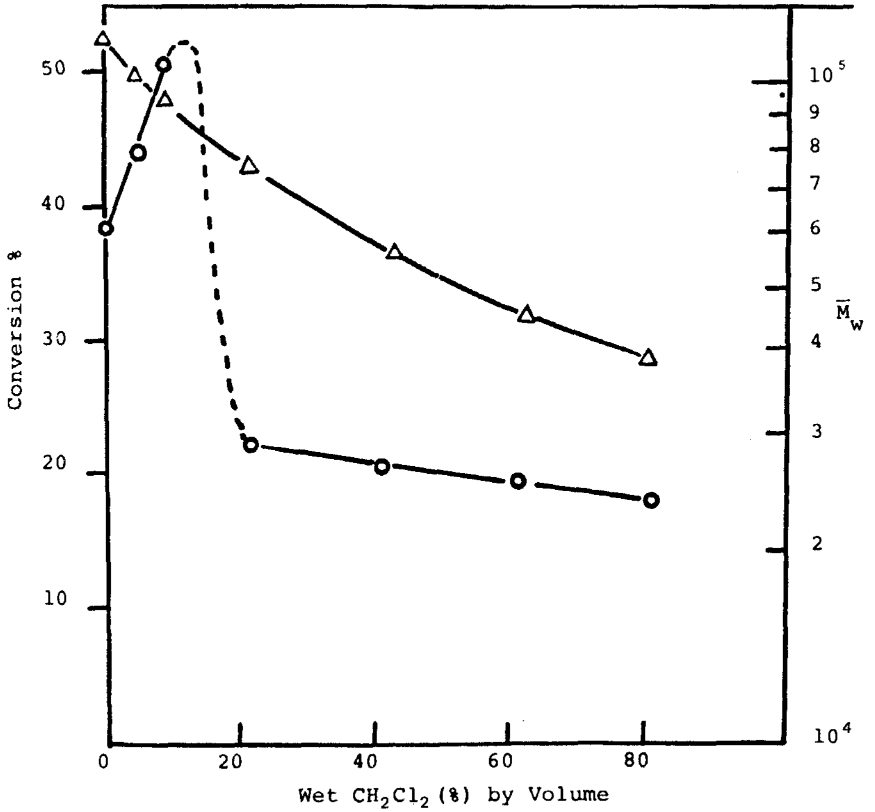
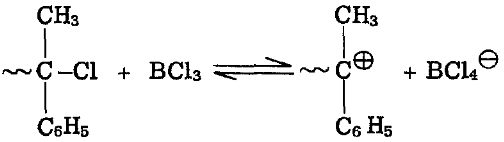


FIG. 1. Effect of H_2O concentration on αMeSt polymerization in the presence of DtBP. ([BCl_3] = 5.0 × 10^{-3} M, [DtBP] = 7.7 × 10^{-3} M, [αMeSt] = 0.62 M, -50°C, 5 min, CH_2Cl_2 solvent).

sufficient BCl_3 would be available in the system to reinitiate the kinetic chain:



$$\sim\!\!\sim \overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{\overset{|}{\underset{|}{C}}}}-Cl + BCl_3 \rightleftharpoons \sim\!\!\sim \overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{\overset{|}{\underset{|}{C}}}}^{\oplus} + BCl_4^{\ominus}$$

Thus in the absence of kinetic termination, polymerizations rapidly go to completion. In the presence of DtBP, conversions cannot reach

TABLE 2. Effect of Solvent Purification on αMeSt Polymerization in the Presence of DtBB ([αMeSt] = 0.32 M, [BCl_3] = 5.0×10^{-3} M, [DtBP] = 5.0×10^{-3} M, CH_2Cl_2, -60°C, 5 min)

Sample	Conversion (%)	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$	Yield/$\overline{M}_n$ (M)
1 CaH_2	54.2	1.1	1.58	2.0×10^{-4}
2 CaH_2 + Na	24.5	1.1	1.52	9.0×10^{-5}

100% because chain transfer to monomer is aborted by terminative proton entrapment, i.e., the proton is intercepted by the DtBP during chain transfer to monomer. Since the polymerization of αMeSt can be stopped at limited conversions by the use of DtBP, the effect of H_2O in the "H_2O"/BCl_3/αMeSt system can be investigated conveniently and rapidly in "open" systems, i.e., not under super-dry high-vacuum conditions, and experiments along these lines have been carried out.

Thus αMeSt polymerizations have been carried out in the presence of different quantities of H_2O (introduced by employing different quantities of "wet" CH_2Cl_2, see Experimental), and the conversions and molecular weights were determined. Figure 1 shows conditions and results.

Conversions first increased from 38 to 52%, then decreased by increasing the H_2O content. Simultaneously, the $\overline{M}_w$'s monotonously decreased from 1.1×10^5 to 3.8×10^4 and the MWD's remained quite narrow $\overline{M}_w/\overline{M}_n = 1.5\text{-}1.7$.

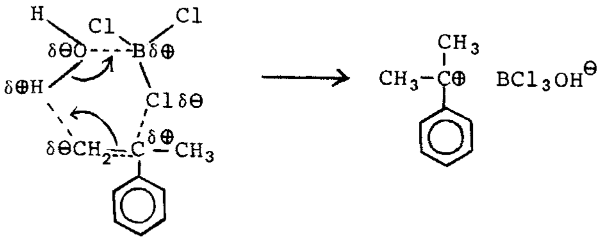
Water plays a dual role in many carbocationic polymerizations: at low concentrations it may be a needed initiator; however, at higher concentrations it often functions as a chain-breaking agent (chain transfer agent and terminating agent). The conversion profile in Fig. 1 which first shows an ascending branch followed by a sharp break and a descending branch may reflect this situation. The monotonically descending $\overline{M}_w$ profile suggests chain breaking with increasing [H_2O]. In the presence of DtBP, terminative proton entrapment operates which would also contribute to the low yields obtained at higher [H_2O].

Table 2 shows the results of another experiment in which αMeSt polymerizations were carried out by the use of solvents dried to different extents. The CH_2Cl_2 of Sample 1 was dried by distillation over CaH_2 whereas that of Sample 2 was further dried by treatment with a Na dispersion (twice, on vacuum line). The conversion was much lower in the experiment with the better dried solvent. Evidently H_2O is the initiator in the "H_2O"/BCl_3/αMeSt/CH_2Cl_2 system.

If each initiator H_2O molecule produces one polymer chain in the presence of DtBP, the number of polymer chains should be equal to the concentration of the H_2O in the system. We found ["H_2O"] = 2-3 × 10^{-4} M by this method. Interestingly, using the same purification method, Higashimura [5] reported that the water concentration in a very similar system determined by the Karl-Fisher method was 2-3 × 10^{-4} M. This is indirect evidence that most chain transfer to monomer was eliminated by DtBP.

The fact that polymerization occurs in the "H_2O"/BCl_3/αMeSt/CH_2Cl_2 system in the presence of DtBP under conventional laboratory conditions suggests that "H_2O" is the initiating cationogen and that DtBP does not interfere with initiation. Since DtBP is a most efficient proton trap, initiation cannot proceed by protonation involving the hypothetical acid $H^{\oplus}BCl_3OH^{\ominus}$. On the basis of these and similar observations with other Friedel-Crafts acid systems, it is postulated that initiation occurs probably by a concerned process in which free protons are absent:

$$H_2O + BCl_3 \rightleftharpoons H_2O\cdot BCl_3 \xrightarrow{+\ \alpha MeSt}$$



B. The Effect of Temperature

The polymerization of αMeSt using the "H_2O"/BCl_3 initiating system and CH_2Cl_2 diluent in the -20 to -60°C range is profoundly affected by the presence of DtBP. Table 3 and Figs. 2 and 3 show representative conversion and molecular weight data. Conversions obtained in the absence of DtBP were invariably 100% over the whole temperature range investigated. Polymerizations were very rapid and complete, and conversions were reached a few seconds after BCl_3 addition at every temperature. In contrast, under identical conditions except in the presence of 2.6 × 10^{-2} M DtBP, much reduced conversions were obtained (Fig. 2). Dependent of the temperature, conversions ranged from 8.4% 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. The effect of temperature on molecular weights is shown by the Arrhenius plot in

TABLE 3. The Effect of DtBP on α-MeSt Polymerization ([DtBP] = 2.6 × 10^{-2} M, [BCl_3] = 1.0 × 10^{-2} M, [αMeSt] = 0.62 M, CH_2Cl_2, 5 min)

Sample	T (°C)	Conversion (%)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$ (± 0.15)	Yield/$\overline{M}_n$ (mol × 10^6)	No. of chain[a] transfers per kinetic chain
1	-20	100	2.0	5.2	2.7	910	162
DtBP	"	8.4	29	48	1.6	5.6	
2	-30	100	4.0	14	3.5	430	82
DtBP	"	12.0	44	71	1.6	5.2	
3	-40	100	6.8	25	3.7	280	40
DtBP	"	22.5	62	110	1.8	7.0	
4	-50	100	11	41	3.9	170	27
DtBP	"	42.0	130	210	1.6	6.2	
5	-60	100	21	78	3.6	90	15
DtBP	"	58.3	190	310	1.6	6.0	

