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Carbocationic Polymerization in the Presence of Sterically Hindered Bases. X. Summary and Quantitative Kinetic Confirmation of the Mechanism

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Carbocationic Polymerization in the Presence of Sterically Hindered Bases. X. Summary and Quantitative Kinetic Confirmation of the Mechanism

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ABSTRACT

The findings presented in the preceding articles of this special issue have been organized, analyzed, and summarized. Commonalities among the various polymerization systems investigated in detail have been identified and phenomena of general validity were found. Increased insight into the mechanism of initiation and chain transfer processes led to the development of a comprehensive kinetic model which was used to describe the assembled data. Excellent quantitative agreement between experimental and calculated data indicates the validity of the mechanistic/kinetic model developed from chemical principles in regard to fast-initiated nonstationary carbocationic polymerizations in the absence and presence of proton traps.

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TABLE 1. The Effect of DtBP on Carbocationic Polymerization

Initiating system initiator/coinitiator				Effect of DtBP on				
Protic	Nonprotic	Solvent	Temperature (°C)	Conversion (%)	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$	Remarks, conclusions	Ref.[a]
Isobutylene								
"H_2O"/$AlCl_3$		n-C_6H_{14} CH_2Cl_2/n-C_6H_{14} CH_2Cl_2	-50	↙	↗	↙	Concerted initiation by "H_2O"·$AlCl_3$ complex. DtBP is proton trap (terminative proton entrapment)	IV
	$\phi C(CH_3)_2Cl/BCl_3$	CH_2Cl_2	-50	↙	↙	↙	Initiation by cumylation DtBP is proton trap (terminative proton entrapment) and terminating agent. PIB end-group control to exo-olefin possible	III
α-Methylstyrene								
"H_2O"/BCl_3		CH_2Cl_2	-20 to -60	↙	↗	↙	Concerted initiation by "H_2O"·BCl_3 complex. DtBP is proton trap (terminative proton entrapment) of indirect chain transfer to monomer. Strong polarity effects on conversion, MW, and MWD	V

"H_2O"/$SnCl_4$		CH_2Cl_2	-60	↙	∧	↙	Concerted initiation by "H_2O"·$SnCl_4$ complex. DtBP is proton trap (terminative proton entrapment)	VI
"H_2O"/$SnCl_4$		C_2H_5Cl	-40 to -122	↙	↗	↙	As above. Change in mechanism at ~ -86°. Strong temperature effect on MWD	5
	$(CH_3)_5\phi CH_2Cl$/ $SnCl_4$	CH_2Cl_2	-30 to -80	↙	↗	↙	Initiation by benzylation. DtBP is proton trap (terminative proton entrapment). $(CH_3)_5$-ϕCH_2Cl is chain transfer agent	VII
	CR-IIR/BCl_3 Cl-IIR/$SnCl_4$ CR/BCl_3 CR/$SnCl_4$	CH_2Cl_2/ MeCH	-50				New grafts. $G_{eff} \simeq 1000$. DtBP aborts. Uncontrolled initiation and chain transfer to monomer (terminative proton entrapment)	VIII
	PIB-Cl/$SnCl_4$	CH_2Cl_2/ n-C_6H_{14}	-50				Diblock; $B_{eff} > 95\%$	IX
	Cl-PIB-Cl/$SnCl_4$		-40				Triblock; $B_{eff} > 95\%$	
	Cl-PIB(-Cl)-Cl/$SnCl_4$		-40 to -59				Tri-arm star block; $B_{eff} > 95\%$	

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[a] Roman numerals correlate with the titles of the articles appearing in this issue.

I. A COMPILATION OF EFFECTS OF STERICALLY HINDERED BASES ON CARBOCATIONIC POLYMERIZATION (TABLE 1)

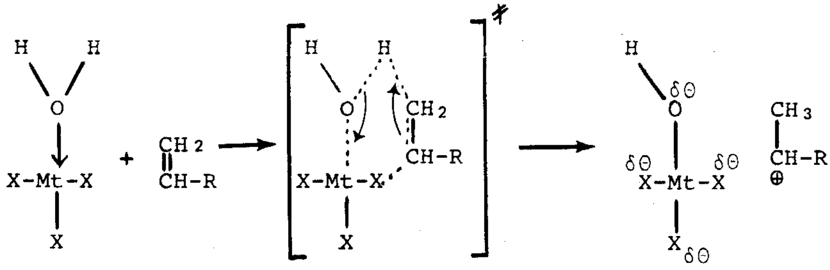
Researchers not actively involved in the investigation of cationic polymerizations may find the very large amount of information uncovered and discussed in the individual articles of this special issue difficult to overview and digest. Therefore we decided comprehensively to organize and present our findings in a more readily absorbable form and to develop a quantitative kinetic theory. For background the reader is referred to the first article in this issue (Setting the Stage) while the subsequent articles contain detailed information.

Table 1 summarizes the polymerization systems examined (monomer, initiating system, solvent, temperature) and the effect of the most-investigated proton trap, 2,6-di-tert-butylpyridine (DtBP), on conversion, molecular weight, and molecular weight dispersity; the arrows in the corresponding columns indicate the direction of the trends observed (↗increasing, ↙decreasing, ∧maximum). The detailed data are in the sources listed in the Reference column.

Two kinds of initiating systems have been examined: protic and nonprotic. In the former systems initiation involves adventitious protogenic impurities (most likely moisture, indicated by "H_2O"). That the proton is necessary for initiation has been proven by stopping experiments, i.e., by investigations carried out in the absence of moisture under high vacuum conditions (see Articles V, VI, VII, VIII, and IX). In nonprotic systems, i.e., with combinations of small and/or large (polymeric) halides in conjunction with Friedel-Crafts acids, initiation occurs by direct cationation, the cation being provided by the halides. Indeed, one of the main justifications for this research was to test our hypothesis that in the presence of DtBP, graft and/or block copolymers can be prepared with ~100% grafting or blocking efficiency by the use of conventional Friedel-Crafts acids. In the absence of DtBP, grafting with conventional Friedel-Crafts acids yields unacceptably low grafting efficiencies [1].

