Quasiliving Carbocationic Poiymerization. III. Quasiliving Polymerization of lsobutylene

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Quasiliving Carbocationic Polymerization. III. Quasiliving Polymerization of Isobutylene

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ABSTRACT

The polymerization of isobutylene has been investigated by the use of the steady, slow, continuous monomer addition technique in the presence of a variety of initiating systems, i.e., "H_2O"/$TiCl_4$, "H_2O"/$AlCl_3$, $C_6H_5C(CH_3)_2Cl/TiCl_4$, p-$ClCH_2 \cdot C_6(CH_3)_4 \cdot CH_2Cl/AlCl_3$ at -50°C. Quasiliving polymerizations have been obtained with the "H_2O" and $C_6H_5C(CH_3)_2Cl/TiCl_4$ systems in 60/40 v/v n-hexane/methylene chloride solvent mixtures with very slow monomer input. After a brief "flash" polymerization, the $\overline{M}_n$ of PIB increased linearly with the cumulative amount

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of monomer added (consumed); however, the number of polymer
molecules formed also increased, indicating the presence of chain
transfer to monomer. With the "H_2O"/$TiCl_4$ initiating system,
$\overline{M}_{n,max}$ was 56,000 and $\overline{M}_w/\overline{M}_n < 2.0$. By the use of the
$C_6H_5C(CH_3)_2Cl/TiCl_4$ initiating system, quasiliving polymeriza-
tion has been achieved and chain transfer could virtually be
eliminated.

INTRODUCTION

Subsequent to the discovery of quasiliving carbocationic polym-
erization of α-methylstyrene in our laboratories [1], several other
monomers have also been found to behave similarly, i.e., isobutyl
vinyl ether [2], methyl vinyl ether [3], p-t-butylstyrene [4], and
styrene [5]. Investigations have also been carried out to demonstrate
quasiliving polymerization with isobutylene; however, initial experi-
ments gave inconclusive data and were in need of confirmation. This
paper concerns a detailed investigation of quasiliving polymerization
of isobutylene, a discussion of advantages/disadvantages of several
initiating systems and monomer addition techniques, and the results
of several series of experiments which illustrate the limitation of
the quasiliving technique with this monomer.

EXPERIMENTAL

Materials

Isobutylene (IB) was dried by passing the gas through a column
packed with a mixture of BaO and molecular sieves (4Å). n-Hexane
was refluxed with concentrated H_2SO_4, washed with distilled water,
dried over molecular sieves (3Å), and distilled from CaH_2 under N_2.
Methylene chloride, n-propyl chloride, n-butyl chloride and chloro-
benzene were purified as described [6]. Nitrobenzene was dried over
molecular sieves (3Å) and fractionated twice from CaH_2 under vacuo.
α-Methylstyrene was extracted with 10% aqueous NaOH, washed neutral
with distilled water, dried over molecular sieves (3Å) and distilled
from CaH under vacuo. Cumyl chloride (CC) (2-chloro-2-phenyl
propane) was prepared from purified α-methylstyrene by hydrochlri-
nation in methylene chloride solution; excess HCl and solvent were
removed by repeated freeze-drying. p-Bis-chloromethyldurene was
recrystallized from chloroform-petroleum ether solvent mixture.
BF_3 and BCl_3 were condensed from a lecture bottle under N_2. $SbCl_5$
was distilled from P_2O_5 under vacuo. $AlCl_3$ [7] was purified by
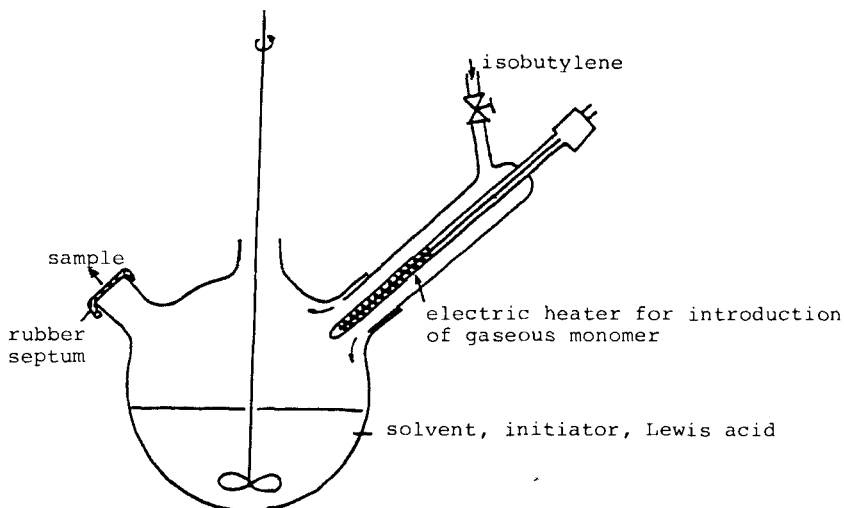repeated extractions with methylene chloride till the solvent remained

FIG. 1. Special heated gas inlet used in the quasiliving polymeri-
zation of isobutylene.

colorless and AlCl$_3$ -methylene chloride suspensions were used in the
experiments. BF$_3$OEt$_2$, SnCl$_4$, and TiCl$_4$ were distilled from P$_2$O$_5$
under N$_2$.