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

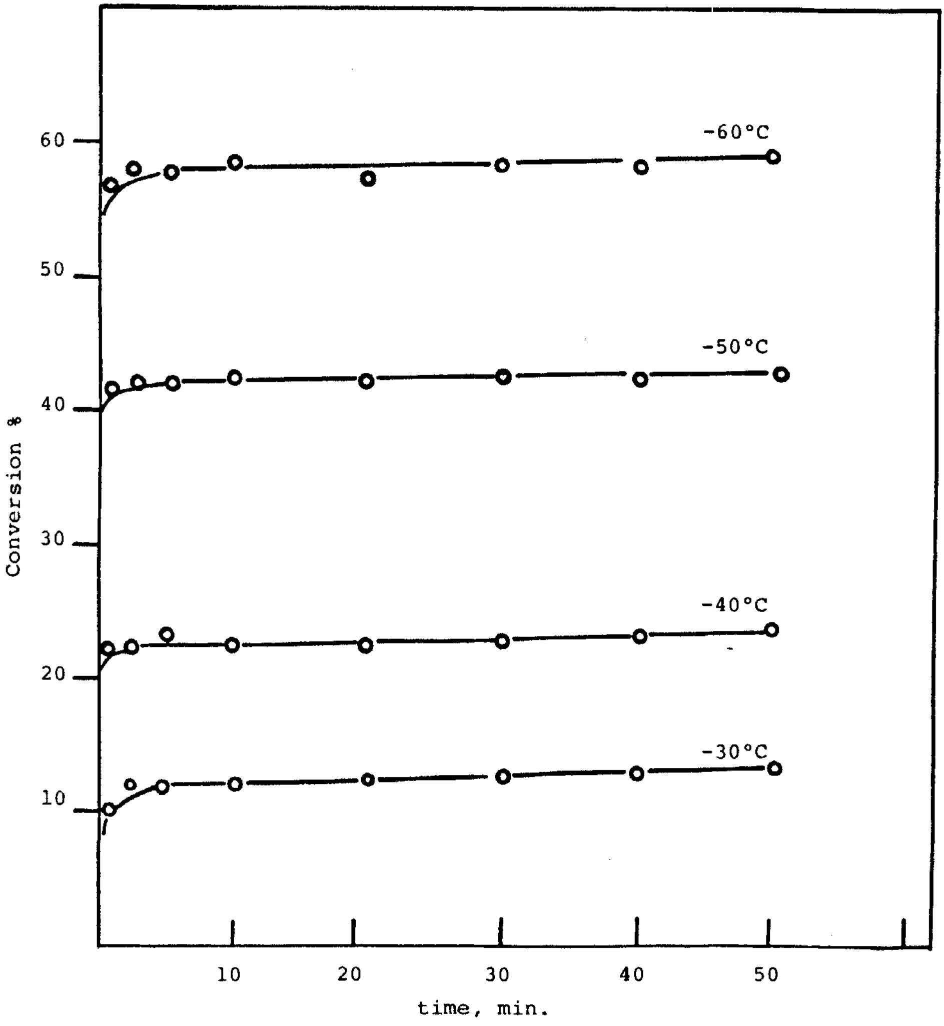


FIG. 2. Conversion versus time plots of αMeSt polymerization in the presence of DtBP at various temperatures. ([αMeSt] = 0.62 M [BCl_3] = 1.0 × 10^{-2} M, [DtBP] = 2.6 × 10^{-2} M, CH_2Cl_2 solvent.)

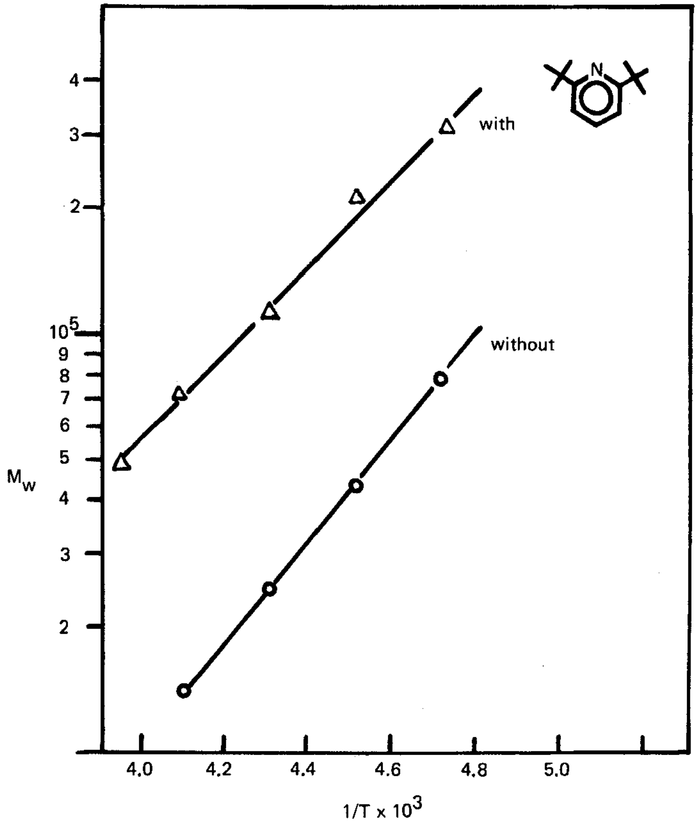


FIG. 3. Effect of temperature on $\overline{M}_w$ of PαMeSt in the presence and absence of DtBP. ([αMeSt] = 0.62 M, [BCl_3] = 1.0×10^{-2} M, [DtBP] = 2.6×10^{-2} M, CH_2Cl_2, 5 min.)

Fig. 3. Molecular weights increase by decreasing temperature, a phenomenon routinely observed in carbocationic olefin polymerization [6]. While the molecular weights obtained in the presence of DtBP are close to an order of magnitude superior to those obtained in the absence of this hindered pyridine, the slopes of the Arrhenius lines, representing the effect of temperature on polymer molecular weight, are identical within what is considered to be experimental variation. This similarity in slopes suggests that the overall molecular-weight-determining mechanisms in these systems are probably identical.

Interestingly, DtBP profoundly affects the polydispersity ratio $\overline{M}_w/\overline{M}_n$; thus $\overline{M}_w/\overline{M}_n$ = 3.0-4.0 in the absence of DtBP whereas $\overline{M}_w/\overline{M}_n$

= 1.6-1.8 in the presence of DtBP. The effect is dramatically illustrated in Fig. 4 which shows GPC traces of PαMeSt samples obtained in the absence and presence of DtBP at -30 and -60° C. The GPC traces of PαMeSt obtained in the presence of DtBP are symmetric and narrow while those obtained in the absence of DtBP are asymmetric and broad. The broad distribution and long tail at high elution volumes of the latter traces are most likely due to chain transfer during polymerization. Indeed, all these results can be explained by assuming highly specific proton scavenging (terminative proton entrapment) by DtBP during chain transfer to monomer (see also Fig. 7).

Thus the low yields obtained in the presence of DtBP are most likely due to proton trapping during the first chain transfer to monomer step. Evidently the kinetic chain cannot progress beyond the first chain transfer (i.e., proton loss/reprotonation) event because the chain carrier (i.e., proton emerging during proton elimination) is immediately trapped by the hindered pyridine. Obviously, the narrower MWD's and higher molecular weights are also consequences of intercepted chain transfer to monomer.

The last two columns in Table 3 give insight into the relative import of chain transfer to monomer at various temperatures and the chain transfer reducing effect of DtBP. The number of polymer molecules (yield/$\bar{M}_n$) obtained in the absence of DtBP decreased with decreasing temperatures, indicating the well-known phenomenon of "freezing out" chain transfer. In contrast, the number of molecules obtained in the presence of DtBP remains largely unaffected (yield/$\bar{M}_n$ = 5-7 × 10^{-6} mol = 2-3× 10^{-4} $\underline{M}$) over the whole temperature range. Dividing the number of molecules obtained in the absence of DtBP with that obtained in the presence of DtBP, and assuming that chain transfer to monomer is absent in the latter experiments, gives the number of chain transfer per kinetic chain in the "control" run. *According to this evidence, chain transfer to monomer can be* efficiently suppressed by the use of DtBP over a broad temperature range.

C. The Effect of Monomer Concentration: Investigation of Chain Transfer to Monomer by Mayo Plots

A cornerstone of the assumptions explaining the effects of DtBP on olefin polymerization is that chain transfer to monomer is essentially absent in the presence of this proton trap. The Mayo equation ($1/DP_n = k_{tr,M}/k_p + k_t/k_p \cdot 1/[M]$) has often been used to determine the relative extent of chain transfer to monomer to termination in cationic polymerizations [7, 8]. The absence of an intercept in the Mayo plot is experimental proof for the absence of chain transfer to monomer.

