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

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ABSTRACT

The effect of 2,6-di-tert-butylpyridine (DtBP) on α-methylstyrene (αMeSt) polymerization induced by the "H_2O"/BCl_3 initiating system has been studied. Yields, molecular weights, (MW's), and molecular weight distributions (MWD's) obtained in the presence of [DtBP] > 1.0×10^{-3} M are invariant with DtBP concentration. Results are explained by the concept of terminative chain transfer, i.e., a process in which the proton which arises in the course of chain transfer to monomer is intercepted by DtBP so that the kinetic chain is terminated. Polymerization goes to completion in the presence of very small amounts of DtBP, i.e., 4.8×10^{-4} M or less; however, MW's and MWD's of the poly(α-methylstyrene) (PαMeSt) formed are still profoundly affected. Thus, in the absence of DtBP, $\overline{M}_n = 1.2 \times 10^4$ and $\overline{M}_w/\overline{M}_n = 3.8$, whereas in the presence of [DtBP] $= 1.0 \times 10^{-4}$ M, $\overline{M}_n = 4.5 \times 10^4$ and $\overline{M}_w/\overline{M}_n = 1.87$. According to Mayo plots, a small but nonnegligible extent of chain transfer to monomer persists even in the presence of DtBP, e.g.,

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$k_{tr,M}/k_p = 6.4 \times 10^{-4}$ and 2.8×10^{-4} at -30 and -50°C, respectively. This, by DtBP unscavengable chain transfer to monomer, is attributed to a concerted chain transfer process. A mechanism is proposed which explains the experimental facts.

INTRODUCTION

The polymerization of αMeSt induced by the "H_2O"/BCl_3 initiating system in CH_2Cl_2 solvent proceeds in the presence of a high concentration of DtBP and gives rise to polymer of higher MW and much narrower MWD than that obtained in the absence of this hindered base [1]. Kinetic analysis suggests that DtBP does not interfere with initiation and propagation; however, it traps the proton that arises during chain transfer to monomer [1].

This presentation concerns observations relative to the effect of DtBP on the yields, MW's, and MWD's obtained in αMeSt polymerization. A mechanism is developed which explains the observations.

EXPERIMENTAL

The source and purity of chemicals used as well as polymerization techniques have been described [1, 2].

RESULTS AND DISCUSSION

Previous studies [1, 2] have suggested that DtBP traps proton or intermediates akin to proton arising during chain transfer in αMeSt polymerization induced by the "H_2O"/BCl_3 initiating system. Investigation of the effect of DtBP concentration on this polymerization system has been continued. A series of experiments has been carried out in which [DtBP] was varied from 0.0 to 1.0×10^{-1} M. Results are shown in Fig. 1. Yields, MW's, and MWD's of P$\alpha\overline{\text{MeSt}}$ obtained in the presence of [DtBP] > 1.0×10^{-3} M are invariant within experimental error. Since yields, MW's, and $\overline{\text{MWD}}$'s remain unaffected over a wide DtBP concentration range, it is safe to conclude that DtBP does not interfere with the elementary events governing these parameters. Evidently DtBP, although a strong base, is neither an inhibitor nor retarder of αMeSt polymerization under the conditions employed.

In view of its hindered pyridine structure, DtBP is regarded as a strong nonnucleophilic base and its effect on αMeSt polymerization is fundamentally different from that of conventional bases. It is

