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Quasiliving Carbocationic Polymerization. II. The Discovery: The α-Methylstyrene System

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ABSTRACT

A detailed analysis of elementary reactions of carbocationic polymerization culminated in the prediction and subsequent experimental demonstration of quasiliving polymerization. Quasiliving polymers are formed in a system provided that the process of chain termination and chain transfer to monomer are absent or reversible, i.e., the propagating ability of the chain end is maintained throughout the experiment, and the molecular weight increases in proportion to the cumulative amount of monomer added. The chain end can be active (carbocation) or dormant (reactivable polymeric olefin or cation source). Chain transfer is suppressed by keeping the monomer concentration low. Quasiliving polymerizations are maintained by continuous slow feeding of dilute monomer to a charge containing the initiating or propagating species (quasiliving polymerization technique). A comprehensive kinetic scheme has been developed that describes quasiliving polymerization in quantitative terms. Quasiliving polymerization was demonstrated experimentally in the "H_2O"/BCl_3/α-methylstyrene and cumyl chloride/BCl_3/α-methylstyrene

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systems. $\overline{M}_n$ versus monomer input plots are linear over wide ranges, indicating quasiliving conditions, and poly(α-methylstyrenes) with $\overline{M}_n > 2 \times 10^5$ have been obtained. Molecular weight distributions were found progressively to narrow and dispersion ratios $\overline{M}_w/\overline{M}_n$ to decrease.

INTRODUCTION

Living polymerization [1, 2] is a unique, extremely valuable tool for the synthesis of well-defined block copolymers and for the control of molecular weights and molecular weight distributions. Living anionic polymerizations provide the basis of several commercial processes, e.g., the production of thermoplastic elastomers [3, 4]. In living polymerizations reactions other than chain initiation and propagation are negligible. Instantaneous initiation yields polymers of narrow (Poisson) molecular weight distribution. Diagnostic proofs of living polymerizations with instantaneous initiation are linear $\overline{M}_n$ versus monomer conversion plots starting at the origin, narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n \approx 1.0$), and the formation of block copolymers by sequential monomer addition.

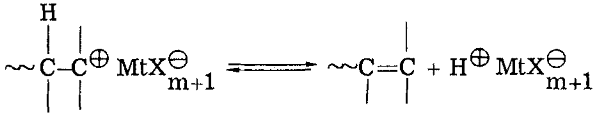
The terminology of living polymerizations or living species has often been misused. For example, recently Higashimura et al. [5-7] claimed living polymerizations in the p-methoxystyrene/iodine/CCl_4 system. Closer examination of the otherwise extremely interesting observations, however, indicates the absence of living polymerizations, i.e., the presence of chain transfer to monomer (see Figs. 2 and 3 in Ref. 7). An attempt to block isobutyl vinyl ether from p-MeOSt$^{\oplus}$ yielded only 39% blocking efficiency due to chain transfer to monomer. According to a recent detailed analysis, the chances for obtaining living carbocationic polymerizations are rather slim [8].

The aim of this research is to overcome the two intrinsic difficulties that prevent the achieving of living carbocationic polymerizations: termination and chain transfer to monomer. Termination (usually by facile ion collapse) is difficult to avoid by manipulating experimental parameters, and the rate of chain transfer to monomer may be reduced but not totally eliminated under select conditions, e.g., low temperatures. Recent insight into the detailed mechanism of these reactions has enabled us to create conditions under which termination and chain transfer to monomer are reversible or avoidable and, indeed, to carry out carbocationic polymerizations which appear as if termination and chain transfer to monomer were absent over a wide range of conditions.

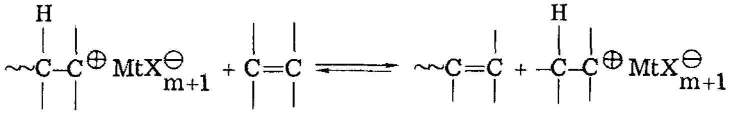
QUASILIVING CARBOCATIONIC POLYMERIZATION: THE PRINCIPLE

We propose that quasiliving polymers can be obtained in systems in which chain transfer to monomer and chain termination are absent or reversible. We introduce the term "quasiliving" to describe these systems and to differentiate them from truly living polymers where termination and transfer reactions are absent. In quasiliving carbocationic polymerization chain transfer and termination may be present but these processes are reversible. The chain ends are not required to remain active throughout the polymerization, they may be temporarily dormant, but they must remain reactivable and able to resume propagation.