Polymerization of αMeSt in the absence of DtBP cannot be stopped at low conversion, and the construction of reliable Mayo plots becomes difficult. However, in the presence of DtBP, limited conversion

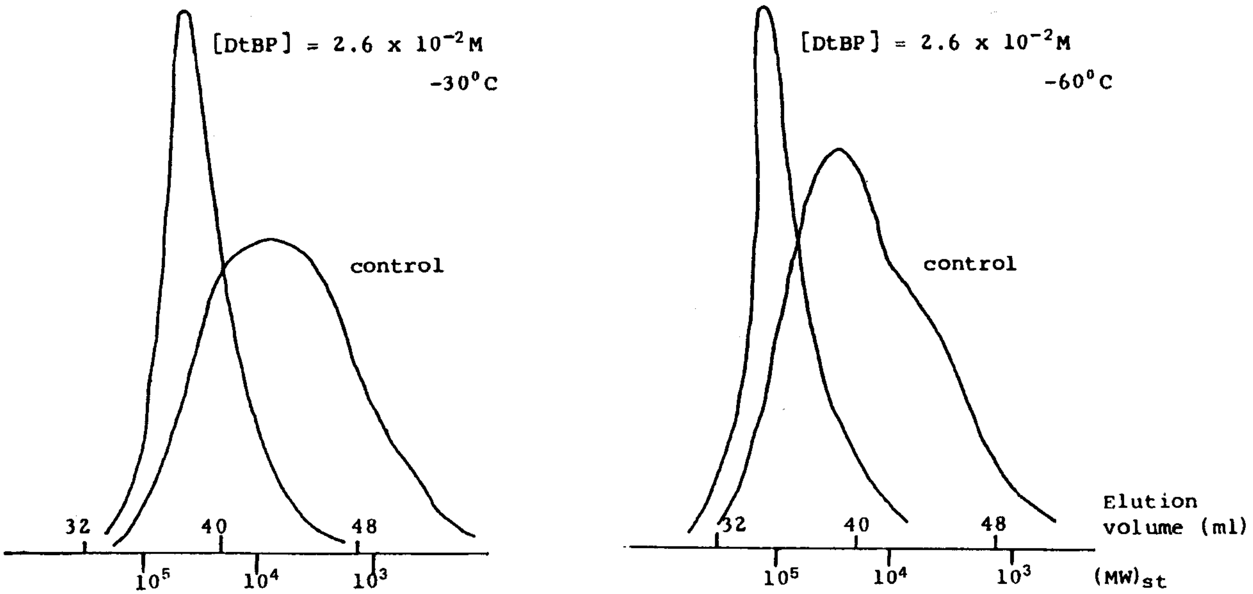


FIG. 4. Typical GPC traces of P(αMeSt) obtained in the presence and absence of DtBP (not normalized).

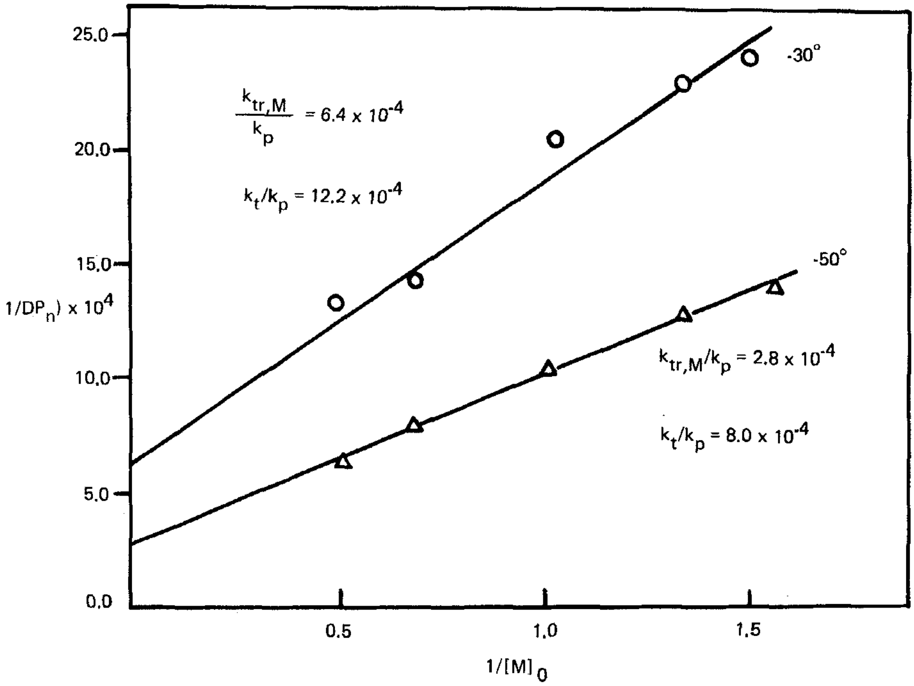


FIG. 5. Investigation of details of chain transfer by Mayo ($1/DP_n = k_{tr,M}/k_p + (k_t/k_p) \times 1/[M]$). ($[BCl_3] = 5.0 \times 10^{-3}$ M, [DtBP] = 7.7 $\times 10^{-3}$ M, CH_2Cl_2.) Solvent polarity was maintained by the use of n-hexane as compensating solvent. $\overline{M}_n$'s were determined by membrane osmometry.

can be obtained. Polymerizations were carried out in the presence of 7.7×10^{-3} M of DtBP at -30 and -50°C and according to the Mayo plots shown in Fig. 5 $k_{tr,M}/k_p = 6.4 \times 10^{-4}$ at -30°C and decreases to 2.8×10^{-4} at -50°C. Evidently a small extent of chain transfer to monomer might still survive even in the presence of DtBP.

It is interesting to speculate that there are two different chain transfer to monomer processes: indirect chain transfer to monomer or chain transfer by counteranion visualized to proceed by proton elimination/reprotonation which is trappable by DtBP:

$$\sim\!\sim C_n^{\oplus}G^{\ominus} \xrightarrow{k_{tr,G^{\ominus}}} \sim\!\sim C_n + H^{\oplus}G^{\ominus} \text{ (trappable proton)}$$

$$H^{\oplus}G^{\ominus} + M \xrightarrow{k_{ri}} HM^{\oplus}G^{\ominus}$$

and direct (concerted) chain transfer to monomer

$$\sim\!\sim C_n^{\oplus}G^{\ominus} + M \rightleftharpoons \left[\sim\!\sim C_n^{\oplus} M\, G^{\ominus}\right] \xrightarrow{k_{tr,M}} \sim\!\sim C_n$$

$$+\ HM^{\oplus}G^{\ominus}\ \text{(nontrappable carbocation)}$$

where $\sim\!\sim C_n^{\oplus}$ is the active propagating carbocation and $\sim\!\sim C_n$ is the "dead" chain after chain transfer to monomer.

Conceptually, the ternary complex $\sim\!\sim C_n^{\oplus}MG^{\ominus}$ proposed to arise in the course of direct chain transfer to monomer is very similar to those previously proposed by Fontana [9] to explain the kinetics of α-olefin polymerization initiated by $HBr/AlBr_3$, by Kennedy and Johnston [10] for isomerization polymerization of 4-methyl-1-pentene, and Kennedy et al. [11] for olefin polymerizations initiated with aromatic compounds. Although the indirect process is much more important than the direct one, the latter still cannot be neglected.

D. The Effect of DtBP Concentration: Conversion Studies

The critical reader may have noticed that all these dramatic differences in yields, molecular weights, and MWD's have been obtained on polymer prepared at quite different conversion levels: samples obtained in the absence of DtBP always reflected complete conversions whereas those prepared in the presence of DtBP formed at much lower conversions. Polymerization of αMeSt under the conditions employed in this research in the absence of DtBP is very difficult to stop (rapid quenching) at less than complete conversion. The question thus arises whether these observations are due to mere differences in conversions and DtBP functions as an inhibitor or retarder, or are these phenomena due to some other effect of DtBP which is independent of its inhibiting or retarding action.

To elucidate this question it was necessary to obtain and compare PαMeSt samples prepared at various conversion levels. Two series of experiments have been designed: In the first series the aim was to study the effect of [DtBP] on polymerization parameters, in particular, conversion. In the second, the aim was to obtain conversion versus time profiles and to characterize samples as to $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ obtained at various conversions.