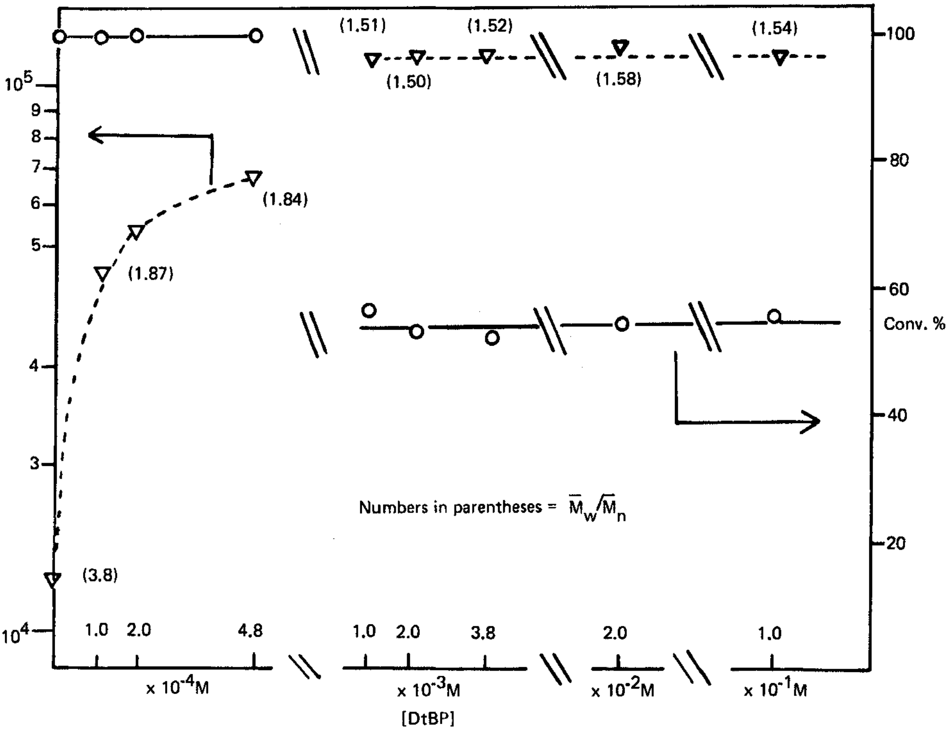
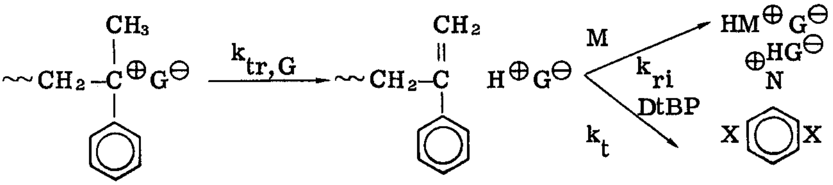


FIG. 1. Effect of [DtBP] on αMeSt polymerization. ([αMeSt] = 0.32 M, [BCl_3] = 5.0 × 10^{-3} M, CH_2Cl_2, -60°C, 5 min.)

proposed that DtBP is able to react with the proton or a species akin to proton that emerges during chain transfer to monomer:



The key point of this proposition is that DtBP, on account of its hindered structure, exclusively and specifically traps proton during chain transfer and that it does not interfere with other elementary events. It is also important to note that according to this mechanism the proton is not transferred directly to monomer but is first transferred to the counteranion G⊖. Thus the rate of proton transfer to G⊖ is

$$R_{tr,G^{\ominus}} = \frac{d[H^{\oplus}G^{\ominus}]}{dt} = k_{tr,G^{\ominus}}[C^{\oplus}G^{\ominus}]$$

where $[\sim\sim C^{\oplus}G^{\ominus}]$ is the concentration of the propagating PαMeSt$^{\oplus}$G$^{\ominus}$ ion pair. Since $k_t \gg k_{ri}$ ($k_t = 4.8 \times 10^8$)[3] and $k_t \gg k_{tr,G^{\ominus}}$,

$$-\frac{d[H^{\oplus}G^{\ominus}]}{dt} = k_t[H^{\oplus}G^{\ominus}][DtBP]$$

i.e., the rate-determining step in proton trapping by DtBP is the rate of proton transfer to G$^{\ominus}$. Thus

$$-\frac{d[H^{\oplus}G^{\ominus}]}{dt} = \frac{d[\sim\sim C^{\oplus}G^{\ominus}]}{dt} = k_{tr,G}[\sim\sim C^{\oplus}G^{\ominus}] = R_t$$

where R_t = rate of termination, termination chain transfer. According to this mechanism, αMeSt polymerization should be independent of DtBP concentration above a certain [DtBP]. This is found experimentally as shown by the data in Fig. 1.

