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# Chain Carriers and Molecular Weight Distributions in Living Isobutylene Polymerizations

**Judit E. Puskas,**[*,†,‡] **Gabor Kaszas,**[†,‡] **and M. Litt**[§]

*Institute of Polymer Research, University of Akron, Akron, Ohio 44325-3909, and Macromolecular Science Department, Case Western Reserve University, Cleveland, Ohio 44118*

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ABSTRACT: The nature of the chain carriers and molecular weight distribution (MWD) in living isobutylene polymerizations are discussed. The evidence presented suggests that the chain carriers in these systems are ion pairs that are in dynamic equilibrium with dormant covalent species (polymeric chlorides). The polymerizations are characterized by "growth periods" and MWDs are described by $\bar{l}$, the average run length, which is the average number of monomer units incorporated during one growth period. $\bar{l}$ can be calculated for constant and varying monomer concentration ($\bar{l}$ and $\bar{l}_0$ for [M] and $[M]_0$, respectively) from experimental MWD data. The effect of the ionization equilibrium (dependence on solvent polarity, the nature and stability of the counteranion, etc.) on $\bar{l}$ is shown by evaluating data presently available on living isobutylene polymerizations; the average run lengths are $\bar{l}_0 = 4.6$ for $CH_3Cl/BCl_3$ at $[M]_0 = 1.57$ mol/L and $\bar{l}_0 = 9.9$ for $CH_3Cl/n\text{-}C_6H_{14}/TiCl_4$ at $[M]_0 = 0.6$ mol/L. In pure $CH_3Cl$ the run length for $TiCl_4$-coinitiated polymerizations is $\bar{l}_0 = 54$ compared to the $\bar{l}_0 = 4.6$ for $BCl_3$ coinitiation. This suggests a higher degree of dissociation or a lower collapse rate in $TiCl_4$-coinitiated systems. $\bar{l}$ was found to be independent of initiator concentration and to increase dramatically with increasing solvent polarity. Very reactive unpaired ions do not appear to participate in the polymerizations.

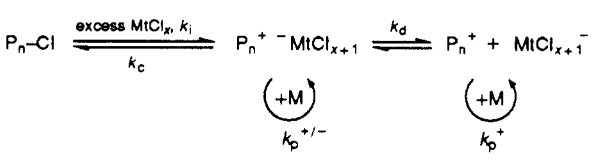
## A. Introduction

One of the most important recent developments in the field of carbocationic polymerizations has been the synthesis of narrow molecular weight distribution polyisobutylenes by living polymerization in the presence of certain electron-pair donors.[1–5] For the first time this development has made possible the synthesis of thermoplastic elastomer block copolymers with polyisobutylene rubbery segments.[6,7]

The electron-pair donors are thought to stabilize the overly reactive carbenium ions, but the exact polymerization mechanism is still obscure. This paper discusses some aspects of the reaction mechanism in living isobutylene polymerizations and describes the MWD by treating the polymerization as a series of growing periods.

## B. Discussion

**B.1. Nature of Chain Carriers in Living IB Polymerizations.** In a recent study[5] on the mechanism of living isobutylene polymerizations, evidence has been presented in favor of an ionic polymerization mechanism as opposed to polymerization by monomer insertion into a polarized covalent species suggested originally for these systems.[8,9] It has been proposed that active ionic species are in dynamic equilibrium with dormant polymers