II. KEY FINDINGS AND CONCLUSIONS

1. One of the important conclusions reached in this work concerns the mechanism of initiation in protic systems. The fact that polymerization readily occurs with "H_2O"/$AlCl_3$, "H_2O"/$SnCl_4$, "H_2O"/BCl_3, and "H_2O"/$TiCl_4$ systems in the presence of specific proton traps like DtBP and other very strong nonnucleophilic bases (see Setting the Stage and Articles IV, V, VI, and VII) leads to the postulate that initiation (or more accurately ion generation) cannot exclusively occur by *free* protons because the proton traps would abort such an event; thus it is suggested that initiation may also proceed by *concerted protonation,* i.e., by a process which does not involve free proton, e.g.,



DtBP would be unable to block such an event because of steric compression. Thus the often-postulated protic initiation mechanism involving the ion generation step, e.g.,

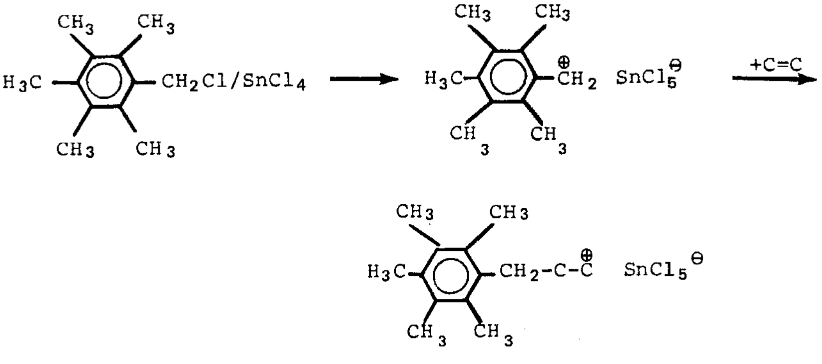
$$H_2O{\cdot}BF_3 \rightleftharpoons H^{\oplus}BF_3OH^{\ominus}$$

followed by protonation of monomer:

$$H^{\oplus}BF_3OH^{\ominus} + M \longrightarrow HM^{\oplus}BF_3OH^{\ominus}$$

probably does not operate in the presence of sufficient amounts of DtBP even in polar media.

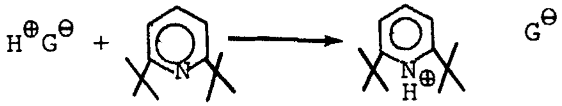
In contrast to protic initiation, nonprotic initiation involving carbenium ion formation followed by rapid cationation seems to operate unmolested even in the presence of large quantities of proton traps, e.g.,



Most likely proton traps are prevented from approaching the carbenium ion site on account of steric compression.

2. A further key finding is evidence for "terminative proton entrapment," i.e., proton trapping during chain transfer to monomer. For

example, the polymerization of α-methylstyrene by conventional Friedel-Crafts acids rapidly proceeds to 100% monomer conversion because kinetic termination is absent and the proton that emerges during chain transfer to monomer sustains the propagation step indefinitely (in the absence of impurities). In the presence of proton traps, e.g., DtBP, the extent of conversions decrease because the DtBP, even if present in very small concentrations, efficiently competes during chain transfer with the monomer for the proton, and by permanently complexing the latter aborts the kinetic chain. Complexation most likely involves quaternization of the nitrogen:



Proton trapping during chain transfer is tantamount to kinetic termination, hence the term *terminative proton entrapment.*

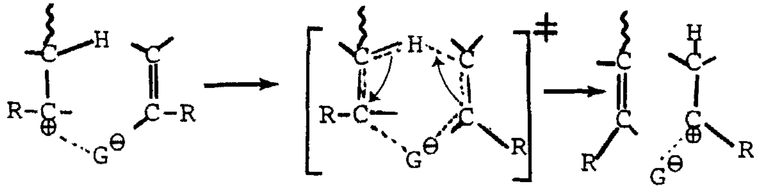
Experiments with DtBP provided evidence for the existence of more than one kind of chain transfer to monomer (Article V). Previously it has been postulated [2-4] that chain transfer to monomer may proceed by an indirect (counteranion assisted, spontaneous) first-order route or by a direct (unassisted) second-order process:

$$-C-C^{\oplus}G^{\ominus} \longrightarrow -C=C + H^{\oplus}G^{\ominus} \xrightarrow{+M} -C=C + HM^{\oplus}G^{\ominus}$$

or

$$-C-C^{\oplus}G^{\ominus} + M \longrightarrow -C=C + HM^{\oplus}G^{\ominus}$$

It seems that proton traps can abort the first-order route, a process in which protons are intermediates. However, they cannot interfere with the second-order route where proton transfer most likely occurs in a concerted manner:



3. The fact that high efficiency grafting and blocking can be obtained in the presence of DtBP by conventional Friedel-Crafts acids is further direct proof for terminative proton entrapment (Articles VIII and IX). Due to uncontrolled initiation by protic impurities and indirect chain transfer to monomer, massive homopolymer formation occurs so that grafting from certain halogenated polymers, i.e., PVC, polychloroprene, and chlorinated butyl rubber, in conjunction with $AlCl_3$, $SnCl_4$, and $TiCl_4$, is a most inefficient undertaking (see Article VIII). In the presence of proton traps, graft copolymer unadulterated by homopolymer can be harvested and grafting efficiencies close to 100% can be readily achieved. Complete monomer utilization during grafting is strong evidence for terminative proton entrapment, i.e., permanent complexing by the DtBP of the proton emerging during chain transfer to monomer. The fact that very high grafting and blocking efficiencies can be obtained in the presence of even relatively small amounts of DtBP suggests that the first-order or indirect route (the one that is aborted by DtBP) is far more important in these polymerizations than the second-order nontrappable route.

4. On the basis of small-molecule organic chemical literature (see Setting the Stage), we have anticipated that DtBP is totally inert toward carbocations in general (indeed, had we not believed this we would not have commenced these investigations). While the weight of evidence is very strong for essentially instantaneous interaction between "free" proton and DtBP, the facts do not bear out the contention that DtBP is inert toward the propagating carbenium ion. According to kinetic findings relative to the cumyl chloride/BCl_3/isobutylene system (Article III), DtBP definitively interacts (complexation?) with the propagating polyisobutylene cation (see Figs. 2 and 3 in Article III).