Under the particular condition used, αMeSt polymerization proceeds to completion at $[DtBP] < 4.8 \times 10^{-4}$ M. Evidently very small amounts of DtBP are insufficient to prevent chain transfer completely; however, the yields, MW's, and MWD's obtained are significantly different from those obtained in control runs (absence of DtBP) at the same conversion level. Pertinent data are shown in Fig. 1.

Further insight into mechanistic details of chain transfer to monomer has been obtained by studying the effect of monomer concentration [M] on $\overline{DP}_n$ (Mayo plots). The Mayo equation $1/\overline{DP}_n = k_{tr,M}/k_p + k_t/k_p[M]$ has often been used to determine the relative extent of monomer transfer to termination in carbocationic polymerization. If chain transfer to monomer occurs only by the above proposed mechanism, it could be completely prevented by the use of DtBP, and Mayo plots constructed with samples obtained in the presence of DtBP should not have an intercept ($k_{tr,M}/k_p = 0$). In contrast to this expectation, as shown by Fig. 2, Mayo plots exhibited a small temperature dependent intercept, i.e., $k_{tr,M}/k_p = 6.4 \times 10^{-4}$ and 2.8×10^{-4} at -30 and -50°C, respectively.

In view of these findings it is proposed that chain transfer to monomer occurs by two routes, a major one involving proton expulsion to G$^{\ominus}$ followed by reinitiation (see above) and a minor one involving concerted proton transfer to monomer without the appearance of a

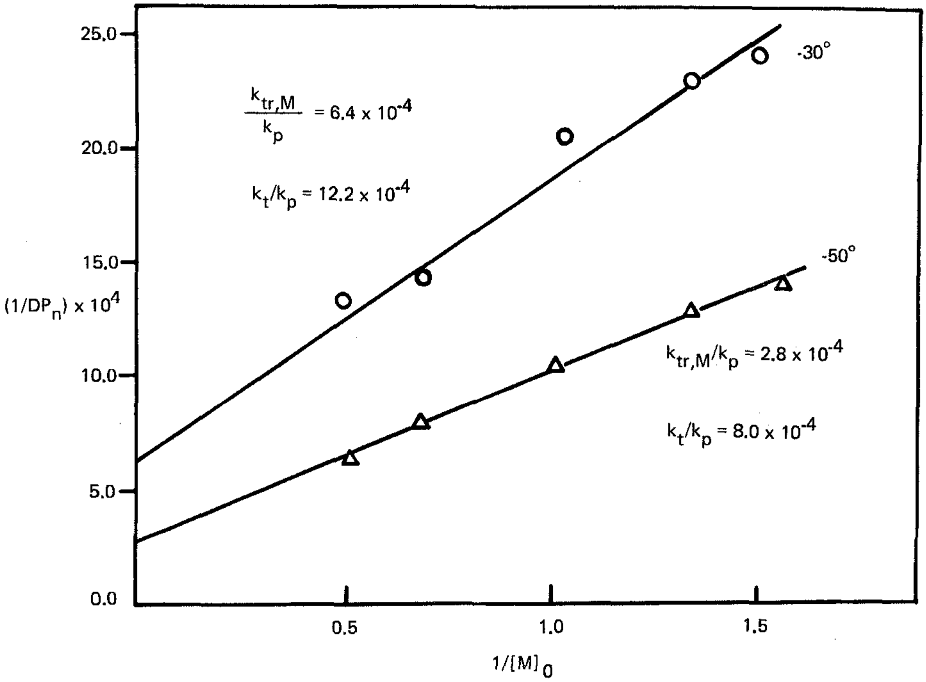


FIG. 2. Investigation of details of chain transfer by Mayo ($1/DP_n = k_{tr,M}/k_p + (k_t/k_p)(1/[M])$). Plots: $[BCl_3] = 5.0 \times 10^{-3}$ M, [DtBP] = 7.7×10^{-3} M, CH_2Cl_2. Solvent polarity was maintained by the use of n-hexane as compensating solvent. $\overline{M}_n$'s were determined by membrane osmometry.