In the first series of experiments the effect of [DtBP] on the polymerization details of αMeSt initiated by the "H_2O"/BCl_3 system has been investigated. Figure 6 shows conversions, $\overline{M}_n$'s, and $\overline{M}_w/\overline{M}_n$'s obtained as a function of [DtBP] from 0 to 1.10^{-1} M. Conversions were 100% in the range from [DtBP] = 0 to 4.8×10^{-4} M, whereas they decreased to ~ 55% and remained constant above

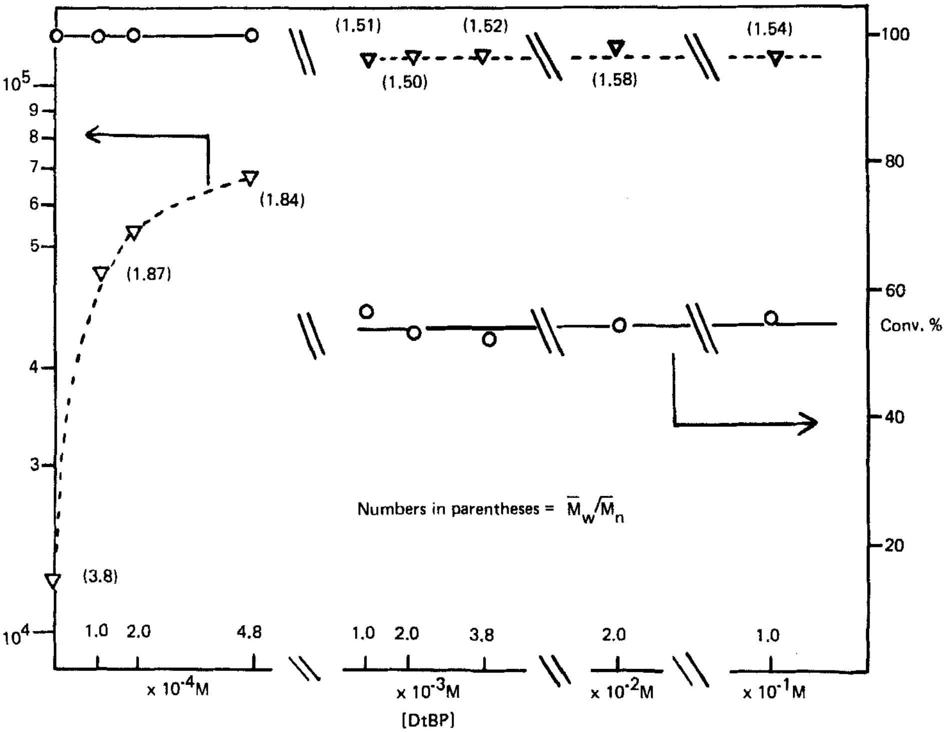


FIG. 6. Effect of [DtBP] on αMeSt polymerization. ([αMeSt] = 0.32 M, [BCl_3] = 5.0 × 10^{-3} M, CH_2Cl_2, -60°C, 5 min.)

[DtBP] = 1.10^{-3} M. Evidently [DtBP] ≈ 4.8 × 10^{-4} M was sufficient completely to suppress chain transfer to monomer. Simultaneously, $\overline{M}_n$'s increased from ~10^4 in the absence of DtBP to 1.1 × 10^5 at [DtBP] ~ 1.10^{-3} M, and remained at this high level even in the presence of large stoichiometric excess of [DtBP] over [BCl_3]. Concurrently, as shown by the GPC scans in Fig. 7, the MWD's gradually narrowed from ~3.8 in the control to ~1.5 at higher [DtBP].

Since polymerization of αMeSt readily proceeds to high molecular weights even in the presence of huge excesses of DtBP, this hindered amine cannot be an inhibitor or retarder of αMeSt polymerizations. Importantly, the $\overline{M}_n$'s and $\overline{M}_w/\overline{M}_n$'s obtained at the same conversion level (100%) in the absence and presence of DtBP are quite different (e.g., $\overline{M}_n$ = 4.5 × 10^4 and $\overline{M}_w/\overline{M}_n$ = 1.87 at [DtBP] = 1.10^{-4} M, whereas $\overline{M}_n$ = 1.2 × 10^4 and $\overline{M}_w/\overline{M}_n$ = 3.8 in the absence of DtBP) which

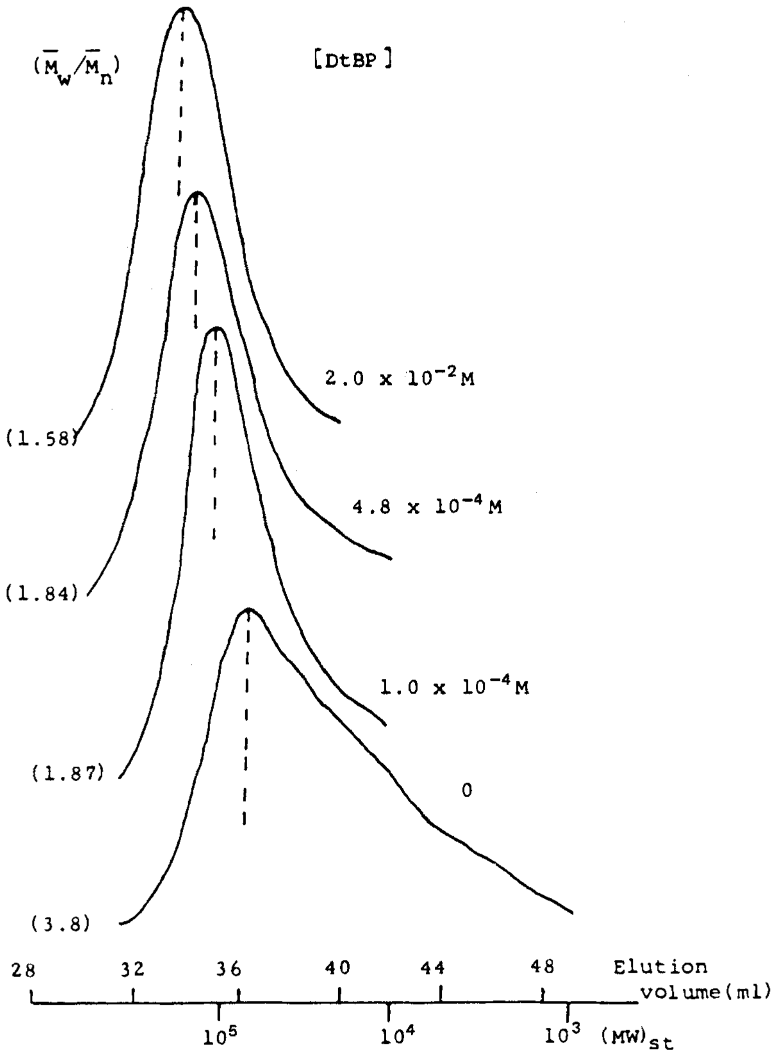


FIG. 7. Effect of [DtBP] on GPC traces of PαMeSt (not normalized, -60°).

demonstrates that these effects and those described earlier, which we set out to elucidate, are not due merely to differences in conversion levels, i.e., monomer concentrations.

In the second series of experiments the aim was to investigate the kinetics of αMeSt polymerization initiated by the "H_2O"/BCl_3 system in the presence of DtBP. Figure 8 shows conversion-time plots obtained in the absence of DtBP and with four different DtBP concentrations. Extremely fast polymerizations occurred at [DtBP] = 0, and conversions reached 100% within seconds after BCl_3 addition. In the presence of an excess (1.5×10^{-2} to 7.7×10^{-3} M), DtBP polymerizations remained extremely rapid; however, conversions leveled off at ~42%. Evidently initiation is not influenced by DtBP. In the presence of 2.5×10^{-4} and 5.0×10^{-4} M DtBP, instantaneous conversions were 70 and 50%, respectively; however, polymerization did not stop but proceeded slowly to higher conversions. A tentative explanation for these observations is suggested below.

$\overline{M}_n$'s and $\overline{M}_w/\overline{M}_n$'s of the samples obtained with [DtBP] = 2.5×10^{-4} M in the conversion range from 69 to 100% have been determined. These data together with two other data points (the control obtained in the absence of DtBP, and one obtained at ~ 41% with [DtBP] = 7.7×10^{-3} M) are shown in Fig. 9. Significantly, the $\overline{M}_n$ and the $\overline{M}_w/\overline{M}_n$ obtained at 100% conversion in the absence of DtBP are much lower and broader, respectively, than those obtained in the presence of [DtBP] = 2.5×10^{-4} M which again proves that this hindered amine is not an inhibitor or retarder. Our insight into the mechanism of this polymerization system is insufficient to explain the linear inverse dependence of log M_n's on conversions.

The relatively narrow $\overline{M}_w/\overline{M}_n$ value of ~ 1.7 obtained at 100% conversion in the presence of DtBP is noteworthy. It would not have been too surprising to find MWD broadening, indicating branching at high conversions. Overberger et al. [12], who investigated the polymerization of styrene with $H_2O/SnCl_4$ over the conversion range from 9.5 to 97%, presented evidence for $\overline{M}_w/\overline{M}_n$ broadening, i.e., branching at high conversions. Conceivably, branching does not occur in the αMeSt system because chain trnasfer to polymer is less likely to occur (absence of benzylic hydrogens) and because ring alkylation by the propagating cumyl cation is sterically more hindered than in the corresponding St system.