Further, according to ^1H NMR spectroscopy the polyisobutylene formed in the presence of DtBP in this particular system is exclusively an exo-olefin ($\sim CH_2{-}C(CH_3){=}CH_2$). Evidently DtBP is able to abstract protons from $-CH_3$ groups adjacent to the propagating carbenium center but cannot do so form the shielded $-CH_2-$ group. This finding may be of value to the macromolecular engineer who is always on the look-out for methods for the synthesis of well-defined functional endgroups. Interestingly, DtBP seems to be neither an inhibitor nor retarder toward the other propagating species examined.

5. In most of the systems studied the molecular weights significantly increase (an exception is the cumyl chloride/BCl_3/isobutylene system, see previous paragraph 4) and molecular weight distributions tend to get narrower in the presence of DtBP. As discussed in detail in the individual chapters (see Articles V and VI), these phenomena suggest interaction, probably complexation, between the growing cation and DtBP. While the nature of these $\sim C^{\oplus}$...DtBP species is obscure, they are system specific and their concentration is affected by reaction conditions (polarity, temperature, reagent concentrations).

6. System polarity (as reflected by the overall dielectric constant ϵ) profoundly affects conversions, molecular weights, and molecular weight distributions in the "H_2O"/BCl_3/α-methylstyrene system; however, these effects are much smaller in the presence of DtBP (Figs. 12-14, Article V). It seems that by the addition of even a relatively small amount of DtBP to a polar (CH_2Cl_2) polymerization system, the mechanism would shift to one characteristic for a nonpolar (n-heptane or CCl_4) system. The lower conversions obtained in nonpolar media and/or in polar media in the presence of DtBP are most likely due to decreased initiation by free protons. Similarly, the higher molecular weight and narrower molecular weight distributions observed in nonpolar media and/or in polar media in the presence of DtBP are due to decreased chain transfer.

7. Close examination of the data indicate subtle but characteristic differences between what appear to be very similar systems at first glance. For example, the slopes of the ln $\overline{M}_n$ versus 1/T (Arrhenius) lines for the "H_2O"/BCl_3/αMeSt and "H_2O"/$SnCl_4$/αMeSt systems obtained in the absence and presence of DtBP are different (compare Fig. 3 in Article V and Fig. 1 in Ref. 5). Other examples abound. Thus the effects due to DtBP are system specific and generalizations should be made only with the utmost care.

III. KINETIC THEORY

Bearing in mind the key findings and conclusions presented in the previous sections, a kinetic model has been developed and tested against available experimental data. The derived equations quantitatively describe the data in respect to the effect of DtBP on yields and molecular weights.

A. The Basic Kinetic Model

A basic model has been developed for carbocationic polymerizations initiated by two-component initiating systems RX/MtX_n where the initiator is a cation source (cationogen, RX) and the coinitiator is a Friedel-Crafts acid (usually metal halide MtX_n).

Except for the details of initiation, the premises of this basic scheme are very similar to those outlined by Burton and Pepper [6] for the sulfuric acid fast-initiated nonstationary styrene polymerization.

1. Initiation = Ion Generation + Cationation

$$RX + MtX_n \rightleftharpoons RX{\cdot}MtX_n \qquad \text{rapid equilibration} \qquad (1)$$

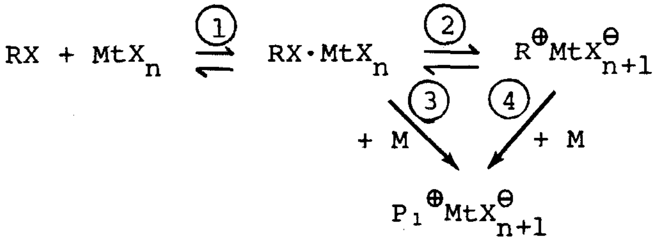
$$RX{\cdot}MtX_n \rightleftharpoons R^{\oplus}MtX^{\ominus}_{n+1} \equiv R^{\oplus}G^{\ominus} \qquad \text{rapid equilibration} \qquad (2)$$

$$RX{\cdot}MtX_n + M \longrightarrow P_1^{\oplus}MtX^{\ominus}_{n+1} \equiv P_1^{\oplus}G^{\ominus} \qquad \text{fast reaction} \qquad (3)$$

$$R^{\oplus}G^{\ominus} + M \longrightarrow P_1^{\oplus}G^{\ominus} \qquad \text{fast reaction} \qquad (4)$$

where RX may be a Bronsted acid (HCl, H_2O, etc.), or active organic halide (tert-butyl chloride, benzylbromide, poly(vinyl chloride), polychloroprene, or active alcohol, (trityl alcohol, benzhydrol), or halogen (chlorine), or interhalogen compounds (iodo chloride); MtX_n is a conventional Friedel-Crafts acid, i.e., $AlCl_3$, BF_3, BCl_3, $SnCl_4$, $TiCl_4$. The cation $R^{\oplus}$ may be proton, carbenium ion, or halonium ion, and the $MtX^{\oplus}_{n+1}$ (or $G^{\ominus}$) is a counteranion formed from the Friedel-Crafts acid and corresponding base. M stands for monomer and $P_1^{\oplus}$ for the first propagating carbocation.

As illustrated by the scheme below, initiation commences by the formation of a loose complex between the initiator and coinitiator, Eq. (1); subsequently the complex may yield the initiating ion pair, Eq. (2), or react by a concerted process with monomer to produce the first propagating unit, Eq. (3). Or else the initiating ion pair formed by Eq. (2) may react with monomer also to produce the first propagating unit, Eq. (4). Whichever route is followed, initiation is rapid.



It is important to bear in mind that in case the initiator is a proton source, i.e., RX = HX or H_2O, initiation may occur by a nontrappable protonless concerted process (via Eq. 3) or it may involve proton ($R^{\oplus} = H^{\ominus}$) in which case it will proceed by a trappable process (Eq. 4).

2. Propagation

$$P_n^{\oplus}G^{\ominus} + M \xrightarrow{k_p} P_{n+1}^{\oplus}G^{\ominus} \tag{5}$$

3. Chain Transfer to Counter Anion (Unimolecular)

$$P_n^{\oplus}G^{\ominus} \xrightarrow{k_{tr,G}} P_n + H^{\oplus}G^{\ominus} \tag{6}$$

rapidly followed by eq. 4 ($H^{\oplus}=R^{\oplus}$)

4. Chain Transfer to Monomer (Bimolecular)

$$P_n^{\oplus}G^{\ominus} + M \xrightarrow{k_{tr,M}} P_n + P_1^{\oplus}G^{\ominus} \tag{7}$$

5. Termination

$$P_n^{\oplus}G^{\ominus} \xrightarrow{k_t} P_n + G \tag{8}$$

where G is the remnant of the Friedel-Crafts acid after termination by ion collapse, e.g., $BCl_3OH^{\ominus} \longrightarrow BCl_2OH$.