where $k_i$, $k_c$, and $k_d$ stand for the rate constants of ionization, collapse, and dissociation to unpaired ions, and $k^{+/-}$ and $k^+$ are the rate constants of ion-pair propagation and unpaired-ion propagation, respectively, M stands for monomer, and $MtCl_x$ is a Lewis acid such as $BCl_3$ and $TiCl_4$. This concept was earlier discussed in terms of a "quasiliving" mechanism.[10] While we believe that $BCl_3$- and $TiCl_4$-coinitiated isobutylene polymerizations can be described by a comprehensive ionic mechanism,[5] it should be noted that in some $BCl_3$-coinitiated systems[5,8] a change seems to occur; a very fast nonequilibrium polymerization is followed by a slow equilibrium polymerization. That reversible termination can take place has been demonstrated by initiating polymerizations from previously produced, tertiary chloride capped polyisobutylenes (with $BCl_3$ in both $CH_2Cl_2$[11] and $CH_3Cl$[5] and with $TiCl_4$ even in nonpolar solvent mixtures.[1–5,12] The above equilibrium has been suggested to be shifted toward the covalent species $P_n$–Cl,[3–5] and the concentration of the active ionic species was estimated to be a $\sim 10^{-4}$–$10^{-7}$ fraction of the covalent species.[13–16] Nuyken[11] showed that the active species in his tertiary chloride/$BCl_3$ system are unpaired ions. The exact nature of the chain carriers (paired and/or unpaired ions) in living isobutylene polymerizations initiated by tertiary ester and ether/Lewis acid ($BCl_3$ or $TiCl_4$) where electron-pair donors are formed in situ[4,5] or by "conventional" tertiary chlorides or tertiary hydroxyls *plus* externally added electron-pair donors,[3,4,17] however, remained obscure. The rate constant of propagation for isobutylene in conventional systems is estimated to be $k_p = 10^4$ L mol$^{-1}$ s$^{-1}$,[18] a composite of $k_p^+$ and $k_p^{+/-}$. The relative magnitude of $k_p^+$ and $k_p^{+/-}$ is debated: some suggest that in cationic systems the reactivity of the carbenium ions does not depend on the degree of dissociation, due to the large size of ions and solvating effects,[13,18] while others propose a several orders of magnitude difference in reactivities in favor of $k_p^+$.[19] (It should be noted that isobutylene polymerizations coinitiated by Lewis acids are done in solvents such as $CH_3Cl$, $CH_2Cl_2$, or their mixture with $n$-hexane or cyclohexane, which have weak solvating power toward the growing carbenium ion.) Conventional isobutylene polymerizations are indeed extremely fast and yield polymers with relatively broad MWDs ($\bar{M}_w/\bar{M}_n > 2$).[12,19] In contrast, living isobutylene polymerizations in the presence of certain electron-pair donors produce

† University of Akron.
‡ Present address: Polysar Rubber Corp., Sarnia, Ontario, Canada N7T 7M2.
§ Case Western Reserve University.

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**Table I**
**$\bar{I}$ and $\bar{I}_0$ Values Calculated Using Equations 14 and 15 from Data Obtained in Living Isobutylene Polymerizations[17]**

(a) TMHDiOH/$BCl_3$/DMA/$CH_3Cl$/IB/−45 °C (ref 17)[a]

| sampling, min | conv, % | $\bar{P}_n$ | $\bar{P}_n$[b] | $\bar{P}_w/\bar{P}_n$ | $\bar{I}$[c] | $\bar{I}_0$[c] |
|---|---|---|---|---|---|---|
| 20 | 25.5 | 14.6 | 57 | 1.36 | 3.1 | 3.5 |
| 40 | 56.7 | 27.1 | 48 | 1.16 | 2.7 | 3.4 |
| 60 | 73.2 | 33.2 | 45 | 1.15 | 3.0 | 4.1 |
| 100 | 91.1 | 40.6 | 45 | 1.14 | 3.3 | 5.2 |
| 140 | 93.7 | 42.1 | 45 | 1.14 | 3.4 | 5.5 |
| 180 | 96.7 | 45.1 | 47 | 1.12 | 3.2 | 5.3 |
| 240 | 98.4 | 46.2 | 47 | 1.12 | 3.3 | 5.5 |