trappable proton. Concerted proton transfer is visualized to occur within a ternary complex $\sim\!\!\sim C_n^{\oplus} MG^{\ominus}$ comprising the growing carbocation-monomer-counteranion. This complex is akin to the one first proposed by Fontana [4] and subsequently explored by Kennedy et al. [5]. Propagation and/or chain transfer can occur via this complex; however, DTBP would not be able to interfere with these processes.

Proton interception of DtBP results in a pyridinium salt $DtBP{\cdot}H^{\oplus}G^{\ominus}$. Dissociation of this salt, a likely process in view of the rather polar medium (ε of CH_2Cl_2 = 12.8 at -50°C), would of course produce the same $G^{\ominus}$ associated with the propagating PαMeSt$^{\oplus}$ cation and thus would suppress dissociation of the latter by the common ion effect. Conversely, in the absence of DtBP the propagating PαMeSt$^{\oplus}$G$^{\ominus}$ ion

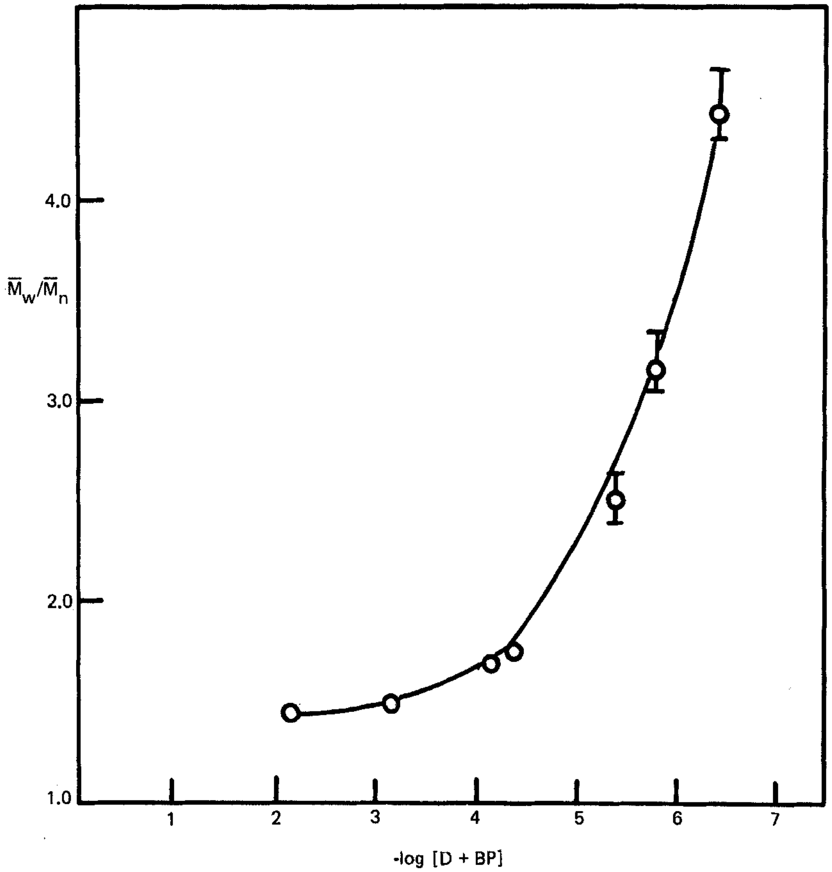
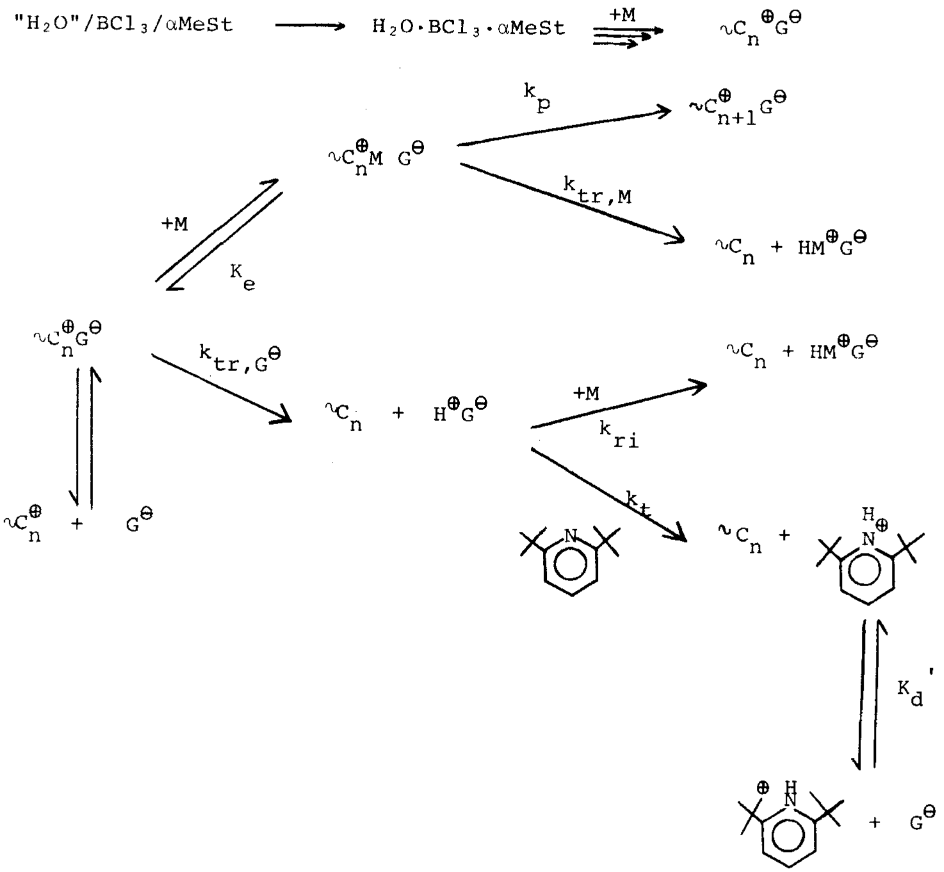