Procedures

   Polymerizations were carried out in a stainless steel enclosure
under dry N$_2$ at -50°C in 300 cm^3 three-neck round-bottom flasks
equipped with stirrer, Teflon plug for monomer addition, and outlet
for sampling. Liquid isobutylene was fed continuously from a
reservoir by the application of N$_2$ pressure. Alternatively, gaseous
monomer was fed continuously through a heated gas inlet (see Fig. 1).
Samples (0.1 cm^3) were withdrawn with a precooled syringe from
the reaction mixture and were injected into capped vials containing
excess methanol. Polymerizations were stopped by adding methanol
to the charge. Conversions were determined gravimetrically and
were found to be 100% in every case. Molecular weights were deter-
mined by a Waters Associates High Pressure GPC apparatus equipped
with four Microstyragel columns (10^5, 10^4, 10^3, and 500 Å) and dual
UV and RI detectors. Molecular weights were calculated from a
calibration curve obtained with fractionated narrow molecular
weight polyisobutylene standards.

RESULTS AND DISCUSSION

Quasiliving polymerization demands rapid initiation and the absence or reversibility of termination [1, 8]:
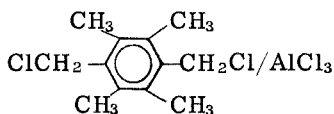
$$
\begin{array}{ccccc}
& \text{CH}_3 & & & \text{CH}_3 \\
& | & & k_t & | \\
\sim\sim\text{CH}_2-\text{C}^{\oplus} & + \text{MtX}^{\ominus}_{n+1} & \rightleftharpoons & \sim\sim\text{CH}_2-\text{C}-\text{X} + \text{MtX}_n \\
& | & & k_{ri} & | \\
& \text{CH}_3 & & & \text{CH}_3
\end{array}
$$
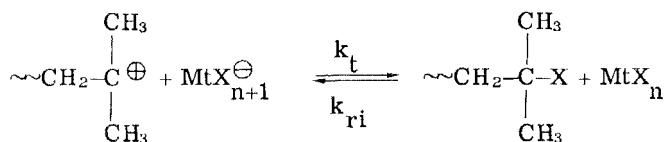
where k_t and k_{ri} stand for the rate constants of termination and re-ionization, respectively. The lifetime of the carbocation must be sufficiently long for propagation in the presence of slow, steady monomer addition. Homogeneous systems, weakly nucleophilic counteranions, and highly electrophilic solvents have also been found to be necessary to obtain quasiliving conditions.

In regard to the quasiliving polymerization of isobutylene, the reionization of the $\sim\sim\text{CH}_2(\text{CH}_3)_2\text{Cl}$ terminus by a Friedel-Crafts acid MtX_n (see above) is of paramount importance. While none of the conventional Friedel-Crafts acids, e.g., AlCl_3, SnCl_4, TiCl_4, SbCl_5, are able to ionize t-BuCl (even the t-BuF/BF_3 or SbF_5 systems contain merely nonionic complexes with somewhat elongated C–F bonds, e.g., t-Bu–F $\rightarrow$ BF_3) [9], the reionization of the tertiary Cl terminus in polyisobutylene is facilitated by internal strain [10]. Thus reionization, i.e., the backward reaction in the above equation, is expected to occur reasonably fast in the presence of AlCl_3 or TiCl_4.

A. Preliminary Studies

Experimentation to achieve quasiliving polymerization of isobutylene started by examining a series of promising Friedel-Crafts acids and solvent systems. Alkylated Friedel-Crafts acids (e.g., MeAlCl_2, Et_2AlCl) have not been tried because irreversible termination by alkylation with these Lewis acids [11] would have prevented reinitiation. Experiments with SnCl_4, SbCl_5 and $\text{BF}_3\cdot\text{OEt}_2$ did not produce polymer and with BF_3 only liquids (oligomers) were obtained with continuous, slow monomer addition, most likely because of relatively slow reinitiation. BCl_3 cannot be used because the $\text{BCl}_4^{\ominus}$ counteranion is very unstable so that the above equilibrium is strongly displaced toward the right [12]. Trials with $\text{C}_6\text{H}_5\text{C}(\text{CH}_3)_2\text{Cl}$ or p-$\text{ClCH}_2\cdot$ $\text{C}_6(\text{CH}_3)_4\cdot\text{CH}_2\text{Cl}/\text{AgSbF}_6$ also failed. Several series of experiments have been carried out with the "H_2O"/AlCl_3 initiating system; however, suitable conditions for quasiliving polymerization could not be found. Trials were also made with