B. Rates and Yields

The number of growing cations in the system is

$$[P^{\oplus}] = \sum_{n=1}^{\infty} [P_n^{\oplus}] \tag{9}$$

and the number of active initiating species is assumed to be equal to the number of initiating events:

$$I_0 = [P^{\oplus}]_0 = [P_1^{\oplus}]_0 \tag{10}$$

In an undisturbed system I_0 includes both nontrappable (I_1) and trappable (I_2) initiations, i.e., $I_0 = I_1 + I_2$.

The yield or conversion is

$$Y = 1 - \frac{[M]}{[M]_0} \tag{11}$$

where $[M]$ and $[M]_0$ are the prevailing and initial monomer concentrations, respectively.

The rate of disappearance of growing cations is

$$- d[P^{\oplus}]/dt = k_t[P^{\oplus}] \tag{12}$$

and the rate of monomer disappearance (neglecting monomer consumption by transfer) is

$$- d[M]/dt = k_p[P^{\oplus}][M] \tag{13}$$

The change in active ion concentration as a function of time (by the use of Eq. 10) is

$$[P^{\oplus}] = I_0 \exp(-k_t t) \tag{14}$$

and the yield (from Eq. 13, by substituting Eqs. 11 and 14) is

$$Y = 1 - \exp\left\{ - \frac{k_p}{k_t} I_0[1 - \exp(- k_t t)] \right\} \tag{15}$$

At the end of the polymerization ($t = \infty$) all active centers disappeared ($[P^{\oplus}]_{\infty} = 0$) and the ultimate conversion

$$Y_{\infty} = 1 - \exp\left(- \frac{k_p}{k_t} I_0\right) \tag{16}$$

In the absence of termination ($k_t = 0$, e.g., α-methylstyrene polymerization) the active center concentration remains constant throughout the polymerization

$$[P^{\oplus}] = I_0 \tag{17}$$

and since

$$\lim_{k_t \to 0} \frac{1 - \exp(-k_t t)}{k_t} = t \tag{18}$$

the time dependence of conversion is

$$Y = 1 - \exp(-k_p I_0 t) \tag{19}$$

which ultimately reaches $Y_\infty = 1$.

C. Degree of Polymerization ($\overline{DP}_n$)

The number-average degree of polymerization is given by the ratio of the total number of monomer molecules polymerized over the total number of macromolecules formed:

$$\overline{DP}_n = \frac{[M]_0 - [M]}{[P]} \tag{20}$$

where $[P]$ includes the number of polymer molecules formed by initiation (I_0) and by chain transfer (n), i.e.,

$$dn/dt = k_{tr,G}[P^{\oplus}] + k_{tr,M}[P^{\oplus}][M] \tag{21}$$

Substituting Eq. (14) for $[P^{\oplus}]$, and Eqs. (11) and (15) for $[M]$, we obtain

$$n = \frac{k_{tr,M}}{k_p}[M]_0 Y + \frac{k_{tr,G}}{k_p}[-\ln(1 - Y)] \tag{22}$$

Thus

$$\overline{DP}_n = \frac{[M]_0 Y}{I_0 + \frac{k_{tr,M}}{k_p}[M]_0 Y + \frac{k_{tr,G}}{k_p}[-\ln(1 - Y)]} \tag{23}$$

At the end of polymerization $Y = Y_\infty$, the ultimate degree of polymerization is

$$\overline{DP}_{n,} = \frac{[M]_0 Y_\infty}{I_0 + \frac{k_{tr,M}}{k_p}[M]_0 Y_\infty + \frac{k_{tr,G}}{k_t} I_0} \tag{24}$$

or

$$\frac{1}{\overline{DP}_{n,\infty}} = \frac{k_{tr,M}}{k_p} + \frac{k_{tr,G} + k_t}{k_t} \frac{I_0}{[M]_0 Y_\infty} \tag{25}$$

Since from Eq. (16)

$$I_0 = -\frac{k_t}{k_p} \ln (1 - Y_\infty) \tag{26}$$

we can write an equivalent expression for Eq. (25):

$$\frac{1}{\overline{DP}_{n,\infty}} = \frac{k_{tr,M}}{k_p} + \frac{k_{tr,G} + k_t}{k_p} \frac{-\ln (1 - Y_\infty)}{[M]_0 Y_\infty} \tag{27}$$

Equation (27) is the integrated form of the Mayo equation and is valid for any ultimate conversion. In case of low ultimate conversions ($Y_\infty < 0.1$)

$$\frac{-\ln (1 - Y_\infty)}{Y_\infty} \approx 1 \tag{28}$$

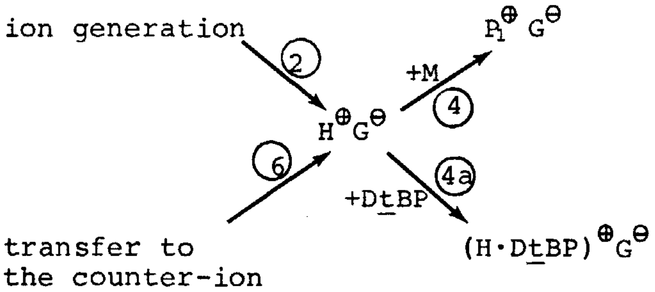
Eq. (27) reverts to the conventional form of the Mayo equation.

D. The Basic Model Modified to Account for the Presence of DtBP

In the presence of DtBP the basic model, Eqs. (1)-(8), must be modified to account for the changes due to the proton trap in the system. On the basis of evidence presented in the earlier articles and earlier sections of this Summary, DtBP will affect carbocationic polymerizations in three ways: 1) In a general manner by forming a loose complex with cations, be these initiating or growing, and thus influencing every process these species are involved:

$$C^{\oplus}G^{\ominus} + DtBP \rightleftharpoons C^{\oplus}DtBP\ G^{\ominus} \qquad (29)$$

2) In a specific manner by proton trapping, i.e., stopping processes in which protons are intermediates. Thus DtBP will specifically abort initiation, i.e., if $R^{\oplus} = H^{\oplus}$ in Eq. (2), and chain transfer to counteranion, Eq. (6):



3) Under certain circumstances DtBP may also function as a conventional terminating agent (see the cumyl chloride/BCl_3/isobutylene system, Article III).