Most of these experiments have been carried out in the presence of stoichiometrically large quantities of DtBP ([DtBP] $> 1.0 \times 10^{-3}$), i.e., DtBP concentrations exceeding that of [BCl_3] and thought to be more than sufficient to trap all potential proton chain carriers $H^{\oplus}G^{\ominus}$ emerging during chain transfer to monomer. It appeared of interest to investigate αMeSt polymerizations in the presence of trace amounts of DtBP, particularly the effect of [DtBP] $< 1.0 \times 10^{-3}$ on conversions, molecular weights, and MWD.

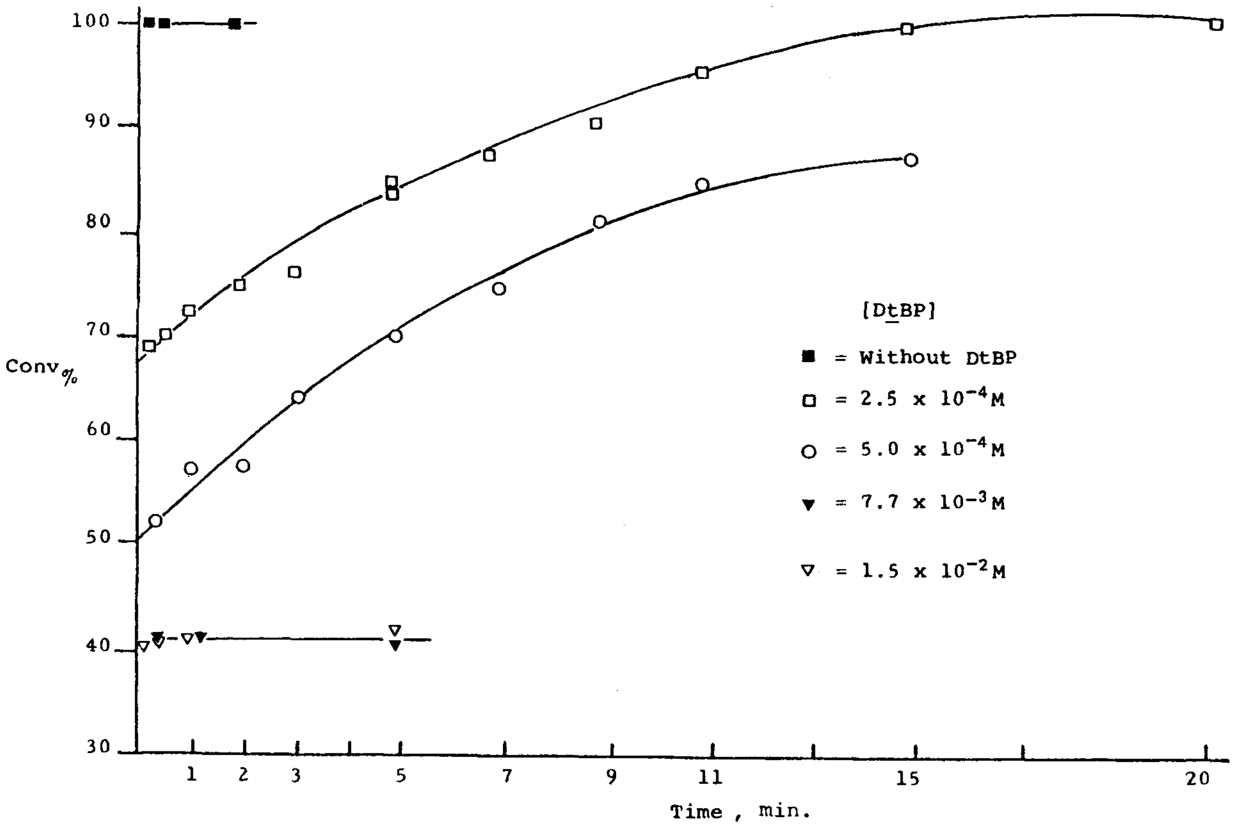


FIG. 8. Conversion versus time plots for αMeSt polymerization in the absence and presence of different [DtBP]'s, ([αMeSt] = 0.62 $\underline{M}$, [BCl_3] = 5.0 × 10^{-3} $\underline{M}$, CH_2Cl_2, -55° C.)

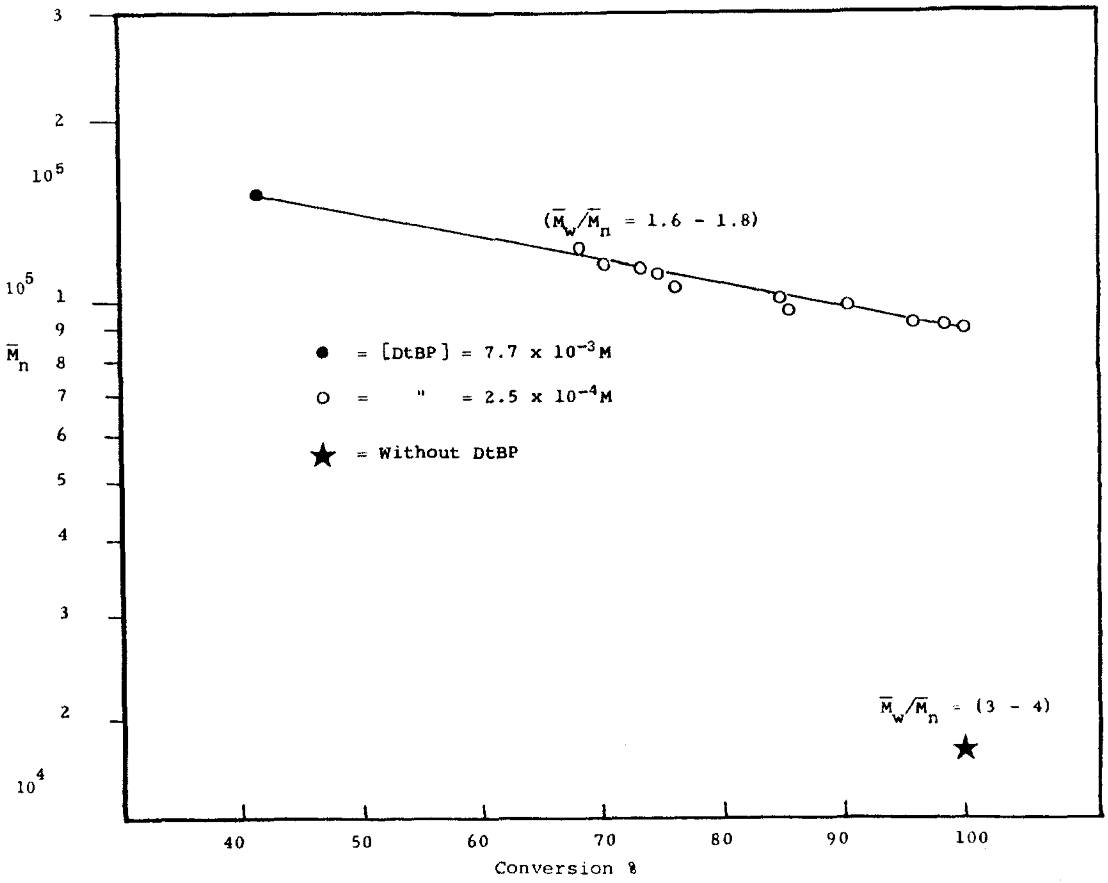


FIG. 9. $\overline{M}_n$ of PαMeSt obtained at different conversions. ([αMeSt] = 0.62 M, [BCl_3] = 5.0×10^{-3} M, CH_2Cl_2, 5 min, -50°C.)

TABLE 4. The Effect of [DtBP] on MW and MWD of P(αMeSt) ([BCl_3] = 5.0×10^{-3} M, [αMeSt] = 0.62 M, -50°C, CH_2Cl_2, 5 min)

Sample	[DtBP] (M)	Conversion (%)	$\overline{M}_n \times 10^{-4}$ (GPC)	$M_w \times 10^{-4}$	$\overline{M}_w/\overline{M}_n$ (± 0.15)
1	7.7×10^{-3}	35.5	16	23	1.47
2	7.7×10^{-4}	32.6	14	22	1.52
3	7.7×10^{-5}	100	6.5	11	1.69
4	3.8×10^{-5}	100	5.4	9.2	1.72
5	3.8×10^{-6}	100	2.4	6.0	2.5
6	1.9×10^{-6}	100	1.6	5.1	3.2
7	3.8×10^{-7}	100	0.8	3.6	4.4
8	0	100	0.64	2.9	4.5

Table 4 shows experimental conditions and results, and Fig. 10 depicts the effect of [DtBP] on MWD. Evidently the presence of even trace amounts of proton trap ([DtBP] = 10^{-7} to 10^{-6}) noticeably affects molecular weight and MWD data. These DtBP concentrations are commensurate with those of unavoidable impurities. These conversion data can be explained by assuming proton trapping by the DtBP during chain transfer. Increasing amounts of DtBP increasingly trap the proton chain carrier and thus reduces conversion (terminative proton entrapment) until the [DtBP] reaches a saturation level beyond which all trappable protons are removed and conversions fall below 100%.