$$\text{ClCH}_2 - \left\langle \underset{\underset{\text{CH}_3 \quad \text{CH}_3}{}}{\overset{\overset{\text{CH}_3 \quad \text{CH}_3}{}}{\bigcirc}} \right\rangle - \text{CH}_2\text{Cl}/\text{AlCl}_3$$

combinations (prepared by mixing saturated $AlCl_3$ in CH_2Cl_2 solutions with p-bischloromethyldurene in CH_2Cl_2 and using the homogeneous deep red liquid in the charge); however, extensive chain transfer to the initiator prevented quasiliving polymerization. These failures, coupled with the difficulties encountered in the purification of $AlCl_3$ and the very low solubility of $AlCl_3$ in solvents suitable for quasiliving polymerization, prompted us to abandon experimentation with this salt. In view of promising preliminary results with $TiCl_4$ (indication of $\overline{M}_n$ growth with slow monomer addition), it was decided to concentrate further investigations on $TiCl_4$-based initiating systems, i.e., $C_6H_5C(CH_3)_2Cl/TiCl_4$ and "H_2O"/$TiCl_4$.

A brief discussion in regard to solvent selection is necessary. A paramount requirement for quasiliving polymerizations is the homogeneity of the system, i.e., the charge including the polymer formed in the charge during experiment must always remain in solution. To meet this requirement a nonpolar solvent is called for; however, ionization of the initiating system and rapid cationation is facilitated by polar media. For stabilizing the counteranion a highly electrophilic solvent having a large acceptor number (AN) [13] is needed. To satisfy these opposing demands a variety of solvents have been examined, e.g., chlorobenzene, n-propyl chloride, n-butyl chloride, nitrobenzene; however, none of them was found to be entirely satisfactory.

After considerable experimentation a suitable compromise was found in the form of n-hexane/CH_2Cl_2 mixtures. Indeed, the best results were obtained in 60/40 v/v n-hexane/CH_2Cl_2 systems.

Thus on the basis of extensive preliminary experiments we selected $TiCl_4$-based initiating systems, i.e., $C_6H_5C(CH_3)_2Cl/TiCl_4$ and "H_2O"/$TiCl_4$, in 60/40 v/v n-hexane/methylene chloride solvent system for further studies on quasiliving polymerization of isobutylene.

B. Quasiliving Polymerizations: The CC/$TiCl_4$/ IB and "H_2O"/$TiCl_4$/IB Systems

In view of extensive orienting experiments (see above) and some promising earlier investigations, detailed studies directed toward the definition of experimental parameters leading to quasiliving polymerization of isobutylene have been undertaken. A series of experiments with the $C_6H_5C(CH_3)_2Cl/TiCl_4$ initiating system have been carried out in which a steady stream of liquid monomer was squirted into well-stirred initiator charges. Figure 2 shows
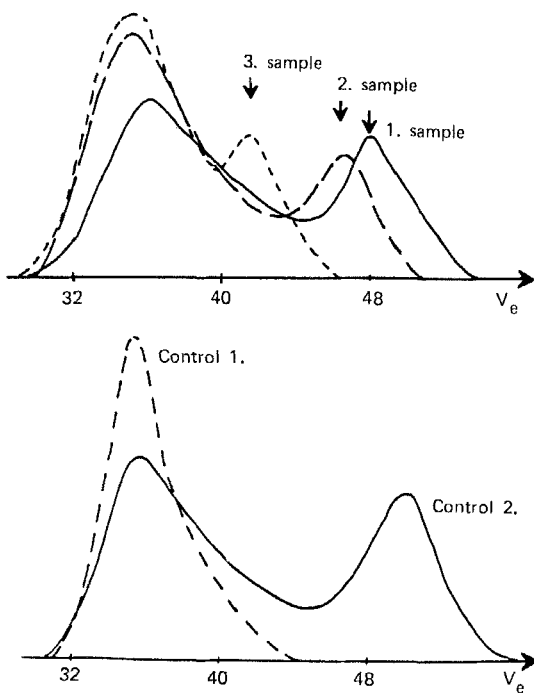
FIG. 2. Top: GPC traces of three polyisobutylene samples pre-
pared by the CC/TiCl$_4$ initiating system using continuous liquid
monomer addition. Normalized curves. Polymerization conditions:
V_0 = 50 cm^3, $[I]_0$ = 2 × 10^{-2} mol/dm^3, $[TiCl_4]_0$ = 3.6 × 10^{-2} mol/
dm^3, A = 6.25 × 10^{-3} mol/min IB. Bottom: GPC traces of polyiso-
butylenes prepared by "controls." Polymerization conditions for
Control 1: "H$_2$O"/TiCl$_4$ initiating system, V_0 = 10 cm^3, $[TiCl_4]$ =
3.6 × 10^{-2} mol/dm^3, $[M]_0$ = 2.4 mol/dm^3. Polymerization conditions
for Control 2: CC/TiCl$_4$ initiating system, V_0 = 10 cm^3, $[I]$ = 2.0
× 10^{-3} mol/dm^3, $[TiCl_4]$ = 3.6 × 10^{-2} mol/dm^3, $[M]_0$ = 2.4 mol/dm^3.