(b) CumOMe/$TiCl_4$/$CH_3Cl$ (40 vol %)/n-Hx (60 vol %)/−80 °C (ref 22)[d]

| $V_0$, mL | $\bar{P}_n$ | $\bar{P}_w/\bar{P}_n$ | $\bar{I}_0$[a] | [CumOMe], mol/L | [$TiCl_4$], mol/L |
|---|---|---|---|---|---|
| 150 | 51.7 | 1.24 | 12.4 | 0.073 | 0.38 |
| 300 | 60.6 | 1.15 | 9.1 | 0.035 | 0.13 |
| 300 | 68.5 | 1.12 | 8.2 | 0.027 | 0.12 |
| 150 | 69.5 | 1.16 | 11.1 | 0.021 | 0.06 |
| 150 | 122.6 | 1.07 | 8.6 | 0.012 | 0.04 |

[a] $V_0$ = 1700 mL, $[BCl_3]_0$ = 0.53 mol/L, $[M]_0$ = 1.57 mol/L (150 g of IB), $[DMA]_0$ = 0.042 mol/L, $[TMHDiOH]_0$ = 0.042 mol/L. Batch polymerizations with sampling. TMHDiOH = 2,4,4,6-tetramethyl-2,6-dihydroxyheptane; DMA = dimethylacetamide; IB = isobutylene. [b] For 100% conversion. [c] The minimum error in these values is ±10% since $\bar{P}_w/\bar{P}_n$ cannot be calculated to better than ±0.1. [d] $[M]_0$ = 0.6 mol/L of IB; incremental monomer addition (3 × (7 mL of IB/5 min) for $V_0$ = 150 mL and 3 × (14 $cm^3$ of IB/5 min) for $V_0$ = 300 mL); convn = 100%. CumOMe = dicumylmethoxy; IB = isobutylene. [e] The minimum error is ±10%.

**Table II**
**Effect of Solvent Polarity in IB Polymerizations Initiated by CumCl/DMA/$TiCl_4$ (Ref 3)[a]**

| $CH_3Cl$, vol % | n-Hx, vol % | convn, % | $\bar{P}_n$ | $\bar{P}_w/\bar{P}_n$ | $\bar{I}$[b] | $\bar{I}_0$[b] |
|---|---|---|---|---|---|---|
| 40 | 60 | 8 | 21 | 1.11 | 1.7 | 1.7 |
| 60 | 40 | 41 | 105 | 1.19 | 10.5 | 12.9 |
| 80 | 20 | 100 | 275 | 1.13 | 18.4 | 36.0 |
| 100 | | 100 | 256 | 1.21 | 27.4 | 54.0 |

[a] $[CumCl]_0$ = 0.0036 mol/L; $[TiCl_4]_0$ = 0.066 mol/L; $[DMA]_0$ = 0.0039 mol/L; $[M]_0$ = 0.87 mol/L; polymerization time = 10 min. CumCl = cumyl chloride; DMA = dimethylacetamide; IB = isobutylene. [b] The minimum error is ±10%.

narrow MWD polymers ($\bar{M}_w/\bar{M}_n$ = 1.1–1.2)[1-5] and are unusually slow; for example, a $BCl_3$-coinitiated polymerization in the presence of the electron-pair donor dimethylacetamide yielded a degree of polymerization $\bar{P}_n$ = 46.2 ($\bar{M}_n$ = 2600) in 4 h(!) (Table Ia and ref 17) while $TiCl_4$ coinitiation produced polymers with $\bar{P}_n$ = 180 ($\bar{M}_n$ = 10 000) in 15–30 min, depending on the strength of the electron-pair donor present (Table II and ref 7). Also, "extension" isobutylene polymerizations using chloride-terminated polyisobutylene macroinitiators yielded a $\bar{P}_n$ = 250 and bimodal distribution in 10 min in the absence of donors[11] and a $\bar{P}_n$ = 15 and monomodal, narrow distribution in 15 min in the presence of the strong donor dimethylacetamide.[5] The large difference in polymerization rates suggests the involvement of chain carriers with different reactivities in the presence and absence of electron-pair donors.