In line with these considerations the basic model was extended to include these contingencies. The subtle difference between the symbols denoting the complexes $(H\cdot DtBP)^{\oplus}$ and $(P^{\oplus}DtBP)$ in the subsequent treatment serves to indicate that the former is visualized as a protonated DtBP, i.e., well-defined quaternary N-cation, whereas the latters are hypothetical constructs involving an undefined loose complex between the electrophile and DtBP.

1. Initiation (Ion Generation + Cationation)

$$RX + MtX_n \rightleftharpoons RX\cdot MtX_n \qquad \text{rapid equilibration} \qquad (1)$$

$$RX\cdot MtX_n \rightleftharpoons R^{\oplus}G^{\ominus} \qquad \text{rapid equilibration} \qquad (2)$$

$$RX\cdot MtX_n + M \longrightarrow P_1^{\oplus}G^{\ominus} \qquad \text{fast reaction} \qquad (3)$$

$$R^{\oplus}G^{\ominus} + M \xrightarrow{k_i} P_1^{\oplus}G^{\ominus} \qquad \text{fast reaction} \qquad (4)$$

and

$$(R^{\oplus}DtBP)G^{\ominus} + M \longrightarrow (P^{\oplus}\ DtBP)G^{\ominus} \qquad \text{fast reaction} \qquad (4')$$

If $R^{\oplus} = H^{\oplus}$, i.e., in the presence of Bronsted acids,

$$H^{\oplus}G^{\ominus} + DtBP \xrightarrow{k_{TPE}} (H{\cdot}DtBP)^{\oplus}G^{\ominus} \qquad \text{fast reaction} \qquad (4a)$$

The latter process is in fact a termination step: terminative proton entrapment (TPE).

2. Propagation

$$P_n^{\oplus}G^{\ominus} + M \xrightarrow{k_p} P_{n+1}^{\oplus}G^{\ominus} \qquad (5)$$

and

$$(P_n^{\oplus}DtBP)G^{\ominus} + M \xrightarrow{k'_p} (P_{n+1}DtBP)G^{\ominus} \qquad (5')$$

3. Chain Transfer to Counteranion (Unimolecular)

$$P_n^{\oplus}G^{\ominus} \xrightarrow{k_{tr,G}} P_n + H^{\oplus}G^{\ominus} \qquad (6)$$

rapidly followed by Eq. (4) ($R^{\oplus} = H^{\oplus}$) or, in competition with Eq. (4) by Eq. (4a), i.e., by TPE.

4. *Chain Transfer to Monomer (Bimolecular)*

$$P_n^{\oplus}G^{\ominus} + M \xrightarrow{k_{tr,M}} P_n + P_1^{\oplus}G \qquad (7)$$

and

$$(P_n^{\oplus}DtBP)G^{\ominus} + M \xrightarrow{k'_{tr,M}} P_n + (P_1^{\oplus}DtBP)G^{\ominus} \qquad (7')$$

5. Termination

$$P_n^{\oplus}G^{\ominus} \xrightarrow{k_t} P_n + G \qquad (8)$$

and

$$(P_n^{\oplus}DtDP)\ G^{\ominus} \xrightarrow{k'_t} P_n + DtBP + G \qquad (8')$$

In exceptional cases when DtBP functions as an active terminating agent:

$$P_n^{\oplus}G^{\ominus} + \text{DtBP} \xrightarrow{k_{t,\text{DtBP}}} P_n + (\text{H}\cdot\text{DtBP})^{\oplus}G^{\ominus} \tag{8a}$$

E. Rates and Yields in the Presence of DtBP

The basic kinetic expressions derived in Section B have been expanded to account for the presence of DtBP. In line with these changes, in order to derive expressions for rates, yields, and molecular weights, one has to use composite rate constants, i.e., rate constants that are combinations of rate constants of more than one reaction. Differential Eqs. (12), (13), and (21) do not change by using these composite constants.

The relative concentration of the two kinds of growing species expressed by Eq. (29) is governed by the equilibrium constant K. Thus the concentration of DtBP-complexed growing cations is

$$[P^{\oplus}\text{DtBP}] = \frac{k[\text{DtBP}]}{1 + K[\text{DtBP}]} I_0 \tag{30}$$

Due to the competition between DtBP and monomer for the proton, only a fraction of the available trappable protons can initiate (i.e., if $R^{\oplus} = H^{\oplus}$ in Eq. 2). Thus in the presence of DtBP the number of effective initiation events is

$$I_0 = I_1 + \frac{1}{1 + \alpha[\text{DtBP}]} I_2 \tag{31}$$

where I_1 denotes the number of nonprotic (nontrappable) initiation events (Eq. 3), I_2 is the number of protic (trappable) initiations (if $R^{\oplus} = H^{\oplus}$ in Eq. 2), and

$$\alpha = k_{\text{TPE}}/k_i[M]$$

if $R^{\oplus} = H^{\oplus}$ in Eq. (4).

Similarly, the rate constant that governs the formation of $P_1^{\oplus}$ by unimolecular transfer to the counteranion, Eq. (6), will be determined by the competition between DtBP and monomer for the proton in $H^{\oplus}G^{\ominus}$:

$$\frac{1}{1+\alpha[\mathrm{DtBP}]}k_{tr,G} \tag{32}$$

By the use of these relationships the following expressions are obtained for the composite rate constants.