In the presence of excess monomer (that is, under conventional polymerization conditions), chain transfer to monomer cannot be prevented since Equilibria (1) and (2) that control monomolecular and bimolecular chain transfer to monomer, respectively, are strongly shifted to the right ($MtX^{\ominus}_{m+1}$ = counterion):



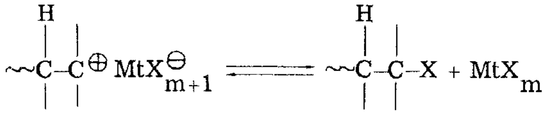
$$\sim\!\sim\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{|}{C}}{}^{\oplus}\,MtX^{\ominus}_{m+1} \rightleftharpoons \sim\!\sim\underset{|}{C}=\underset{|}{\overset{|}{C}} + H^{\oplus}MtX^{\ominus}_{m+1} \tag{1}$$



$$\sim\!\sim\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{|}{C}}{}^{\oplus}\,MtX^{\ominus}_{m+1} + \underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}} \rightleftharpoons \sim\!\sim\underset{|}{C}=\underset{|}{\overset{|}{C}} + -\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{|}{C}}{}^{\oplus}\,MtX^{\ominus}_{m+1} \tag{2}$$

Reaction (1) is rapidly followed by protonation of a monomer which completes the chain transfer to monomer process. In the virtual absence of monomer, these reactions are shifted to the left. Chain transfer can therefore be suppressed by continuous monomer addition at a very low rate, i.e., by maintaining a suitably low monomer concentration [M] in the charge. The incoming monomer would be consumed exclusively by propagation after initiation is complete. Under these quasiliving conditions, provided initiation is practically instantaneous, $\overline{M}_n$ would increase for a considerable period of time in proportion to the amount of monomer introduced, and $\overline{M}_n$ versus monomer input plots would be linear for an experimentally meaningful period reminiscent of $\overline{M}_n$ versus conversion plots obtained in truly living anionic or oxonium ion systems.

The requirement of reversible termination (Eq. 3) could be met in systems in which termination (i.e., the collapse of the propagating cation/counter anion pair) is in equilibrium with ionization:



$$\sim\!\sim \overset{H}{C}\!-\!C^{\oplus}\,MtX^{\ominus}_{m+1} \rightleftharpoons \sim\!\sim \overset{H}{C}\!-\!C\!-\!X + MtX_m \qquad (3)$$

Reversible termination may occur in many carbocationic polymerizations coinitated by $AlCl_3$, $TiCl_4$, BF_3, $SnCl_4$ and similar fully halogenated strong Lewis acids, provided the monomer and reaction conditions are correctly chosen (see below).

The numerical values of the three equilibrium constants (Eqs. 1, 2, and 3):

$$K_H = k_{-H}/k_{+H}, \qquad K_{tr} = k_{tr,M}/k_{tr,M_n^=}, \qquad \text{and } K_t = k_t/k_{ri} \qquad (4)$$

would determine the fraction of the chains that are in the active carbocation form $M_n^{\oplus}$ or in the temporarily dormant forms (i.e., reversibly terminated M_nX or deprotonated carrying an unsaturated chain end $M_n^=$).

QUASILIVING CARBOCATIONIC POLYMERIZATION: QUANTITATIVE TREATMENT

The following kinetic expressions are needed to define the reaction scheme envisioned:

Initiation:

$$I^{\oplus} + M \xrightarrow{k_i} M^{\oplus} \qquad (5)$$

Propagation:

$$M^{\oplus} + M \xrightarrow{k_p} M_2^{\oplus} \qquad (6)$$

$$M_n^{\oplus} + M \xrightarrow{k_p} M_{n+1}^{\oplus} \qquad (6a)$$

Proton explusion from chain end:

$$M_n^{\oplus} \xrightarrow{k_{-H}} M_n^= + H^{\oplus} \qquad (7)$$

Proton expulsion from monomer cation:

$$M^{\oplus} \xrightarrow{k_{-H}} M + H^{\oplus} \tag{7a}$$

Protonation of monomer:

$$H^{\oplus} + M \xrightarrow{k_{+H}} M^{\oplus} \tag{8}$$

Reprotonation of olefinic chain end:

$$H^{\oplus} + M_n^{=} \xrightarrow{k_{+H}} M_n^{\oplus} \tag{8a}$$

Chain transfer to monomer:

$$M_n^{\oplus} + M \xrightarrow{k_{tr,M}} M_n^{=} + M^{\oplus} \tag{9}$$

Chain transfer to olefinic polymer terminus:

$$M^{\oplus} + M_n^{=} \xrightarrow{k_{tr,M_n^{=}}} M + M_n^{\oplus} \tag{10}$$

Termination (ion collapse):