representative results of an experiment in which a series of samples
has been withdrawn. The sequence of samples is given in the figure
(for experimental details see the legend to Fig. 2).
    According to the GPC traces, polyisobutylene samples withdrawn
during a run exhibit two sets of peaks: one at higher molecular
weights that remains unchanged during the experiment, and another
that shifts toward higher molecular weights with monomer addition,
i.e., exhibits quasiliving character. The set of peaks at the higher
molecular weights is most likely due to initiation by "H$_2$O" (proto-
genic impurities) whereas the one gradually shifting toward higher

molecular weights is probably due to the $C_6H_5C(CH_3)_2Cl/TiCl_4$ initiator system. This assumption has been borne out by a set of two "control" experiments, i.e., experiments in which the monomer was added in one rapid dose to stirred charges of "H_2O"/$TiCl_4$ and $C_6H_5C(CH_3)_2Cl/TiCl_4$, respectively. The positions of the GPC peaks obtained with the "H_2O"/$TiCl_4$ control on the one hand and those remaining unchanged at higher molecular weights in the continuous monomer addition experiment on the other hand coincide. Also, the bimodal GPC peak obtained with the $C_6H_5C(CH_3)_2Cl/TiCl_4$ control indicates a population at higher molecular weights, most likely due to "H_2O"/$TiCl_4$, and another at lower molecular weights arising from initiation by the $C_6H_5C(CH_3)_2Cl/TiCl_4$ system.

It is of interest to speculate why the $\overline{M}_n$'s obtained by the "H_2O"/$TiCl_4$ system are consistently higher but remain unchanged whereas those produced by the $C_6H_5C(CH_3)_2Cl/TiCl_4$ combination are lower to start with but tend to undergo quasiliving growth. There is reason to believe that the counteranion $TiCl_4OH^{\ominus}$ arising from the "H_2O"/$TiCl_4$ initiating system is more stable (less nucleophilic) than the $TiCl_5^{\ominus}$ produced from the $C_6H_5C(CH_3)_2Cl/TiCl_4$ combination [14]; thus the "loser" propagating ion pair $\sim\sim CH_2C^{\oplus}(CH_3)_2TiCl_4OH^{\ominus}$ propagates faster and produces higher $\overline{M}_n$ polymer than the "tighter" ion pair $\sim\sim CH_2C^{\oplus}(CH_3)_2TiCl_5^{\ominus}$. Because of extremely rapid initiation and propagation in the presence of the $TiCl_4OH^{\ominus}$ counteranion, initial mixing may be inadequate and the monomer concentration may locally remain high. The monomer is mainly used up by the more active "H_2O"/$TiCl_4$/IB system producing high $\overline{M}_n$ polymer while the rest of the monomer undergoes quasiliving polymerization with the $C_6H_5C(CH_3)_2Cl/TiCl_4$ initiating system.

Locally high monomer concentration could be avoided by perfect mixing so that termination by

$$\sim\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{}^{\oplus} TiCl_4OH^{\ominus} \longrightarrow \sim\sim CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-Cl + TiCl_3OH$$

may occur. Since excess $TiCl_4$ is available in the system, reinitiation could occur and after a while all the growing species would be $\sim\sim CH_2C^{\oplus}(CH_3)_2\cdot TiCl_5^{\ominus}$. In disagreement with earlier workers [9], termination by hydroxylation by $TiCl_4OH^{\ominus}$ is thought to be much less likely than termination by chlorination.