Rate constant of propagation:

$$K_p = \frac{1}{1+K[\mathrm{DtBP}]}(k_p + k_p{}'K[\mathrm{DtBP}]) \tag{33}$$

Rate constant of chain transfer to counteranion:

$$K_{tr,G} = \frac{1}{1+K[\mathrm{DtBP}]} + \frac{1}{1+\alpha[\mathrm{DtBP}]}k_{tr,G} \tag{34}$$

Rate constant of chain transfer to monomer:

$$K_{tr,M} = \frac{1}{1+K[\mathrm{DtBP}]}(k_{tr,M} + k'_{tr,M}K[\mathrm{DtBP}]) \tag{35}$$

Rate constant of termination:

$$K_t = \frac{1}{1+K[\mathrm{DtBP}]}(k_t + k_{tr,G}\frac{\alpha[\mathrm{DtBP}]}{1+\alpha[\mathrm{DtBP}]} + k'_tK[\mathrm{DtBP}] + k_{t,\mathrm{DtBP}}[\mathrm{DtBP}]) \tag{36}$$

With [DtBP] ⟶ 0 the composite constants approach the simple constants. Assuming that these composite constants are true "constants," they can be used to derive expressions for active center concentration (by Eq. 14), for monomer conversions (by Eqs. 15, 16, or 19), and for the degree of polymerization (by Eqs. 23, 24, 25, or 27).

Although the exact values of the composite constants may change with DtBP and monomer concentrations during polymerizations, we have assumed that they remain unchanged and have used them quantitatively to describe select data. Excellent agreement between calculated and experimental data (see next section) suggests that this assumption was justifiable, particularly in regard to the description of various DtBP concentration effects.

F. Testing of the Kinetic Scheme

By the use of the above kinetic expressions the experimental results obtained in the following systems have been quantitatively described:

"H_2O"/$SnCl_4$/α-methylstyrene	Article VI
"H_2O"/BCl_3/α-methylstyrene	Article V
Cumyl chloride/BCl_3/isobutylene	Article III

Attempts have also been made to describe the "H_2O"/$AlCl_3$/isobutylene system; however, these efforts remained unsuccessful, conceivably because of the microheterogeneity (insolubility) of the $AlCl_3$ in the media used, peculiarities in the initiation mechanism (self-initiation by $AlCl_2^{\oplus}AlCl_4^{\ominus}$ (?)), etc.

In our calculations we disregard bimolecular termination by DtBP (Eq. 8a) because the effect of this event is indistinguishable from that of the complex formed in Equilibrium (29). The two effects are mathematically unseparable because only the sum of the last two terms in Eq. (36) is available:

$$(k_t'K + K_{t,DtBP})[DtBP] = k[DtBP]$$

Thus we assumed $k_{t,DtBP} \approx 0$ even for the cumyl chloride/BCl_3/isobutylene system although direct evidence exists for bimolecular termination by DtBP.

TABLE 2

Table 2 is a summary of relative rate constants estimated by an iterative process by comparing experimental with calculated data. In the protic systems, I_1 and I_2 have also been estimated. For the cumyl chloride/BCl_3/isobutylene system the I_1 value is an experimental quantity. The initial monomer concentrations, $[M]_o$, are experimental values. By the use of the quantities in Table 2 we constructed yield versus ln [DtBP] and $\overline{M}_n$ versus ln [DtBP] plots.

TABLE 2. Parameters Used to Construct Figs. 1-3

			CC/BCl$_3$/ IB: Article III	"H$_2$O"/BCl$_3$/ αMeSt: Article V	"H$_2$O"/SnCl$_4$/ αMeSt: Article VI
1	$\frac{k_p}{k_t + k_{tr,G}}$	(M^{-1})	8.74×10^2	9.19×10^3	7.41×10^3
2	$\frac{k_p'}{k_p}K$	(M^{-1})	4.96×10^3	Very small[a]	1.58×10^2
3	$\frac{k_t'}{k_t + k_{tr,G}}K$	(M^{-1})	3.09×10^5	Very small[a]	1.23×10^4
4	$\frac{k_{tr,M}}{k_p}$	(-)	ϕ[c]	5.94×10^{-4}	5.02×10^{-4}
5	$\frac{k_{tr,M}'}{k_{tr,M}}K$	(M^{-1})	ϕ[c]	Very small[a]	9.70×10^{-4}
6	$\frac{k_{TPE}}{k_i}$	(-)	(-)[b]	$3.18 \quad 10^3$	5.08×10^5
7	$\frac{k_t}{k_t + k_{tr,G}}$	(-)	1[c]	ϕ[c]	ϕ[c]
8	I$_1$ (protonless initiation)	(M)	4.91×10^{-4}	7.95×10^{-5}	2.26×10^{-4}
9	I$_2$ (trappable initiation)	(M)	ϕ[c]	4.28×10^{-4}	3.95×10^{-4}
10	$[M]_0$	(M)	1	0.32	0.924

[a] Final calculations performed by assuming zero for this value.

[b] Irrelevant since chain transfer and protic initiation are absent.

[c] Assumed value in line with previous extensive experimental evidence.