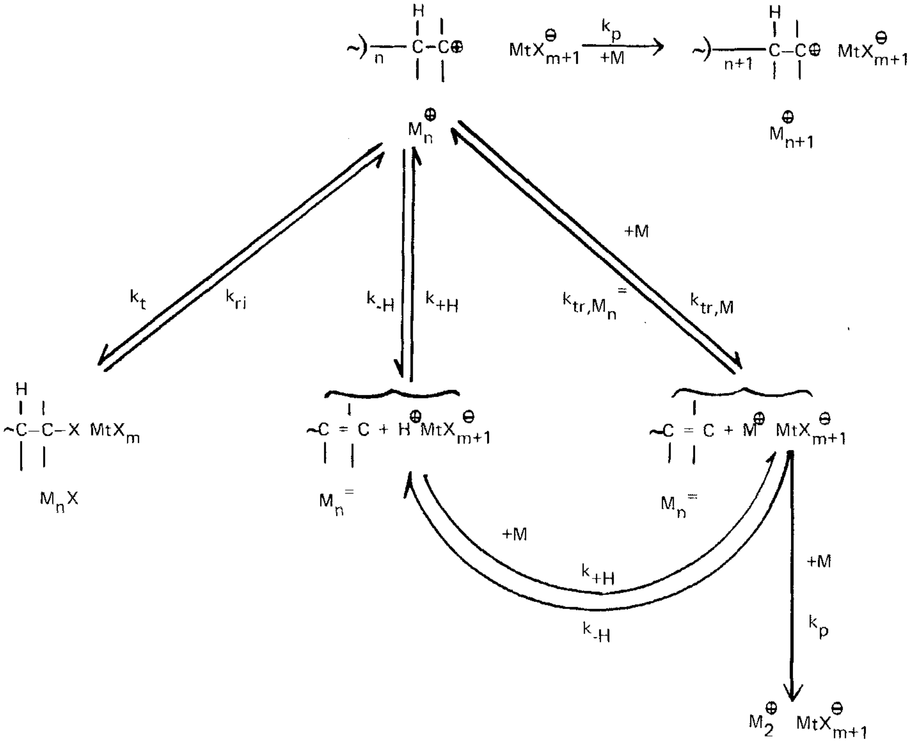
$$M_n^{\oplus}\, MtX_{m+1}^{\ominus} \xrightarrow{k_t} M_nX + MtX_m \tag{11}$$

Reionization:

$$M_nX + MtX_m \xrightarrow{k_{ri}} M_n^{\oplus}\, MtX_{m+1}^{\ominus} \tag{12}$$

where M is monomer; $M_n^{=}$ is polymer with olefinic chain end; M_nX is polymer with halogenated chain end; $I^{\oplus}$, $M^{\oplus}$, and $M_n^{\oplus}$ are initiator-, monomer-, and polymer-cations; $H^{\oplus}$ is proton; MtX_m is Friedel-Crafts acid coinitiator, and $MtX_{m+1}^{\ominus}$ is counterion. The subscript "n" denotes degrees of polymerization from 2 to ∞.

Unlikely reactions, reactions that occur only under special conditions, or reactions that do not have an effect on the concentration of species in the system (e.g., attack of propagating carbocation on olefin-terminated polymer, chain transfer to solvent or polymer) have not been considered.



SCHEME 1.

Inspection of the above equations shows that except for initiation (Eq. 5) and propagation (Eqs. 6 and 6a) which can proceed only in the forward direction, all other reactions are parts of equilibria: (7) ⇌ (8a), (7a) ⇌ (8), (9) ⇌ (10), and (11) ⇌ (12). Under conventional conditions, i.e., in the presence of excess monomer, or when adding the initiating system to a charge of monomer, the rates of Reactions (8) and (9) are high. Thus except for Reactions (7a), (8a), and (10), which become important only in the presence of very low [M], this scheme is identical to that valid for conventional carbocationic polymerizations.

Scheme 1 helps to visualize the detailed kinetic scheme. Thus two monomer molecules are consumed to start a new polymer chain by the irreversible Reaction (6). The formation of a new polymer chain is second order while propagation is first order in monomer; thus decreasing the monomer concentration decreases the rate of polymer generation (of which chain transfer to monomer is the first step) more than that of propagation. In quantitative terms, using Equilibria (1) and (2) and assuming $k_{tr,M} = k_{tr,M_n^=}$:

$$\frac{\text{rate of polymer generation}}{\text{rate of propagation}} = \frac{k_p[M^{\oplus}][M]}{k_p[M_n^{\oplus}][M]} = \frac{[M]}{[M_n^{=}]} \qquad (13)$$

The degree of polymerization equation can be derived by the following considerations. The differential equations describing the changes in the concentration of monomer and in the concentration of polymer species are as follows:

$$\frac{-d[M]}{dt} = k_p([M^{\oplus}] + [M_n^{\oplus}])[M] + k_i[I^{\oplus}][M] + k_{tr,M}[M_n^{\oplus}][M]$$

$$- k_{tr,M_n^{=}}[M^{\oplus}][M_n^{=}] + k_{+H}[H^{\oplus}][M] - k_{-H}[M^{\oplus}] \qquad (14)$$

$$\frac{d[M_n^{\oplus}]}{dt} = k_p[M^{\oplus}][M] + k_{+H}[H^{\oplus}][M_n^{=}] + k_{tr,M_n^{=}}[M^{\oplus}][M_n^{=}]$$

$$+ k_{ri}[M_nX][MtX_m] - k_t[M_n^{\oplus}]$$

$$- k_{-H}[M_n^{\oplus}] - k_{tr,M}[M_n^{\oplus}][M] \qquad (15)$$

$$\frac{d[M_n^{=}]}{dt} = k_{-H}[M_n^{\oplus}] - k_{+H}[H^{\oplus}][M_n^{=}] + k_{tr,M}[M_n^{\oplus}][M]$$

$$- k_{tr,M_n^{=}}[M^{\oplus}][M_n^{=}] \qquad (16)$$

$$\frac{d[M_nX]}{dt} = k_t[M_n^{\oplus}] - k_{ri}[M_nX][MtX_m] \qquad (17)$$

Equation (14) expresses the rate of monomer consumption by Processes (5), (6), (6a), (7a), (8), (9), and (10). Under our conditions of quasiliving carbocationic polymerization, the monomer consumed by these reactions is continuously replenished, i.e., the rate of monomer addition A and that of monomer consumption are equal:

$$-d[M]/dt = A \tag{18}$$

and monomer conversion is practically 100%.