To clarify the results discussed above, four series of experiments have been carried out with continuous slow addition of isobutylene to well-stirred "H_2O"/$TiCl_4$ charges. Table 1 shows the results. In the first series undiluted isobutylene was used. The $\overline{M}_n$'s are

PUSKAS ET AL.

TABLE 1. Polymerization of Isobutylene with "H$_2$O"/TiCl$_4$ Initiating System Using Continuous Liquid Monomer Addition[a]

Samples	Time of sampling t (min)	Cumulative amount of consumed monomer (mol $\times 10^3$)	$\overline{M}_n$ $\times 10^{-3}$	$\overline{M}_w/\overline{M}_n$	[P] $\times 10$ mol	$\overline{DP}_n$ $\times 10^{-2}$	$\overline{DP}_{n,max}$ calc	[I]$_0$ $\times 10^4$ mol
		$A = 50.4 \times 10^{-3}$ mol/min (undiluted)						
FF 12	1	50.4	75.8	1.91	0.37	13.5		
13	2	100.8	82.9	1.84	0.68	14.8		
14	3	151.2	85.0	1.68	1.00	15.2		
15	4	201.6	88.4	1.67	1.28	15.8		
16	5	252.0	89.8	1.64	1.57	16.0		
		$A = 12 \times 10^{-3}$ mol/min (dilute monomer: 50 vol% IB + 50 vol% solvent mixture						
FF 17	5	60	49.2	1.86	1.02	8.8		
18	10	120	50.6	1.73	1.72	9.0		
19	15	180	46.2	1.88	2.02	8.2		
20	20	240	53.4	1.77	2.60	9.5		

A = 2.88 × 10⁻³ mol/min (dilute monomer: 10 vol% IB + 90 vol% solvent mixture)

HH	6	10	28.8	18.3	1.97	0.87	3.3	1.2
	7	20	57.6	22.4	2.03	1.44	4.0	
	8	30	86.4	24.7	1.88	1.96	4.4	1087
	9	40	115.2	28.4	1.96	2.26	5.1	
	10	50	144	31.4	1.86	2.57	5.6	
	11	60	172.8	35.6	1.62	2.74	6.3	

A = 1.6 × 10⁻³ mol/min (dilute monomer: 10 vol% IB + 90 vol% solvent mixture)

LL	1	15	24.2	–	–	–	–	
	2	30	48.4	22.3	2.04	1.10	4.0	
	3	45	72.6	24.6	1.96	1.65	4.4	
	4	60	96.8	28.1	1.95	1.94	5.0	1000
	5	75	121.0	31.0	1.90	2.20	5.5	
	6	90	145.2	33.8	1.73	2.42	6.0	0.96

$^aV_0 = 100$ cm^3, $[TiCl_4]_0 = 3.6 \times 10^{-2}$ mol/dm^3, T = 50°C; in every experiment conversion = 100%.

last sample
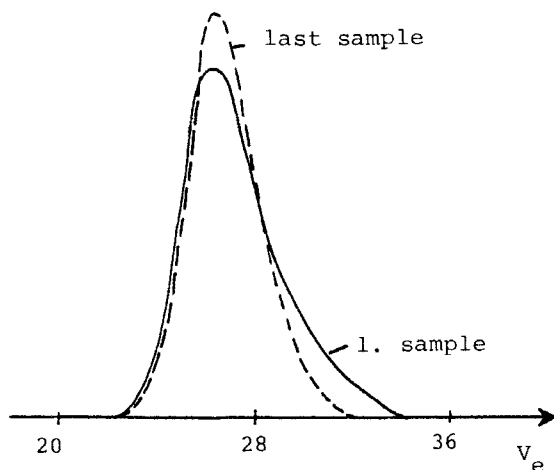
1. sample

20   28   36 V_e

FIG. 3. GPC traces of polyisobutylene samples obtained by "H_2O"/
$TiCl_4$ initiating system using continuous addition of undiluted liquid
monomer (Runs FF 12-16, Table 1).

relatively high and seem to be increasing with time. However, a
closer inspection of the data and the GPC traces of the first and the
last samples shown in Fig. 3 reveals that molecular weight growth
is not due to quasiliving polymerization but rather to a progressing
narrowing of the molecular weight distribution, i.e., to the disappear-
ance of the low molecular weight tail. Conceivably, impurities in the
system are gradually scavenged by the growing carbenium ions and
the relative contribution of the low molecular weight fraction to the
average molecular weights decreases. The fact that the number of
macromolecules $[P]$ (calculated by using $[P] = At/\overline{DP}_n$ and given,

for convenience, in moles) increases about fourfold during the run,
indicates the presence of unacceptable chain transfer to monomer in
the system. As discussed above, locally high monomer concentrations
may have prevented the attainment of quasiliving conditions. Thus
the next experiment was carried out with a dilute stream of monomer.
According to the data in Table 1 (Experiments FF 17-20), however,
quasiliving polymerization still could not be achieved.