The question arises as to what are the active center chain carriers in living isobutylene polymerizations in the presence of electron pair donors. Let us consider first the case of unpaired ions in a rapid equilibrium with dormant covalent species

$$\text{PIB–Cl} + \text{MtCl}_x \underset{k_c}{\overset{k_i}{\rightleftharpoons}} \text{PIB}^+ + \text{MtCl}_{x+1}^- \qquad \text{PIB}^+ \xrightarrow[k_p^+]{(+\text{M})}$$

The lifetime of the cation will be determined by $k_c$. The shortest possible lifetime of the active carbocations can be estimated assuming diffusion-controlled collapse with the counteranion ($k_D \sim 10^9$ L mol$^{-1}$ s$^{-1}$); thus a $k_c = 10^{10}$ L mol$^{-1}$ s$^{-1}$ can be assumed for the rate constant of collapse. The selection of a polymerization rate constant of $k_p^+ = 10^5$ L mol$^{-1}$ s$^{-1}$ seems reasonable for this case ($k_p = 10^4$ L mol$^{-1}$ s$^{-1}$ for isobutylene, see above, and the most credible values of $k_p^+$ for styrene in chlorinated solvents of medium dielectric constants ($D \sim 10$ at 300 K) lie in the $10^4$–$10^6$ L mol$^{-1}$ s$^{-1}$ range.[20] From the polymerization rate expression

$$\ln \frac{[M]_0}{[M]} = k_p^+[P_n^+]t$$

Table I shows conversion–time data for a living isobutylene polymerization in the presence of the strong donor dimethylacetamide taken from ref 17. The ln $[M]_0/[M]$–$t$ plot yielded $k_p^+[P_n^*] = 3.63 \times 10^{-4}$ s$^{-1}$; with $k_p = 10^5$ L mol$^{-1}$ s$^{-1}$ we get $[P_n^+] = 3.63 \times 10^{-9}$ mol/L.

The lifetime of the carbocation, $\tau$, can be calculated as follows:

$$\tau = \frac{[P_n^+]}{k_c[P_n^+][MtCl_{x+1}^-]} = \frac{1}{k_c[P_n^+]} = 0.026 \text{ s}$$

With [M] = 1.57 mol/L, $\bar{P}_n$ of the polymer formed during the lifetime of the active species, i.e., in 0.026 s, should be

$$\bar{P}_n = k_p^+[M]\tau = 4100$$

Thus, polymerization assuming unpaired-ion chain carriers with a lifetime of 0.026 s, the shortest possible with reasonable assumptions, gives a $\bar{P}_n$ of 4100 versus the $\bar{P}_n$ of 40.6 found (see Table I). This is certainly a striking difference. If the collapse is viewed to involve the breaking of a covalent bond $Cl_xMtCl^-$, the rate constant would be in the range of $10^7$ L mol$^{-1}$ s$^{-1}$),[14] which would yield a longer lifetime and thus an even higher molecular weight polymer. On the basis of the above exercise, we can conclude that the chain carriers in living isobutylene polymerizations in the presence of electron-pair donors are most likely not unpaired ions. If even a small proportion of the polymerization were through unpaired ions, there should be a bimodal distribution with some high molecular weight polymer. This conclusion leaves us with two theoretically possible active species: the covalent species and paired ions.

In the case of an insertion mechanism, the covalent species should be polymerization-active. However, evidence has shown that the tertiary ester or ether/$TiCl_4$ complexes are inactive in a 1:1 molar ratio.[2,5] Also, data suggest that tertiary ester, tertiary ether, tertiary chloride + donor, tertiary alcohol + donor, and mixed tertiary ester + tertiary chloride/$TiCl_4$ initiated polymerizations proceed by the same mechanism,[3-5,17] and very recently the same conclusion has been reached for isobutylene–diene copolymerizations initiated by tertiary ester and ether/$TiCl_4$ initiating systems.[21] All the references cited reported the formation of tertiary chloride capped polymers, regardless of the structure of the initiator used, demonstrating ion exchange at the active sites. These evidences are interpreted to indicate that the covalent species are not polymerization-active. The ionic mechanism is further supported by the fact that polymerization rates were found to increase with decreasing temperatures.[21,22]

The above arguments leave us with the conclusion that almost certainly in living isobutylene polymerizations in the presence of certain electron-pair donors the active centers are paired ions.