Integration of (18) gives the total number of monomer molecules consumed, i.e., the cumulative amount of monomer added in 1 dm^3 mixture during the time interval (0, t):

$$[M]_{total} = At \tag{19}$$

The concentration change of polymeric species is given by the sum of Eqs. (15-17):

$$\frac{d[M_n^-]}{dt} + \frac{d[M_n^\oplus]}{dt} + \frac{d[M_nX]}{dt} = k_p[M^\oplus][M] \tag{20}$$

where $[M_n]$ stands for the polymer concentration, i.e., for the total number of polymer molecules present in 1 dm^3 mixture.

Let us consider a short time interval, t' $\ll$ t - t', during the initial stages of polymerization, i.e., during which initiation rapidly goes to completion and every initiator molecule initiates one kinetic chain. During time t'

$$\int_0^{t'} k_p[M^\oplus][M] = [I]_0 \tag{21}$$

i.e., the number of polymer chains starting to grow is equal to the number of kinetic chains initiated by $[I]_0$. Considering Eq. (21), integration of (20) yields

$$[M_n] = [I]_0 + \int_{t'}^{t} k_p[M^\oplus][M]\,dt \tag{22}$$

Since the degree of polymerization at any time t is

$$\overline{DP}_n = \frac{\text{number of monomer molecules consumed}}{\text{number of polymer molecules present}} = \frac{[M]_{total}}{[M_n]} \tag{23}$$

from (19) and (22) we obtain

$$\overline{DP}_n = \frac{At}{[I]_0 + \int_{t'}^{t} k_p[M^\oplus][M]\,dt} \tag{24}$$

The system behaves as a living system as long as the condition

$$[I]_0 \gg \int_{t'}^{t} k_p[M^{\oplus}][M]\, dt \tag{25}$$

is fulfilled. During this period, which can be extended by lowering the monomer concentration, i.e., the monomer addition rate, we have

$$\overline{DP}_n \approx At/[I_0] \qquad \text{and} \qquad \overline{M}_n \approx [M]_{total}/[I]_0 \tag{26}$$

EXPERIMENTAL

Materials

α-Methylstyrene (αMeSt) was extracted with 10% aqueous NaOH, washed neutral with distilled water, dried over molecular sieves, and distilled from CaH_2 under vacuum at 35°C. Methylcyclohexane (MeCH) was refluxed with oleum for 1 h to remove unsaturated impurities, then washed with distilled water, 5% aqueous $NaHCO_3$, distilled water, dried over molecular sieves, and distilled from CaH_2 under N_2 at 101°C. Methylene chloride (CH_2Cl_2) was dried over molecular sieves, distilled from CaH_2, refluxed, and distilled from Et_3Al at 40°C under nitrogen. Cumyl chloride (2-chloro-2-propylbenzene) was prepared from purified α-methylstyrene by hydrochlorination in CH_2Cl_2 solution; excess HCl and solvent were removed by repeated freeze-drying. BCl_3 was condensed from a lecture bottle under N_2 in the dry box.

Procedures

Polymerizations were performed at -50°C in a stainless steel enclosure (dry box) under N_2 in round-bottom, three-neck flasks equipped with stirrer, Teflon plug for monomer addition, and outlet for sampling. Liquid αMeSt was introduced continuously by a Waters Associates chromatography pump Model 6000A into solvent charges of 50 mL. Samples were withdrawn by a syringe through a serum cap and were injected into excess methanol in capped vials.

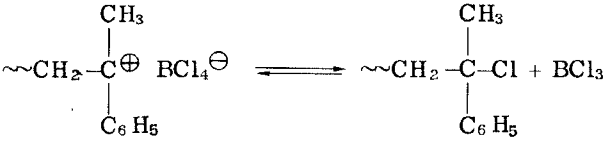
Molecular weights were obtained by a Waters Associates High Pressure GPC equipped with five Microstyragel columns (10^6, 10^5, 10^4, 10^3, and 500 Å) and dual UV and RI detectors, and a universal calibration curve using polystyrene standards.

RESULTS AND DISCUSSION: EXPERIMENTAL DEMONSTRATION OF QUASILIVING POLYMERIZATION

Keeping in mind the above kinetic requirements, we selected the "H_2O"/BCl_3/αMeSt and the cumyl chloride/BCl_3/αMeSt systems to achieve quasiliving polymerization. Based on previous experience we believed that in these systems (a) termination is reversible; (b) conditions can be found under which irreversible chain transfer to monomer (i.e., chain transfer to monomer leading to indane-skeleton formation) can be suppressed, while reversible chain transfer to monomer (i.e., chain transfer to monomer leading to polymeric olefin) can be maintained; (c) the rate of initiation R_i will be equal to or greater than the rate of propagation R_p; and (d) the rate of monomer addition can be reduced so as to maintain a very low monomer concentration throughout the experiment. These conditions will now be examined.