Further reductions in the monomer addition rate led to more
encouraging results: the $\overline{M}_n$'s of the samples increased with the

cumulative amount of monomer added (Experiments HH 6-11 with
$A = 2.88 \times 10^{-3}$ and LL 1-6 with 1.6×10^{-3} mol IB/min, Table 1).
These data are further illustrated by shifts of the monomodal GPC
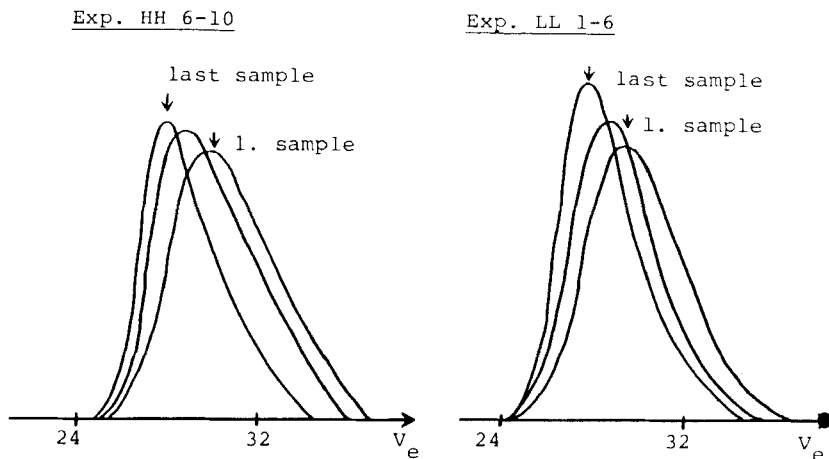traces toward higher molecular weights in Fig. 4. Figure 5 shows

Exp. HH 6-10

last sample

1. sample

Exp. LL 1-6

last sample

1. sample

24   32 V_e

24   32 V_e

FIG. 4. GPC traces of polyisobutylenes prepared with the "H_2O"/ $TiCl_4$ initiating system using continuous addition of diluted liquid monomer (Runs HH and LL, Table 1).

$\overline{M}_n \times 10^{-3}$

40

30

20

10

0

0   100   200

$A \cdot t \times 10^3$ mole

FIG. 5. $\overline{M}_n$ vs monomer consumption plots of polyisobutylenes prepared with the "H_2O"/$TiCl_4$ initiating system using continuous addition of diluted liquid monomer (Runs HH and LL, Table 1).
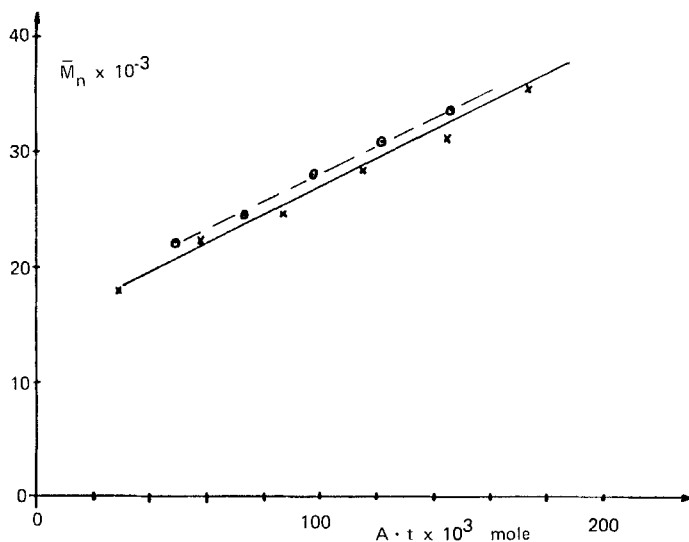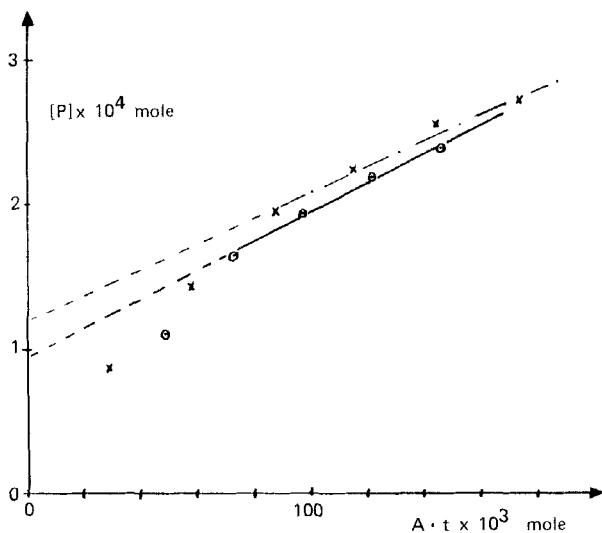
FIG. 6. [P] vs monomer consumption of polyisobutylenes obtained by "H₂O"/TiCl₄ initiating system using continuous addition of diluted liquid monomer (Runs HH and LL, Table 1).