Coupled to these effects are equilibria that have to be considered:

$$H^{\oplus}G^{\ominus} + DtBP \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} H^{\oplus}DtBP\cdot G^{\ominus} \overset{K_d}{\rightleftharpoons} H^{\oplus}DtBP + G^{\ominus}$$

In the presence of excess DtBP, i.e., ~1.0×10^{-3} M under our conditions, k_{-t} is suppressed.

The slow polymerizations obtained with [DtBP] = 2.5×10^{-4} and 5.0×10^{-4} M shown in Fig. 8 may be explained by considering the above equilibria. It may be that at these low DtBP concentrations all DtBP has been converted to $H^{\oplus}DtBP\cdot G^{\ominus}$ which slowly releases $H^{\oplus}G^{\ominus}$ (by k_{-t}) which in turn slowly reinitiates the kinetic chain. This process may lead to slow but complete monomer consumption as shown by the data in Fig. 8.

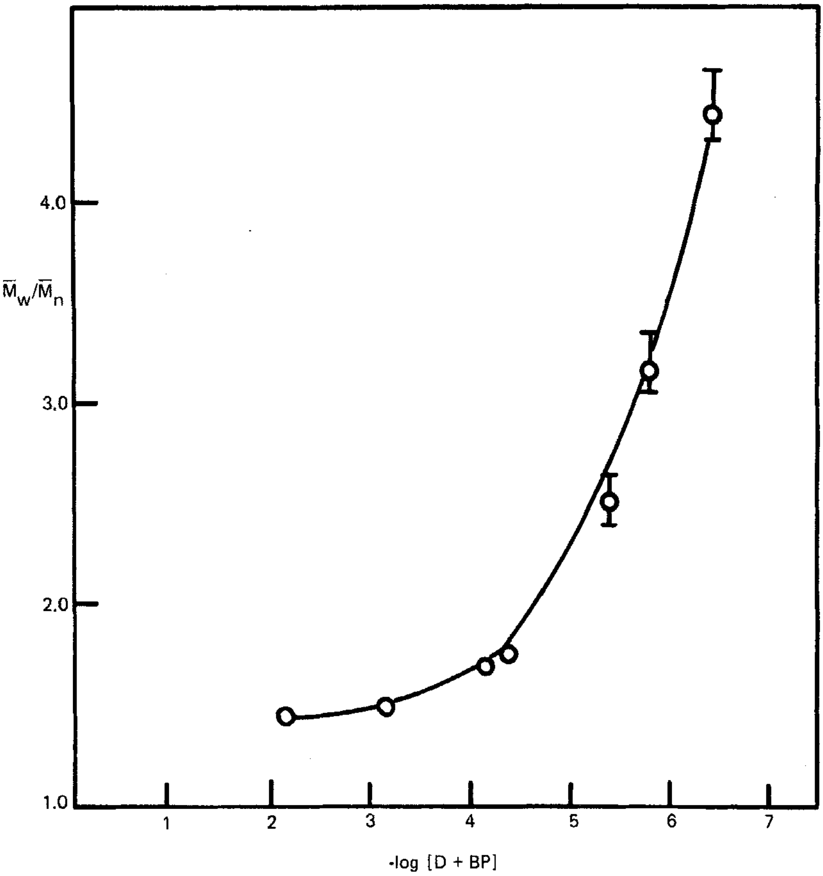


FIG. 10. The effect of DtBP concentration on polydispersity ratio of PαMeSt. ([αMeSt] = 0.62 M, [BCl_3] = 5.0×10^{-3} M, -50°C, CH_2Cl_2, 5 min.)

E. The Effect of BCl_3 Concentration

A series of experiments have been carried out to determine the effect of [BCl_3] on the polymerization of αMeSt. Table 5 shows the reaction conditions employed and the results. Evidently [BCl_3] in the range employed does not affect the rate (conversion), molecular weights, and their dispersities. These results support the statement made in the previous section that the true initiating entity is "H_2O" whose concentration remained constant during this series of experiments (constant conversions, etc.). Self-initiation by BCl_3 must also be absent.

TABLE 5. Effect of BCl_3 Concentration on αMeSt Polymerization in the Presence of DtBP ([αMeSt] = 0.62 M, [DtBP] = 7.7×10^{-3} M, CH_2Cl_2, -60°C, 5 min)

Sample	BCl_3 $\times 10^3$ M	Conversion (%)	$\overline{M}_n$ $\times 10^{-5}$	$\overline{M}_w$ $\times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
1	1.0	63.8	1.0	1.6	1.6
2	5.0	62.5	1.0	1.5	1.5
3	10.0	61.5	1.0	1.5	1.5
4	15.0	69.7	1.0	1.6	1.6

F. The Effect of Solvent Polarity

The effect of solvent polarity has been studied by a series of experiments in which the polar/nonpolar composition of the solvent (mixtures of $CH_2Cl_2/n\text{-}C_6H_{14}$ and CH_2Cl_2/CCl_4) was systematically changed. The dielectric constant ϵ of CH_2Cl_2 is 12.8 at -50°C; those of CCl_4 and $n\text{-}C_6H_{14}$ are 2.2 and 1.9, respectively. CH_2Cl_2 and CCl_4 are good solvents for PαMeSt while $n\text{-}C_6H_{14}$ is not. Figures 11 and 12 give experimental details and show data.

Judging by the virtually identical data trends obtained with $n\text{-}C_6H_{14}$ and CCl_4 mixtures with CH_2Cl_2 (compare Figs. 11 and 12), solubility differences of PαMeSt in these experiments do not seem to affect the results.

With increasing polar solvent in the medium in the absence of DtBP, conversions were consistently 100%, the molecular weights gradually decreased, and MWD's broadened from ~1.5 to ~4.5. In contrast, under the same conditions except in the presence of DtBP, conversions were much lower than 100% (ranges obtained are given in the figures). The molecular weights were much higher and, although they showed a monotonically decreasing trend, the drop was much less than in the absence of DtBP. Interestingly, the molecular weight dispersities remained unchanged (MWD ≈ 1.5) within what is considered to be experimental variation over the entire polarity range. Figure 13 shows the GPC traces obtained in the $CH_2Cl_2/n\text{-}C_{16}H_{14}$ experiment and further emphasizes the finding that polarity profoundly affects MWD in the absence of DtBP, while in the presence of this proton trap MWD's remain unusually narrow (MWD ≈ 1.5) irrespective of medium polarity.

Figure 14 is a comparison of MWD data obtained in the absence and presence of DtBP as a function of the overall dielectric constant of the medium (calculated from weighted volume means). In the absence of proton trap the MWD's show an S-shaped curve: below ϵ ≈ 5, MWD's are low and virtually unchanged with $\overline{M}_w/\overline{M}_n \approx 1.5$; in