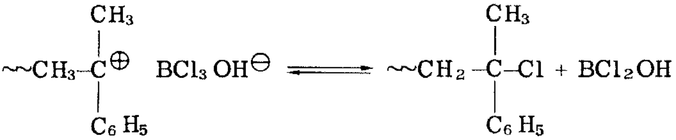
(a) Reversibility of Termination

Previous studies in our laboratories indicated [9] that termination is absent or reversible in αMeSt polymerization coinitiated by BCl_3:

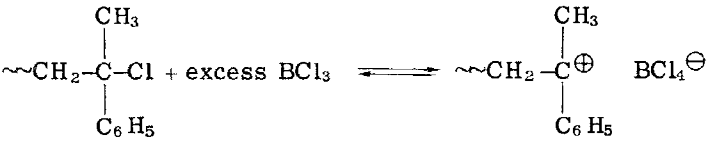


$$\sim\!\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{C^{\oplus}}}\ BCl_4^{\ominus} \rightleftharpoons \sim\!\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{C}}-Cl + BCl_3 \qquad (27)$$

The counteranion becomes $BCl_4^{\ominus}$ even in "H_2O"-initiated systems because of the following sequence of events:



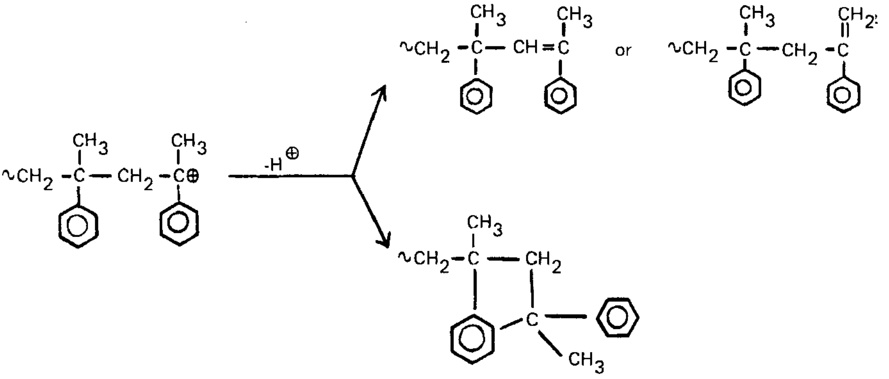
$$\sim\!\sim CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{C^{\oplus}}}\ BCl_3OH^{\ominus} \rightleftharpoons \sim\!\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{C}}-Cl + BCl_2OH \qquad (28)$$



$$\sim\!\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{C}}-Cl + \text{excess } BCl_3 \rightleftharpoons \sim\!\sim CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle C_6H_5}{C^{\oplus}}}\ BCl_4^{\ominus} \qquad (29)$$

(b) Reversibility of Chain Transfer to Monomer

Chain transfer to monomer in cationic αMeSt polymerization may give rise to polymeric olefin (reversible) or to a polymeric indane derivative (irreversible):



Proton NMR spectra of low molecular weight PMeSt fractions, prepared at +25 and -20° C, did not show olefinic protons and the ratio aliphatic/aromatic protons suggested indane endgroups. However, indane formation was found to be negligible at -50° C using a rather nonpolar medium, i.e., 25/75 v/v CH_2Cl_2/MeCH.

Thus, in low polar media at low temperatures, chain transfer to monomer has been restricted to olefin formation, the equilibrium of which can be shifted toward recationation by maintaining low monomer concentration in the system.

(c) $R_i \geq R_p$

Although instantaneous initiation is not a mandatory requirement, it greatly facilitates the diagnosis of quasiliving polymerizations.

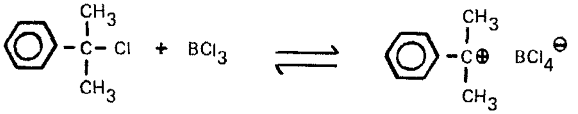
Initiation in carbocationic polymerization is visualized to involve slow ionization:

$$IX + MtX_m \rightleftharpoons I^{\oplus} MtX^{\ominus}_{m+1} \qquad (30)$$

where IX is usually an active halogen-containing compound, followed by rapid cationation of monomer (Eq. 5):

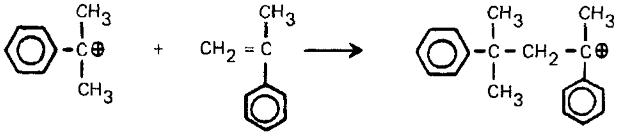
$$I^{\oplus} + M \xrightarrow{k_i} M^{\oplus} \qquad (31)$$

Initiation in the "H_2O"/BCl_3/αMeSt system was thought to be due to ubiquitous impurities (the quotation marks around H_2O indicate impurity) [10]. "H_2O" in the system is expected to be present in sufficient quantity ($\sim 10^{-3}$ mol/dm^3) to yield rapidly the highly reactive ion pair $H^{\oplus}/BCl_3OH^{\ominus}$ prior to monomer introduction. Thus by choosing this particular system we hoped to assure rapid initiation by "H_2O"; however, we sacrificed exact knowledge of the initiator concentration $[I]_0$. It was anticipated and subsequently demonstrated (see below) that $[I]_0$ can be calculated from $\overline{M}_n$ versus monomer input plots. Fast initiation was thought to be achievable with the cumyl chloride/BCl_3/αMeSt system by adding monomer to premixed cumyl chloride/BCl_3 mixtures. Premixing these ingredients would lead to the ion pair



(32)

which would rapidly effect initiation by cumylation:



(33)

since the structure of the initiating cumyl cation and that of the propagating PαMeSt$^{\oplus}$ cation are practically identical. Thus fast initiation was expected to occur by the addition of monomer to "H_2O"/BCl_3 or premixed cumyl chloride/BCl_3 systems since ion generation could take place in the absence of monomer.