the corresponding $\overline{M}_n$ versus monomer consumption plot (since the conversion is complete, $\xi = 1$, the amount of consumed monomer At). After a very rapid initial increase in $\overline{M}_n$, an extended slower phase of quasiliving growth proceeds. The "flash" increase in $\overline{M}_n$ at the beginning of the reaction may be due to insufficient mixing (stirring). Figure 6 is a plot of [P] versus cumulative weight of monomer consumption; the increasing number of polymer molecules indicates chain transfer to monomer i.e., a QL_{R1} system [8]. The initial nonlinear portion of the [P] versus At plot is most probably due to chain transfer to water impurities ("H₂O") in the system. The linear portion of the [P] versus At plot provides $\overline{DP}_{n,max}$ by

$$[P] = \frac{At}{\overline{DP}_n} = [I]_0 + \frac{1}{\overline{DP}_{n,max}} At$$

where $\overline{DP}_{n,max}$ stands for k_p/k_{tr}. By using this equation, $[I]_0$ can be obtained by extrapolating the linear portion of the plots. Table 1 shows these data. According to these runs, the "H₂O" concentration

TABLE 2. Polymerization of Isobutylene with the "H₂O"/TiCl and CC/TiCl₄ Initiating System Using Continuous Gaseous Monomer Addition[a]

Sample	Time of sampling t (min)	Cumulative amount of consumed monomer (mol × 10³)	$\bar{M}_n \times 10^{-3}$	$\overline{DP}_n \times 10^{-2}$	$[P] \times 10^4$	$\bar{M}_w/\bar{M}_n$	$\overline{DP}_{n,max}$	$[I]_0$ (mol)
		$A = 7.2 \times 10^{43}$ mol/min; $V_0 = 100$ cm³						
E 9	5	36	18.3	3.26	1.00	3.05	963	0.9
10	10	72	24.6	4.39	1.64	1.96		
11	15	108	26.5	4.72	2.29	1.98		
12	20	144	31.6	5.64	2.56	1.85		
13	25	180	24.7	6.19	2.91	1.82		
14	30	216	35.9	6.40	3.38	1.76		
		$A = 5.5 \times 10^{-3}$ mol/min; $[I]_0 = 1 \times 10^{-2}$ mol/dm³ cumyl chloride; $V_0 = 50$ cm³						
F 1	10	55	9.2	1.64	3.35	4.5		4.3
2	20	110	14.4	2.57	4.28	4.5		
3	30	165	23.0	4.10	4.02	4.0		
4	40	220	26.3	4.69	4.69	3.1		
5	50	275	40.4	7.20	3.81	2.60		

[a] $[TiCl_4]_0 = 3.6 \times 10^{-2}$ mol/dm³; T = -50°C; in every experiment conversion = 100%.
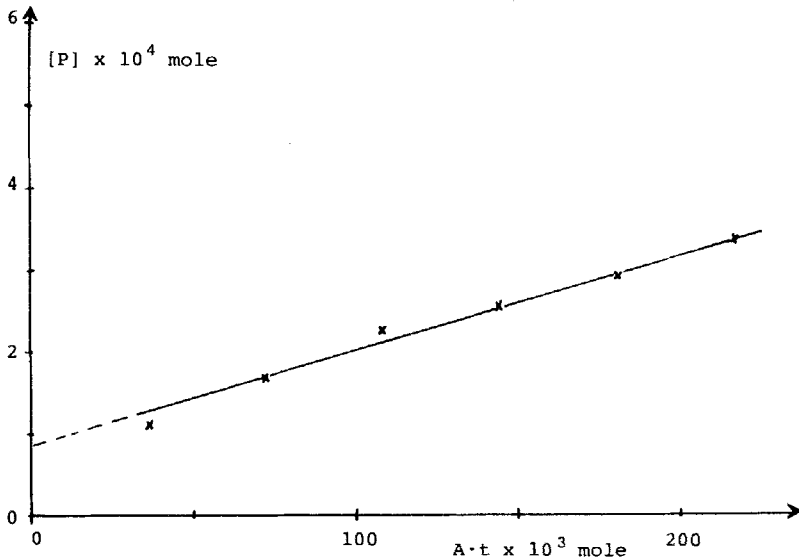
FIG. 7. $[P]$ vs monomer consumption plot of polyisobutylenes prepared with the "H_2O"/$TiCl_4$ initiating system using continuous gaseous monomer addition (Run E, Table 2).

in the system is $\sim 1 \times 10^{-3}$ mol/dm^3 and $\overline{DP}_{n,max}$ is around 1000 ($\overline{M}_{n,max} \cong 56,000$).