FIG. 3. The effect of DtBP concentration on polydispersity ratio of PαMeSt. ([αMeSt] = 0.62 M, [BCl_3] = 5.0 × 10^{-3} M, -50°C, CH_2Cl_2, 5 min.)



SCHEME 1. Mechanism of αMeSt polymerization in the presence of DtBP.

pair would tend to dissociate into free ions which would induce a great variety of reactions having rate constants different from those induced by ion pairs and thus result in complicated kinetics. Interception of chain transfer by DtBP and suppression of the dissociation of the propagating PαMeSt$^{\oplus}$G$^{\ominus}$ ion pair during polymerization will result in the narrowing of MWD as illustrated by the data in Fig. 3.

Scheme 1 summarizes the processes outlined and presents an overall view of the mechanism of αMeSt polymerization occurring in the presence of DtBP.

This mechanism accounts for the experimental observations. 1) It explains the observed limited conversion obtained in the presence of suitable amounts of DtBP. 2) It explains that αMeSt polymerization can proceed even in the presence of a high concentration of DtBP. 3) It explains that yields, MW's, and MWD's do not change over a wide range of DtBP concentration above [DtBP] = 1.0×10^{-4} M. 4) It explains the presence of an intercept observed in Mayo plots. 5) It explains that the MW's of PαMeSt obtained in the presence of DtBP are much higher than those produced in control runs. 6) It helps, at least qualitatively, to rationalize that MWD's of PαMeSt's obtained in the presence of DtBP are invariably narrower than those of controls.

ACKNOWLEDGMENT

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