(d) Maintenance of Low Monomer Concentration

The mandatory requirement of maintaining low [M] has been established by a series of preliminary runs in which the monomer input rate was varied. Quasiliving polymerizations have been achieved by continuously feeding 0.725 g αMeSt (undiluted or diluted by suitable solvents) per minute into well-stirred charges of "H_2O"/BCl_3 (2×10^{-2} mol/dm^3) in CH_2Cl_2/MeCH (25/75 v/v) at -50°C (for details, see the Experimental section and the Table 1 title). Frequent samples have been withdrawn during the experiment and $\overline{M}_n$ and $\overline{M}_w/\overline{M}_n$ have been determined. The experiments have usually been continued until the increasing viscosity of the homogeneous charges (at 25-35% polymer content) prevented sampling and rendered stirring difficult.

TABLE 1. Quasiliving Polymerization of α-Methylstyrene Initiated by "H_2O"/BCl_3 (CH_2Cl_2/MeCH) 25/75 v/v; -50; [BCl_3] = 2×10^{-2} mol/L) and $C_6H_5C(CH_3)_2Cl/BCl_3$ Systems

Initiator	Rate of monomer addition (g/min)	M_{total} (g)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	Conversion (%)
"H_2O"	0.725[a]	1.45	28.8	69.2	2.4	
		2.90	90.0	136.2	1.51	
		4.35	105.9	147.6	1.39	
		5.80	105.3	172.0	1.63	
		7.25	162.7	238.5	1.46	100
"H_2O"	0.725[a]	3.63	105.3	164.5	1.56	
		7.26	167.0	265.0	1.59	
		10.89	188.4	276.6	1.47	
		14.52	218.5	307.0	1.41	
		18.15	221.1	306.0	1.38	100
"H_2O"	0.73	3.66	109.6	181.5	1.65	
		7.32	183.4	285.2	1.56	
		10.59	209.1	297.8	1.42	
		14.64	232.9	324.4	1.39	
		18.30	234.9	330.1	1.42	100

(continued)

TABLE 1 (continued)

Initiator	Rate of monomer addition (g/min)	M_{total} (g)	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	Conversion (%)
"H_2O"	Control	2.19	158.0	273.0	1.73	100
"H_2O"	Control	2.19	120.1	217.6	1.80	100
"H_2O"	Control	2.19	115.1	210.5	1.83	100
1.88×10^{-4} mol of $C_6H_5C(CH_3)_2Cl$	3.66	3.66	27.6	44.3	1.61	
		7.32	50.9	75.8	1.49	
		10.98	70.2	97.1	1.38	
		16.47	78.0	100.1	1.28	
		21.46	83.7	121.0	1.45	100
1.88×10^{-4} mol of $C_6H_5C(CH_3)_2Cl$	3.66	3.66	24.5	42.0	1.72	
		7.32	41.1	62.8	1.53	

		10.98	58.7	86.8	1.48	
		14.64	67.0	94.2	1.41	
		21.96	63.5	98.4	1.44	100
9.4×10^{-5} mol of $C_6H_5C(CH_3)_2Cl$	1.83	1.83	13.1	34.6	2.64	
		3.66	33.5	51.3	1.53	
		7.32	68.0	96.0	1.41	
		14.64	84.0	123.6	1.47	
		21.96	94.7	146.9	1.55	100
$C_6H_5C(CH_3)_2Cl$[b]	Control	2.19	55.6	110.4	1.98	100
$C_6H_5C(CH_3)_2Cl$[b]	Control	2.19	49.0	72.4	1.49	100

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[a] Monomer was added in solution (45% αMeSt, 30% MeCH, 25% CH_2Cl_2).

[b] 2.83×10^{-3} mol/dm^3 cumyl chloride was used.

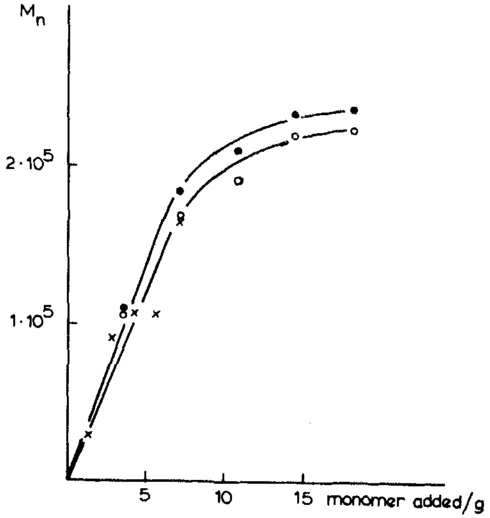

FIG. 1. $\overline{M}_n$ vs monomer input plot of "H_2O"/BCl_3/αMeSt polymerization system; (×, ○) monomer added in solution; (●) pure monomer added.