Subsequent to experiments with liquid dilute monomer injection, a run was carried out in which gaseous monomer was fed into the reactor by means of a heated inlet and was continuously condensed on the surface of the cold, stirred charge (Fig. 1). It was hoped that by gaseous monomer introduction the cumulative amount of "H_2O" impurity in the reactor could be reduced and efficient mixing of the monomer with the charge could be achieved. Results are compiled in Table 2 (Runs E 9-14) and the $[P]$ versus At plot is shown in Fig. 7. Apparently the results obtained in this experiment and those obtained with liquid dilute monomer introduction are identical within experimental error; evidently protogenic impurities reaching the system with the dilute stream of liquid monomer does not affect the polymerization.

Subsequently an experiment was carried out with the $C_6H_5C(CH_3)_2Cl$ /$TiCl_4$ initiating system by using the gaseous monomer addition technique in which the $C_6H_5C(CH_3)_2Cl$ initiator concentration was increased to 1×10^{-2} mol/dm^3, i.e., 10 times that of the level of suspected water impurities in the system. Results are compiled in Table 2 (Runs F 1-5). According to the $\overline{M}_n$ versus monomer input
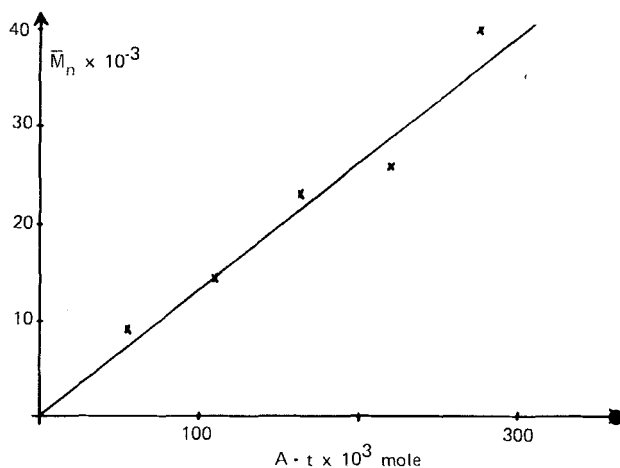
FIG. 8. $\overline{M}_n$ vs monomer consumption plot of polyisobutylenes obtained by $C\overline{C}/TiCl_4$ initiating system using continuous gaseous monomer addition (Run F, Table 2).

plot shown in Fig. 8, $\overline{M}_n$'s increased linearly with monomer intro-duction and $[P]$ remained essentially unchanged, suggesting quasi-living conditions and the practical absence of chain transfer (QL_{R0}). The broad MWD values, however, may reflect the presence of two propagating centers, $\sim C^{\oplus}(CH_3)_2 TiCl_4 OH^{\ominus}$ and $\sim C^{\oplus}(CH_3)_2 TiCl_5^{\ominus}$

In sum, quasiliving carbocationic polymerization of isobutylene may be achieved by the use of "H_2O"/$TiCl_4$ and $C_6H_5 C(CH_3)_2 Cl$/ $TiCl_4$ initiating systems in n-hexane/methylene chloride solvent mixtures by carefully controlled slow and continuous monomer addition. With the "H_2O"/$TiCl_4$ system "flash" polymerizations at the beginning of the reactions prevented controlled slow growth and although $\overline{M}_n$ increased linearly with monomer consumption after this initial jump in $\overline{M}_n$, chain transfer could not be avoided, leading to limited $\overline{DP}_{n,max}$ values.

Due to unavoidable traces of water in the charges, the $C_6H_5 C(CH_3)_2 -Cl/TiCl_4$ system was most likely always contaminated with "H_2O"/ $TiCl_4$, giving rise to two propagating species. By the use of a large excess of $C_6H_5 C(CH_3)_2 Cl$ initiator, quasiliving polymerization has been achieved and chain transfer could be virtually eliminated. It is predicted that in the total absence of moisture, quasiliving polymerization of isobutylene with a single propagating active center could be achieved by the use of the $C_6H_5 C(CH_3)_2 Cl/TiCl_4$ initiating system in n-hexane/methylene chloride solvent at $-50°C$.

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