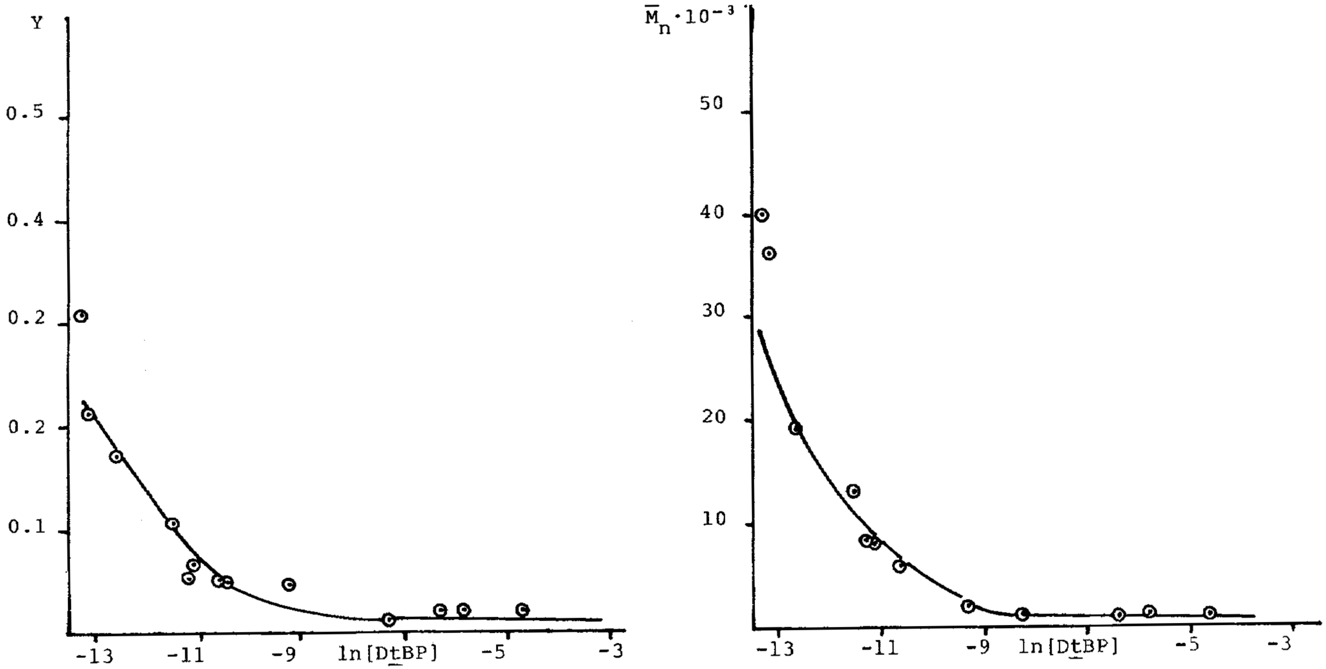


FIG. 1. The effect of [DtBP] on conversion and $\overline{M}_n$ in the cumyl chloride/BCl_3/isobutylene system (Article III).

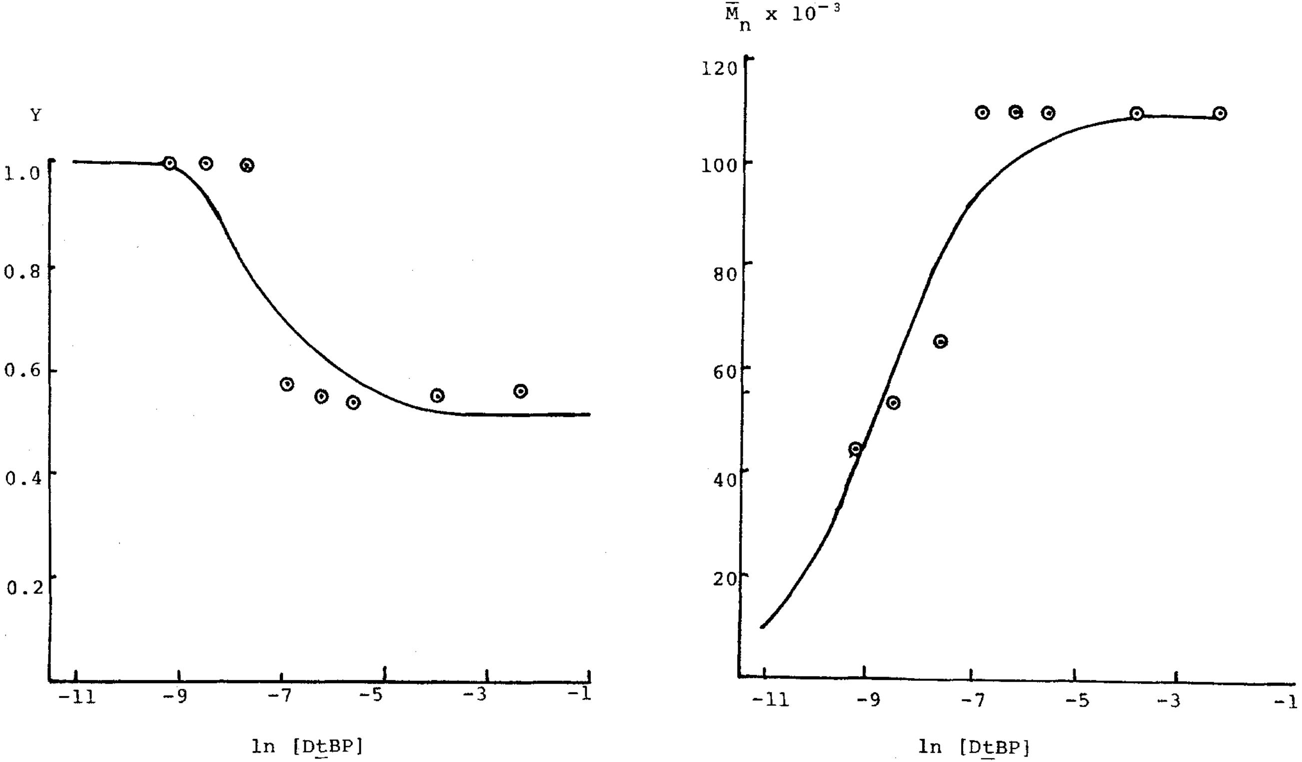


FIG. 2. The effect of [DtBP] on conversion and $\overline{M}_n$ in the "H_2O"/BCl_3/α-methylstyrene system (Article V).