Table 1 and Figs. 1 and 2 show the results. Figure 1 shows three series of experiments carried out under quasiliving conditions. In two of the experiments the polarity of the monomer feed and that of the BCl_3 solution were essentially identical (feed: αMeSt/MeCH/CH_2Cl_2 = 45/30/25; charge: MeCH/CH_2Cl_2 = 75/25) whereas in the third one, undiluted αMeSt was fed into the same charge. The excellent agreement between the data obtained in the first two runs carried out with dilute αMeSt solutions demonstrates the reproducibility of our experimental technique. Further, the close agreement of the slopes of the $\overline{M}_n$ versus monomer input plots obtained for experiments carried out with dilute and undiluted αMeSt indicates that slight differences in polarities do not affect the results (the difference between the two lines is considered to be within experimental variation). Significantly, the $\overline{M}_n$ versus monomer input plots are linear over a wide monomer addition range, indicating quasiliving polymerization.

The rate of monomer introduction is critical for quasiliving polymerization. Linear $\overline{M}_n$ versus monomer input plots cannot be obtained when the rate of αMeSt addition is too high or too low, or in highly viscous polymer solutions. If the rate of monomer addition is too high, monomer concentration may become too high, leading to enhanced chain transfer to monomer and irreversible

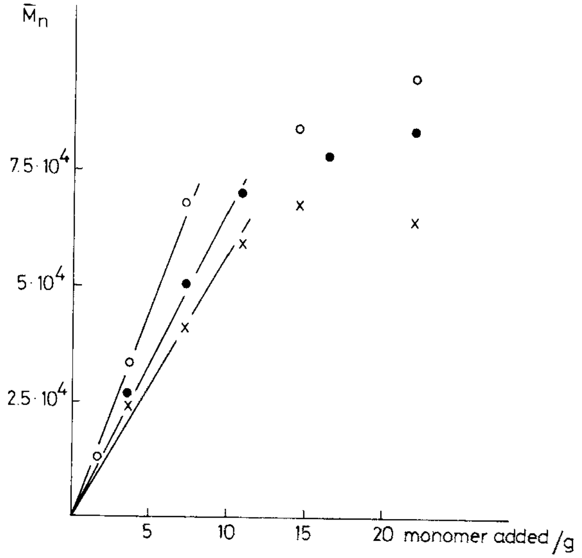

FIG. 2. $\overline{M}_n$ vs monomer input plot of $C_6H_5C(CH_3)_2Cl/BCl_3/\alpha$MeSt polymerization system at different initiator concentrations: (×, •) $[I]_0 = 1.88 \times 10^{-4}$; (○) $[I]_0 = 9.4 \times 10^{-5}$ mol.

polymer formation. Under these conditions the $\overline{M}_n$ versus monomer input plot will tend to deviate from and fall below the straight line very soon. If the rate of monomer addition is too low, the rate of chain transfer to α-methylstyrene by indane formation compared to the rate of propagation is no longer negligible. The formation of indane endgroups is unacceptable for quasiliving conditions because when endgroup reversibility is lost, the indane terminus cannot be reprotonated to active chain end.

It should be emphasized that the particular monomer input rate (i.e., 0.725 g αMeSt/min) found to lead to quasiliving polymerization in the "H_2O"/BCl_3/αMeSt system is not an absolute value but is characteristic only of the particular moisture content prevailing in the system. Assuming that every H_2O molecule initiated one polymer chain (a not unreasonable assumption in view of the relatively high concentration of BCl_3 used, 2×10^{-2} mol/dm^3), the linear portion of the $\overline{M}_n$ versus monomer input line gives $[I]_0$ = ["H_2O"] = $7\text{-}8 \times 10^{-4}$ mol/dm^3.

In experiments with cumyl chloride, initiator $[I]_0$ is known and the above uncertainty is avoided. Since the concentration of initiator was higher than that of moisture impurity, the rate of monomer addition was increased in proportion. Polymerizations were performed at two different initiator concentrations and the corresponding data are plotted in Fig. 2. (Experiments with 1.88×10^{-4} mol initiator, identified by ○ and ×, are duplicates and reflect experimental variation.) Similarly to the "H_2O"/BCl_3 systems, quasiliving polymerizations existed up to a certain point beyond which the $\overline{M}_n$ versus monomer input plots started to deviate from linearity. Initiator efficiency, calculated by $[I]_0 = [M]_{total}/\overline{M}_n$ in the linear quasiliving region for each experiment, was found to be reasonably close to 100% (117, 83, and 97%, respectively).