## C. Molecular Weight Distribution

Having arrived at the conclusion that living isobutylene polymerizations in the presence of electron-pair donors are characterized by an equilibrium between dormant polyisobutylene–chlorides and active ion pairs, we will derive the molecular weight distribution for these systems.

The MWD in similar living anionic systems, where active and dormant species coexist, was treated by Figini and Schultz.[23] In a treatment given for quasiliving polymerizations[24] MWD was discussed in terms of reversible transfer and termination, but the effect of reversible termination was not considered.

Figini and Schultz treated such polymerizations as a series of well-defined successive events, namely, the addition of monomer droplets into a polymerizing mixture.[23] The above authors and later Litt[25] used this concept in evaluating the effect of inadequate mixing on the MWD in living anionic polymerizations. We will consider the living cationic polymerization of isobutylene as successive growing periods (productive ionization periods) and derive equations for the MWD for the cases of constant and varying monomer concentrations.

**C.1. MWD for Constant Monomer Concentration.** In living isobutylene polymerizations characterized by a dynamic equilibrium between dormant polymers and ion pairs

$$\mathrm{P_n{-}A} \underset{k_c}{\overset{k_i}{\rightleftharpoons}} \mathrm{P_n^+\ {}^-A} \ (+\mathrm{M})\ k_p^{+/-} \equiv k_p$$

the probability of ion-pair propagation is given as

$$\alpha = \frac{k_p[\mathrm{M}][\mathrm{P_n}^+]}{k_p[\mathrm{M}][\mathrm{P_n}^+] + k_c[\mathrm{P_n}^+]} = \frac{k_p/k_c[\mathrm{M}]}{1 + k_p/k_c[\mathrm{M}]} \quad (1)$$

where $k_i$, $k_p$, and $k_c$ stand for the initiation, propagation, and collapse rate constants, respectively, [M] stands for the monomer concentration, and $[\mathrm{P_n}^+]$ is the ion-pair concentration. If true Poisson growth takes place, then

$$k_p/k_c[\mathrm{M}] \ll 1 \quad (2)$$

and the ion pair ionizes and collapses many times per monomer addition, and it is unlikely that more than one monomer unit will be added before a collapse. When the ion pair can add several monomer units before collapsing, the distribution per addition is broadened to the most probable distribution. However, the number of times an active center ionizes and collapses during the course of the polymerization must follow a Poisson distribution for all the active centers. Similarly, the number of times an active center ionizes and adds at least one monomer before collapsing, a productive ionization, must follow a Poisson distribution for all the active centers.

We can define those centers that have ionized productively $i$ times as $N_i$

$$N_i = \exp(-\bar{z})\frac{\bar{z}^i}{i!} \quad (3)$$

where $\bar{z}$ is the average number of times the centers ionize productively. The average degree of polymerization for any population, $N_i$, is easily defined in terms of $\alpha$, the probability of propagation (past the first monomer unit) in a productive ionization

$$\bar{P}(1)_n = \frac{1}{1-\alpha}; \quad \bar{P}(1)_w = \frac{1+\alpha}{1-\alpha} \quad (4)$$

where $\bar{P}(1)$ is the average degree of polymerization of those ion pairs per productive ionization. The other average degrees of polymerization can be written[23] as

$$\bar{P}(i)_n = \frac{i}{1-\alpha}; \quad \bar{P}(i)_w = \frac{i+\alpha}{1-\alpha} \quad (5)$$