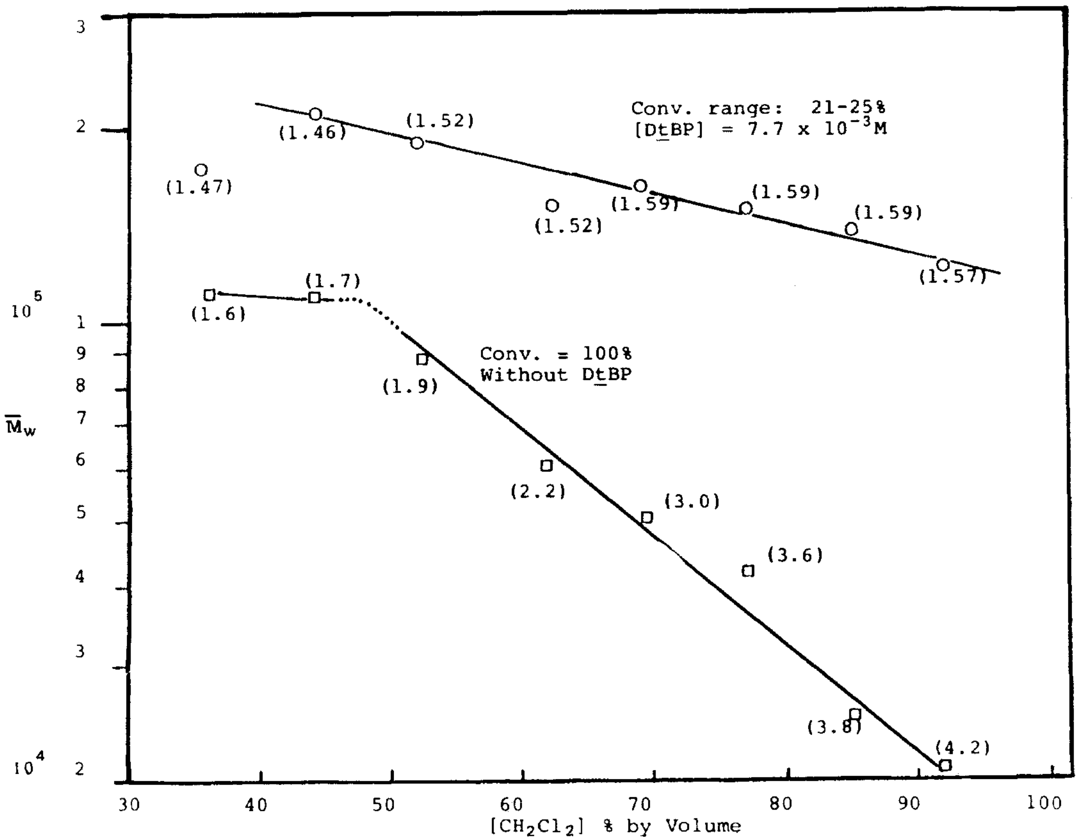


FIG. 11. The effect of solvent polarity on αMeSt polymerization in the presence and absence of DtBP. (CH_2Cl_2/hexane, [αMeSt] = 0.62 M, [BCl_3] = 5.0 × 10^{-3} M, -50° C; numbers in parentheses = $\overline{M}_w/\overline{M}_n$.)

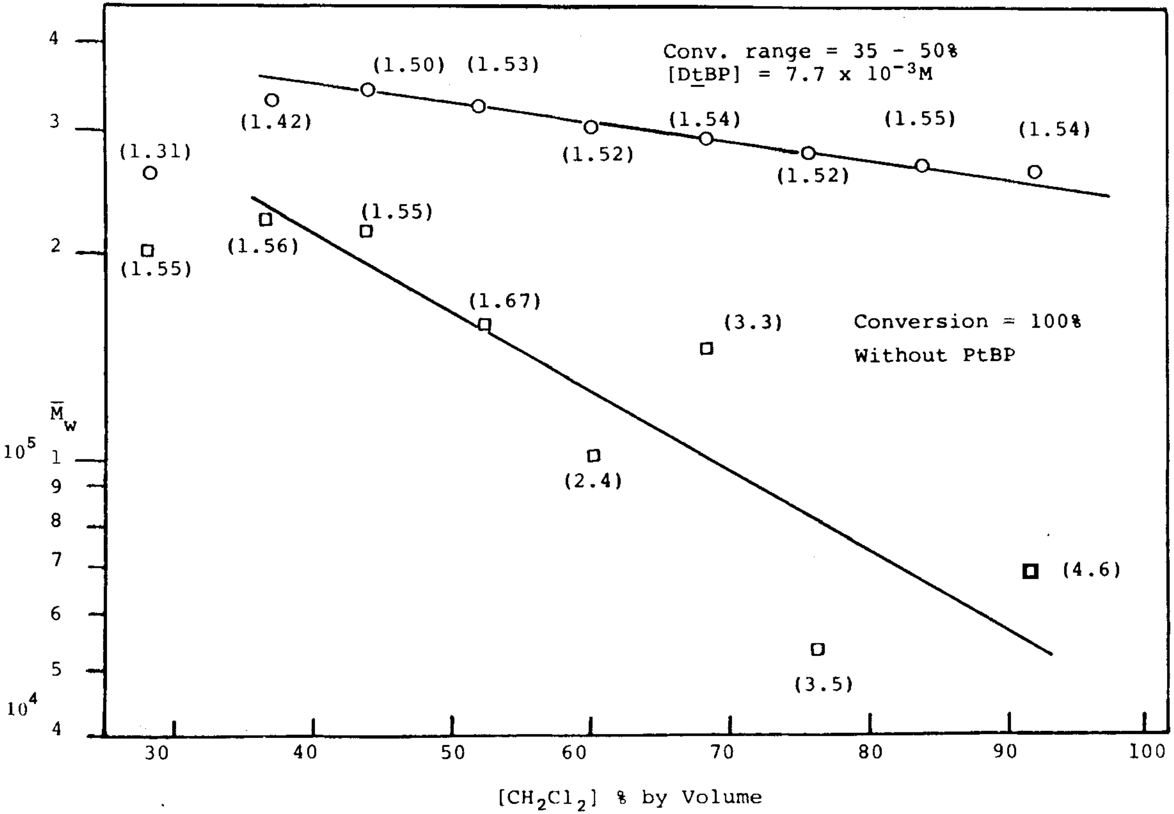


FIG. 12. The effect of solvent polarity on αMeSt polymerization in the presence and absence of DtBP, (Solvent = CH_2Cl_2/CCl_4, [αMeSt] = 0.62 M, [BCl_3] = 5.0×10^{-3} M, -50°C; numbers in parentheses = $\overline{M}_w/\overline{M}_n$.)

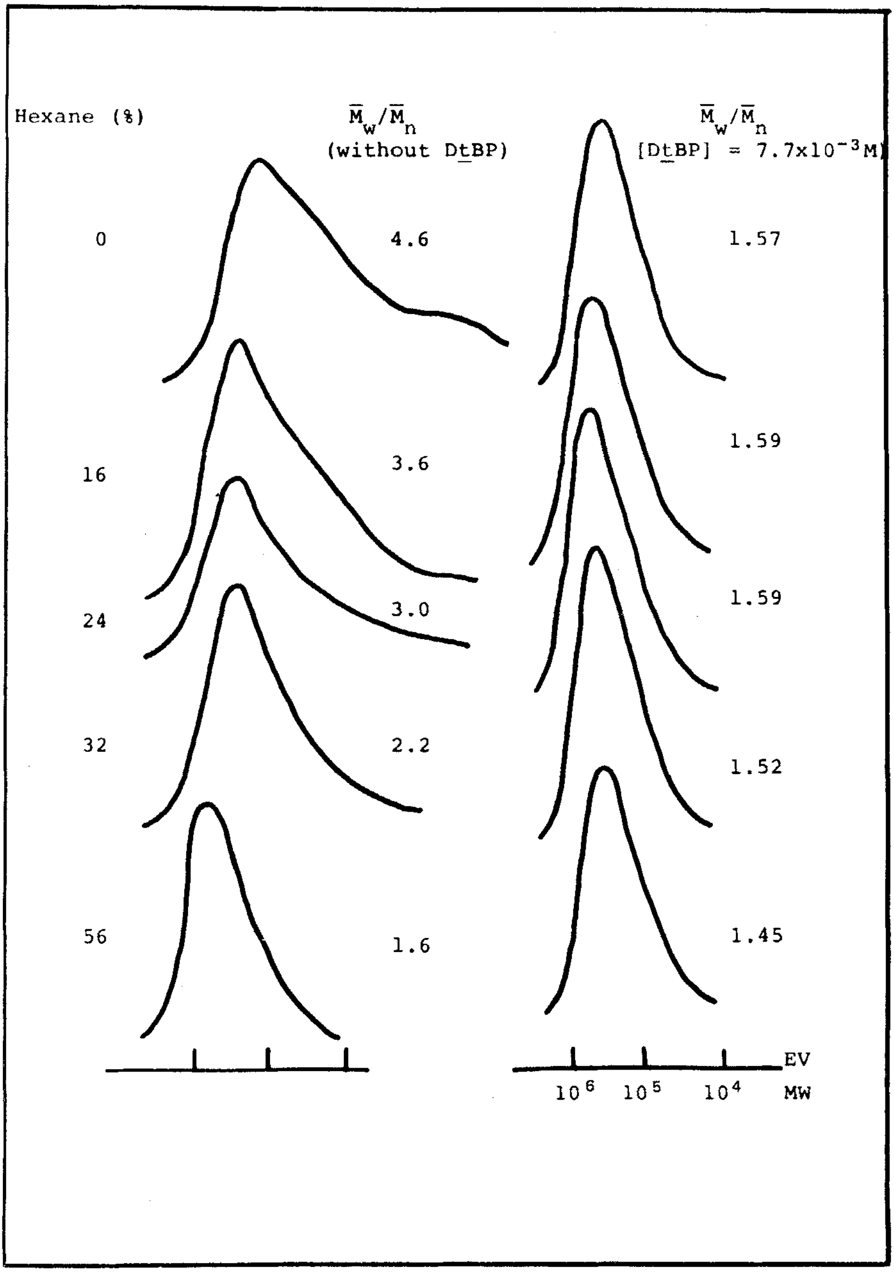


FIG. 13. The effect of solvent polarity on the MWD of PαMeSt obtained in the presence and absence of DtBP. (Solvent = CH_2Cl_2/n-C_6H_{14}, [αMeSt] = 0.62 M, [BCl_3] = 5.0×10^{-3} M, -50° C; Conversion: without DtBP ~100%, with DtBP ~25%.)