For comparison with these experiments whose aim was to demonstrate the existence of quasiliving polymerizations, control experiments by the conventional method have also been carried out. The composition and concentration of reaction mixtures are shown in Table 1. Control polymerizations were initiated at -50°C by introducing BCl_3 (2×10^{-2} mol/dm^3) solutions into charges consisting of 2.4 mL αMeSt in 20 mL solutions in one dose. A series of temperature increases may occur. Initiation efficiciencies in quasiliving and in control polymerizations were quite different. In quasiliving systems initiated by cumyl chloride where ionization occurred in the absence of monomer, initiator efficiency was ~100%. In contrast, in control runs the number of polymer chains produced was only about half the number of cumyl chloride added although in this system polymer could also have been formed by chain transfer to monomer. Evidently in the control runs monomer is completely consumed long before ionization is complete.

The $\overline{M}_n$ versus monomer input plots exhibit significant deviation from linearity when the amount of polymer becomes high in the reaction mixture during the later phases of polymerization (see Figs. 1 and 2). Although a deviation from linearity is caused by the cumulative amount of polymer molecules generated by chain transfer, the deviation may also be due to additional factors, e.g., diffusion control, uneven monomer distribution caused by improper mixing. The following facts indicate that viscosity may affect the system: (a) the reproducibility which is satisfactory in the linear region becomes poor after the plots start to deviate from linearity (see Fig. 2, symbols ○ and ×), (b) the molecular weight region where the deviation occurs depends on the polymer concentration in the charge, and (c) the deviation from linearity occurs after the charge becomes highly viscous (25-35% w/w polymer at -50°C). This phenomenon is reminiscent of those studied in the free radical polymerization of styrene and methyl methacrylate, where diffusion control of propagation was observed even at elevated temperatures [11]. Difficulties caused by improper mixing have been discussed by Szwarc [12].

Molecular Weight Distribution

The quasiliving character of the above systems is also reflected by their molecular weight distribution characterized by the dispersion ratio $\bar{M}_w/\bar{M}_n$, and by the trend of $\bar{M}_w/\bar{M}_n$ values during quasiliving conditions. Polymers formed in conventional polymerization exhibit $\bar{M}_w/\bar{M}_n = 2$ if the monomer concentration remains constant, or $\bar{M}_w/\bar{M}_n > 2$ if [M] decreases during the run. In contrast, polymers obtained under quasiliving conditions possess $\bar{M}_w/\bar{M}_n < 2$, and this value tends to decrease with increasing molecular weight. In living polymerizations, provided initiation is instantaneous, all polymer chains are approximately of equal length all the time. The chains grow continuously as long as monomer is present and incorporate the same number of monomers over a unit time. As a consequence $\bar{M}_w/\bar{M}_n \approx 1.0$ for polymers obtained under living conditions. Under quasiliving conditions, even if initiation is practically instantaneous, the chain ends cannot incorporate the same number of monomers during a unit time because temporarily they may be dormant i.e., in the form of $M_n^{=}$ of M_nX (see kinetic scheme). The less time the polymer chain end spends in the dormant state, the more monomer it can incorporate over a unit time, and vice versa. These differences between individual polymer chains will tend to disappear in time because, on the average, they will spend the same length of time in the dormant state. This equalizing process is reflected in the narrowing of molecular weight distributions and diminution of $\bar{M}_w/\bar{M}_n$ values with time. In our experiments a progressive decrease in $\bar{M}_w/\bar{M}_n$ values is evident (see Table 1).

The molecular weight distribution of polymers formed in quasiliving systems is invariably narrower than those of the corresponding control experiments. In some cases the dispersion ratio obtained in control runs is also significantly lower than 2; this phenomenon is not exceptional and several authors have observed $\bar{M}_w/\bar{M}_n < 2$ in carbocationic polymerizations. However, this phenomenon has not yet been explained.

Quasiliving polymerization may become of great theoretical and practical significance. This new process points the way toward new possibilities for the synthesis of novel block and graft copolymers, chain end functionalization, etc. Investigation along these lines is under way.

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REFERENCES

[1] M. Szwarc, Nature, 178, 1168 (1956).
[2] M. Szwarc, M. Levy, and R. Milkovich, J. Am. Chem. Soc., 78, 256 (1956).
[3] A. Noshay and J. McGrath, Block Copolymers, Academic, New York, 1977.
[4] D. C. Allport and W. H. Janes, Block Copolymers, Wiley, New York, 1973, pp. 354-355.
[5] T. Higashimura, O. Kishiro, and T. Takeda, J. Polym. Sci., Polym. Chem. Ed., 14, 1089 (1976).
[6] T. Higashimura and O. Kishiro, Polym. J., 9, 87 (1977).
[7] T. Higashimura, M. Mitshuhashi, and M. Sawamoto, Macromolecules, 12, 178 (1979).
[8] D. C. Pepper, J. Polym. Sci., Polym. Symp., 50, 51 (1975).
[9] J. P. Kennedy, S. Y. Huang, and S. C. Feinberg, J. Polym. Sci., Polym. Chem. Ed., 15, 2869 (1977).
[10] J. P. Kennedy, Cationic Polymerization of Olefins, Wiley-Interscience, New York, 1975.
[11] K. Horie, I. Mita, and H. Kambe, J. Polym. Sci., Polym. Chem. Ed., 6, 2663 (1968).
[12] M. Szwarc, Carbanions, Living Polymers and Electron Transfer Processes, Wiley-Interscience, New York, 1968, p. 47.