Since we define the fraction of centers that have ionized productively $i$ times and can write the average $\bar{P}(i)_n$ and $\bar{P}(i)_w$, we can sum those to determine the weight-average and the number-average degrees of polymerization for the whole system

$$\bar{P}_n = \frac{\sum_{i=1}^{\infty} N_i \bar{P}(i)_n}{\sum_{i=1}^{\infty} N_i} \quad (6)$$

where $\bar{P}(i)_n$ is the number-average degree of polymerization of these molecules. Similarly

$$\bar{P}_w = \frac{\sum_{i=1}^{\infty} w_i \bar{P}(i)_w}{\sum_{i=1}^{\infty} w_i} = \frac{\sum_{i=1}^{\infty} N_i \bar{P}(i)_n \bar{P}(i)_w}{\sum_{i=1}^{\infty} N_i \bar{P}(i)_n} \quad (7)$$

From Figini and Schultz[23]

$$\bar{P}_n = \sum_{i=1}^{\infty} \exp(-\bar{z})\frac{\bar{z}^i}{i!}\frac{i}{1-\alpha} = \frac{\bar{z}}{1-\alpha} \quad (8)$$

$$\bar{P}_w = \frac{\exp(-\bar{z})\sum_{i=1}^{\infty}\frac{\bar{z}^i}{i!}\frac{i}{1-\alpha}\frac{i+\alpha}{1-\alpha}}{\exp(-\bar{z})\sum_{i=1}^{\infty}\frac{\bar{z}^i}{i!}\frac{i}{1-\alpha}} \quad (9)$$

Equation 9 can be summed to give

$$\bar{P}_w = \frac{\bar{z}^2 + \bar{z}(1+\alpha)}{\bar{z}(1-\alpha)} = \frac{\bar{z}}{1-\alpha} + \frac{1+\alpha}{1-\alpha} = \bar{P}_n + \bar{P}(1)_w \quad (10)$$

When $\alpha$ is very small, eqs 8 and 10 simplify to the normal Poisson distribution. When $\alpha$ approaches 1, several monomer units add at each ionization and the distribution broadens.

The average number of monomer units added per productive ionization is defined in eq 4 and can be called the "run number", $\bar{l}$. Thus

$$\bar{l} = \frac{1}{1-\alpha} = 1 + k_p/k_c[\mathrm{M}] \quad (11)$$

In these terms eq 10 can be rewritten as

$$\frac{\bar{P}_w}{\bar{P}_n} = 1 + \frac{2\bar{l} - 1}{\bar{P}_n} \quad (12)$$

Thus, if $\bar{P}_n$ and $\bar{P}_w$, the number- and weight-average degrees of polymerization, are known, we can calculate $\bar{l}$, the average number of monomer units polymerized per productive ionization.

**C.2. MWD for Varying Monomer Concentration.** When a batch polymerization is carried out, monomer concentration will drop toward zero as the monomer is consumed. Therefore, $\alpha$ drops toward zero as the polymerization progresses. Since we are discussing living isobutylene polymerizations, initially the polymer could grow in larger jumps while the last portion will grow one unit at a time. This can be taken into account very easily by averaging $\bar{l}$ over the monomer concentration

$$\bar{l} = \frac{\int_{[\mathrm{M}]_0}^{[\mathrm{M}]} \bar{l}\, \mathrm{d}[\mathrm{M}]}{\int_{[\mathrm{M}]_0}^{[\mathrm{M}]} \mathrm{d}[\mathrm{M}]} = \frac{\int_{[\mathrm{M}]_0}^{[\mathrm{M}]} (1 + k_\mathrm{p}/k_\mathrm{i}[\mathrm{M}])\, \mathrm{d}[\mathrm{M}]}{\int_{[\mathrm{M}]_0}^{[\mathrm{M}]} \mathrm{d}[\mathrm{M}]} = 1 + \frac{k_\mathrm{p}[\mathrm{M}]_0\left(1 + \frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right)}{2k_\mathrm{c}} \tag{13}$$