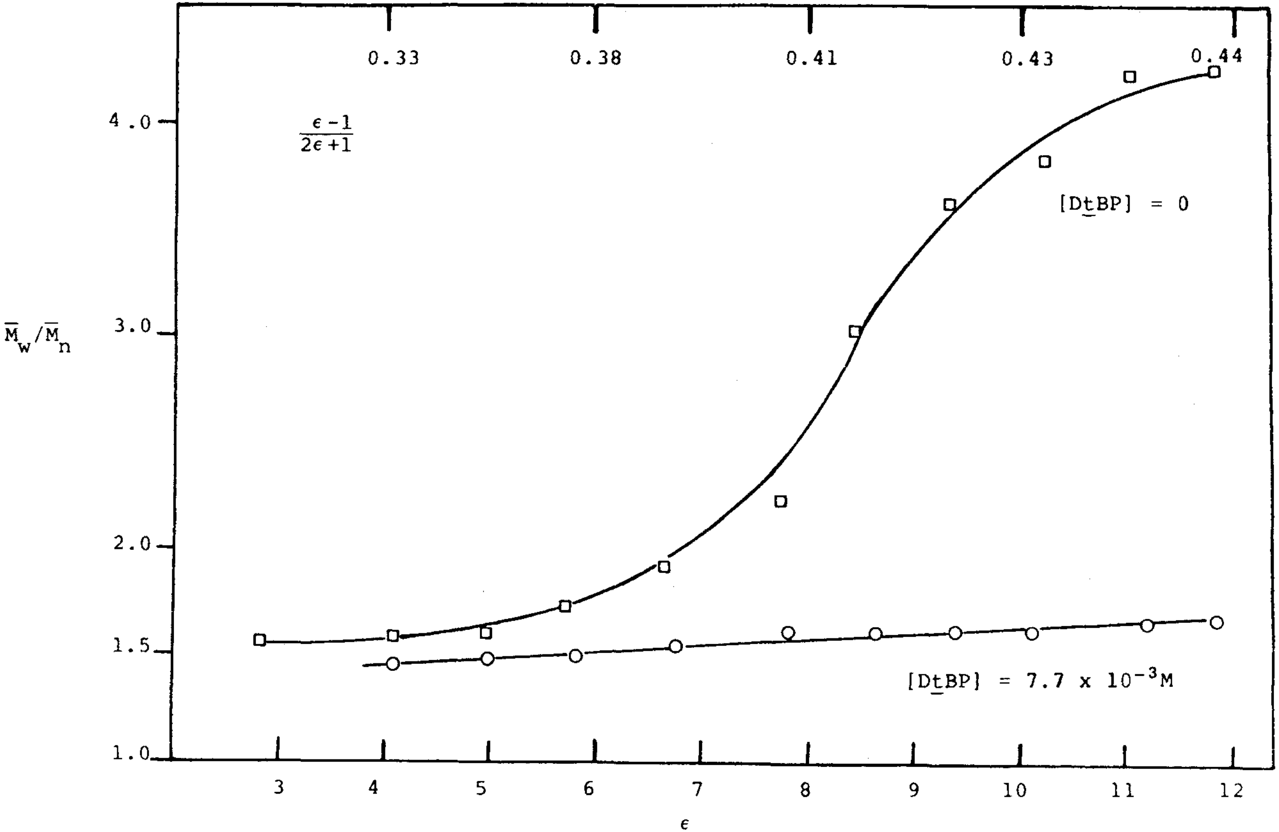


FIG. 14. The effect of dielectric constant of the polymerization medium on the polydispersity ratio.

the range ϵ = 5-10, MWD's increase rapidly; and beyond $\epsilon \approx 11$, $\bar{M}_w/\bar{M}_n$ seems to level off at ~ 4.5. Obviously the mechanism of αMePSt polymerization changes rapidly with medium polarity. In contrast, in the presence of DtBP, MWD's are largely independent of ϵ. Apparently, the addition of DtBP to a polar medium alters the mechanism as if the polymerization would proceed in a nonpolar medium: phenomenologically the presence of DtBP changes the mechanism from a polar to a nonpolar one.

The effect of medium polarity and/or the addition of DtBP to nonpolar media on conversions, molecular weights, and molecular weight dispersities (i.e., the findings represented in Figs. 11-14) may be explained by postulating that in nonpolar media, or in polar media but in the presence of DtBP, processes involving the proton are slowed down. Obviously, in nonpolar systems all ionic processes including those involving protons occur only with difficulty; in polar media in the presence of DtBP, ionic processes are accelerated except those proceeding by free (trappable) protons. Thus the lower conversions observed in nonpolar systems and/or in polar systems in the presence of DtBP may be due to reduced (protic) initiation. Similarly, the higher molecular weights and narrower molecular weight distributions found in nonpolar systems and/or in polar systems in the presence of DtBP may be explained by decreased protic chain transfer to monomer.

II. Preliminary Conclusions Concerning the Mechanism of αMeSt Polymerization in the Presence of DtBP Proton Trap

The aim of the above detailed kinetic examination of the "H_2O"/BCl_3/αMeSt system was the construction of a comprehensive polymerization mechanism which would account for all the observations described in the previous section. While the quantitative description of the data in the framework of a comprehensive theory appears to be a formidable task and is still under investigation (the scheme shown in Ref. 2 is currently being examined) [13], a number of qualitative conclusions concerning the mechanism have been reached.

Initiation most likely occurs by a concerted free-protonless process, i.e., by a mechanism in which free or trappable protons are not involved. Thus the acid $H^{\oplus}BCl_3OH^{\ominus}$, whose involvement in the initiation process might have been assumed in the absence of information presented in this paper, must be absent because DtBP would immediately trap the proton and abort initiation.

As discussed in the first article in this issue and in Section I-A, DtBP is regarded to be a valuable diagnostic tool for the exploration of protic initiation in cationic polymerizations in general.

The fact that polymerization readily occurs in the presence of DtBP with "H_2O"/BCl_3 and similar "H_2O"/Friedel-Crafts acid systems, e.g., with "H_2O"/$SnCl_4$ [14], "H_2O"/$AlCl_3$ [15], and "H_2O"/$TiCl_4$ [16], suggests that initiation in these systems is protonless and probably proceeds by an intramolecular reorganization within the three-component complex:

$$\text{"}H_2O\text{"}\cdot BCl_3\cdot M \longrightarrow HM^{\oplus}BCl_3\,OH^{\ominus}$$

The protonated monomer ($HM^{\oplus} = (CH_3)-\overset{\oplus}{C}-C_6H_5$) is evidently quite inert toward DtBP and starts the propagation. The proton trap is unable to intercept the chain transfer to monomer process, perhaps because steric hindrance prevents the approach of DtBP in the transition state.

In contrast, chain transfer to monomer that proceeds via proton elimination to the counteranion followed by protonation of M (i.e., indirect chain transfer to monomer or chain transfer by counteranion) is trappable by DtBP. In the presence of a stoichiometric excess of DtBP, proton trapping is extremely rapid and complete and

$$H^{\oplus}G^{\ominus} + M \xrightarrow{k_{ri}} HM^{\oplus}G^{\ominus}$$

does not occur (see Section I-C).

Proton entrapment is in fact a termination reaction since the chain carrier $H^{\oplus}G^{\ominus}$ is trapped by complexation with DtBP, hence the term "terminative proton entrapment." In the "H_2O"/BCl_3/αMeSt system DtBP is apparently virtually completely nonnucleophilic (see Section I-B and I-D) and the rate of terminative proton entrapment is controlled by the rate of deprotonation. This, in this system, termination may be viewed as an incomplete chain transfer to monomer reaction. It needs to be emphasized that in the absence of DtBP, kinetic termination does not occur in the "H_2O"/BCl_3/αMeSt system and polymerization rapidly reaches 100% conversion (see Sections I-A, I-B, and I-D).

This simple mechanism accounts for the conversion data obtained in the "H_2O"/BCl_3/αMeSt/DtBP system in solvents of various polarities over the -20 to -60° C range.

In regard to molecular weights and MWD's, the key observations are as follows: The molecular weights and MWD's obtained in the presence of DtBP are always significantly higher and narrower, respectively, than under identical conditions except in the absence of this proton trap, and above a rather low threshold [DtBP] the molecular weights and MWD's are independent of [DtBP] (see Fig. 6). Evidently DtBP is not an inhibitor or retarder. Furthermore, the Arrhenius lines are essentially parallel (see Fig. 3), demanding that the activation enthalpy differences of the underlying molecular-weight-determining events remain identical. Qualitatively these observations can be explained by assuming the existence of a necessarily weak but still nonnegligible (dipole-ion?) interaction between the propagating site and DtBP which results in relatively unimpeded propagation and delayed chain transfer to monomer. Similarly, the narrowing of molecular weight dispersities in the presence of DtBP may be explained by assuming that the rate of fast initiation remains unaffected; however, the rate of propagation is slightly reduced by DtBP. Quantitative theories are currently being developed and are planned to be published at a future date.

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