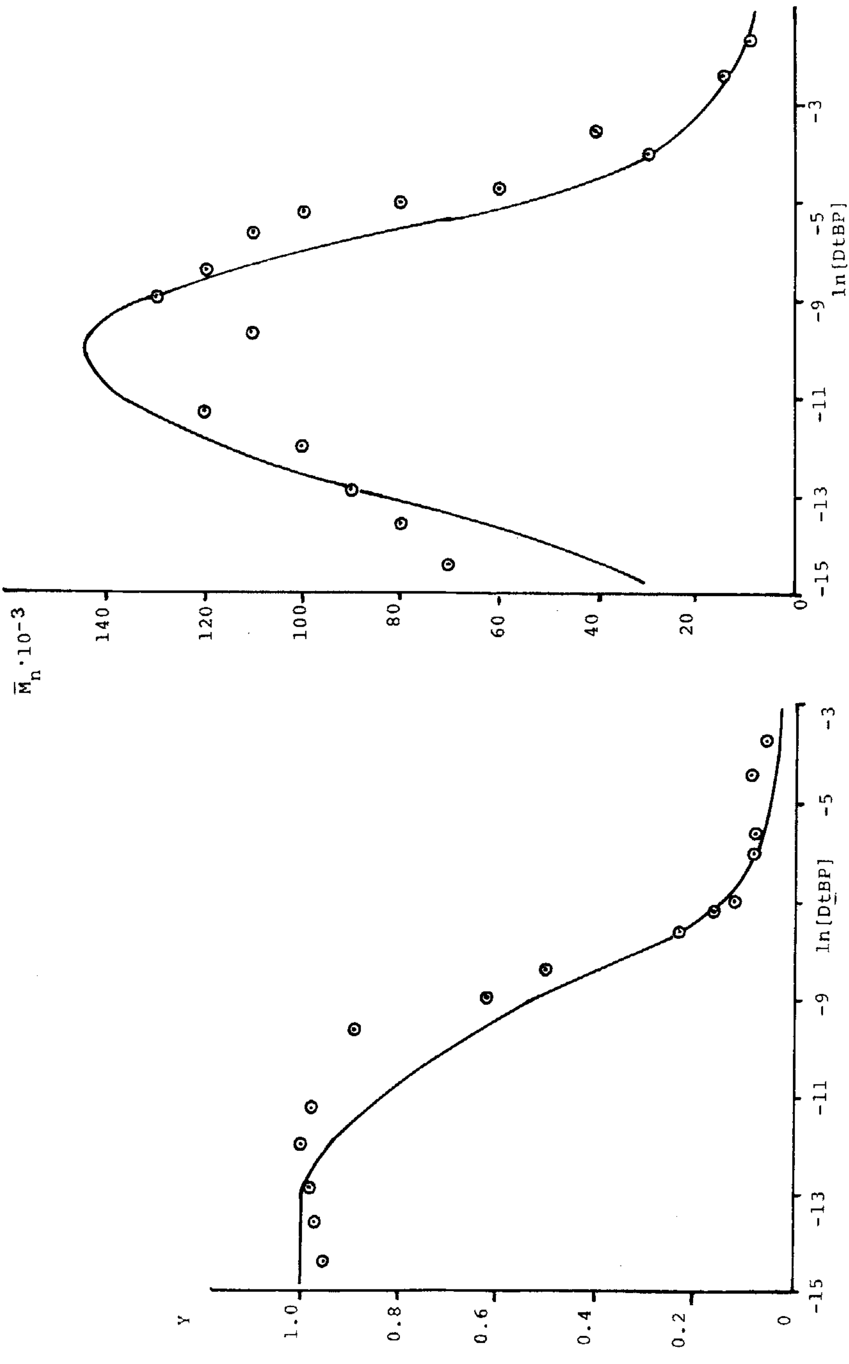


FIG. 3. The effect of [DtBP] on conversion and $\overline{M}_n$ in the "H_2O"/$SnCl_4$/α-methylstyrene system (Article VI).

Figures 1-3 show the results. The agreement between the experimental data and calculated lines are most satisfactory.

These results quantitatively substantiate the basic assumptions made in regard to the effect of DtBP on the mechanism of carbocationic polymerizations. In view of the large number of elementary steps (and constants) involved, however, the numerical values of the constants are necessarily arbitrary and similar sets of parameters may also satisfactorily describe the data.

A detailed examination of the relative constants and parameters in Table 2 leads to the following quantitative information.

A. In Regard to the Cumyl Chloride/BCl_3/Isobutylene System (Article III)

1. Chain transfer to monomer is absent (see Line 4) while termination occurs (see Line 7). Since $k_t/(k_t + k_{tr,G}) = 1$, $k_{tr,G}$ must also be zero.

2. Assuming that the DtBP-complexed cation propagates slower than the uncomplexed one, k_p'/k_p should be < 1; thus K must be > 5000 (see Line 2), i.e., DtBP complexation is strong. Accordingly, $k_t'/k_t \leq 62$, i.e., the DtBP-complexed cation terminates faster than the uncomplexed one.

B. In Regard to the "H_2O"/BCl_3/α-Methylstyrene System (Article V)

1. There is no complexation between DtBP and the growing carbenium ion (K = 0) see Lines 2, 3, and 5).

2. While kinetic termination is absent ($k_t = 0$; see Line 7), transfer to the counteranion and to monomer occur (see Lines 1 and 4).

3. As $k_{tr,M}[M]_0/k_{tr,G} \simeq 1.6$ (see product of parameters in Lines 1, 4, and 10), chain transfer to monomer and chain transfer to counteranion are about of the same significance till [M] is reasonably high.

4. TPE is important (see Line 6).

5. About 84% of initiation is trappable [$I_2/(I_1 + I_2) = 0.84$, see Lines 8 and 9].

C. In Regard to the "H_2O"/$SnCl_4$/α-Methylstyrene System (Article VI)

1. DtBP-uncomplexed carbenium ions do not terminate ($k_t = 0$; see Line 7) but they are involved in chain transfer to counteranion or to monomer (see Lines 1, 3, 4, and 5).

2. Assuming that the DtBP-complexed carbocation propagates slower than the uncomplexed one, k_p'/k_p should be < 1; thus K must be > 160 (see Line 2) which suggests relatively strong complexation. Accordingly $k_t'/k_{tr,G} \leq 77$, i.e., termination by the DtBP-complexed species is faster than chain transfer to the counteranion (see Line 3). In contrast, $k_{tr,M}'/k_{tr,M} \leq 6 \times 10^{-6}$ i.e., chain transfer to monomer by the DtBP-complexed carbenium ion is negligible (see Line 5).

3. $k_{tr,M}[M]_0/k_{tr,G} = 3.4\ M^{-1}$ (see the product of parameters in Lines 1, 4, and 10), i.e., $k_{tr,M}$ is more significant than $k_{tr,G}$ until [M] is reasonably high.

4. About 64% of initiation is trappable [$I_2/(I_1 + I_2) = 0.64$, see Lines 8 and 9].

5. TPE is important (see Line 6). In view of the conclusions in Lines 3 and 4, the role of DtBP is more important in regard to trapping the proton evolving from the initiator than that evolving from the propagating carbocation.

It is noteworthy that DtBP-complexed carbocations exist in the CC/BCl_3/isobutylene and "H_2O"/$SnCl_3$/α-methylstyrene systems, whereas DtBP complexation is very small in the "H_2O"/BCl_3/α-methylstyrene system (see Lines 2, 3, and 5). Conceivably the nature of counteranions ($BCl_4^{\ominus}$ and $SnCl_4OH^{\ominus}$ on the one hand, and $BCl_3OH^{\ominus}$ on the other hand), the size of counteranions, and/or the carbocations involved may explain these phenomena.

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