At complete conversion [M] = 0 and $\bar{l} = (\bar{l}_0 + 1)/2$

$$\frac{\bar{P}_\mathrm{w}}{\bar{P}_\mathrm{n}} = 1 + \frac{2\bar{l} - 1}{\bar{P}_\mathrm{n}} = 1 + \frac{\bar{l}_0}{\bar{P}_\mathrm{n}} \tag{14}$$

and at intermediate conversions

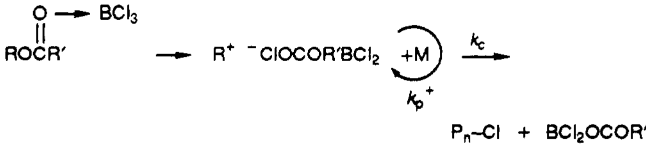
$$\bar{l} = 1 + \frac{\bar{l}_0 - 1}{2}\left(1 + \frac{[\mathrm{M}]}{[\mathrm{M}]_0}\right) \tag{15}$$

where $\bar{l}_0$ is the run number at $[\mathrm{M}] = [\mathrm{M}]_0$.

Figure 1 displays $\bar{P}_\mathrm{w}/\bar{P}_\mathrm{n}$ plots for various $\bar{l}$ values calculated by using eq 14. The MWD narrows with increasing $\bar{P}_\mathrm{n}$ values, and the smaller the $\bar{l}$, the narrower the MWD for the same $\bar{P}_\mathrm{n}$ value. Small $\bar{l}$ values can yield MWDs close to the Poisson values at reasonably high $\bar{P}_\mathrm{n}$.

Living IB polymerizations have often been carried out by using the incremental monomer addition technique.[8] Incremental monomer addition allows the use of smaller $[\mathrm{M}]_0$ compared to a conventional batch polymerization. Smaller $[\mathrm{M}]_0$ yields smaller $\bar{l}_0$ and consequently narrower MWD. MWD can then be minimized by using continuous monomer addition and maintaining low monomer concentration (high conversion). Quasiliving polymerizations[12,26] conducted under these conditions indeed yielded narrower MWDs than conventional batch polymerizations.

In the next section we will use the above approach to evaluate MWD data available for living IB polymerizations. We find it important to emphasize here that our treatment is not applicable to isobutylene polymerizations initiated by tertiary ester and ether/$BCl_3$ where a marked shift in ionization equilibria occurs during initiation and/or propagation, leading to an abrupt change in polymerization rate[8,9] and in $\bar{l}$. Those polymerizations are very rapid initially, indicating the involvement of unpaired ions in the initial phase of propagation:




Collapse with the $BCl_2OCOR'Cl^-$ or $BCl_2OR'Cl^-$ counteranion, however, yields a tertiary chloride capped polyisobutylene and a donor compound ($BCl_2OCOR'$ or $BCl_2OR'$) and propagation will proceed by ion pairs.[5] In these systems the molecular weight distribution of the polymers is relatively broad, as opposed to the narrow distributions obtained in the presence of certain electron-pair donors.

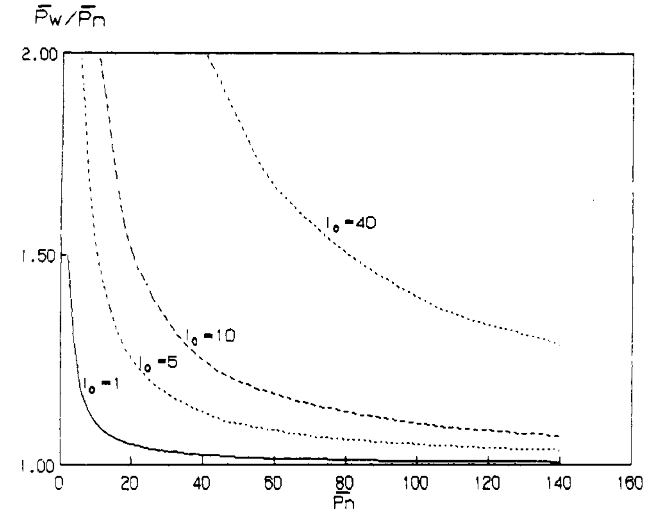



**Figure 1.** $\bar{P}_\mathrm{w}/\bar{P}_\mathrm{n}$ vs $\bar{P}_\mathrm{n}$ plots for various $\bar{l}_0$ values.

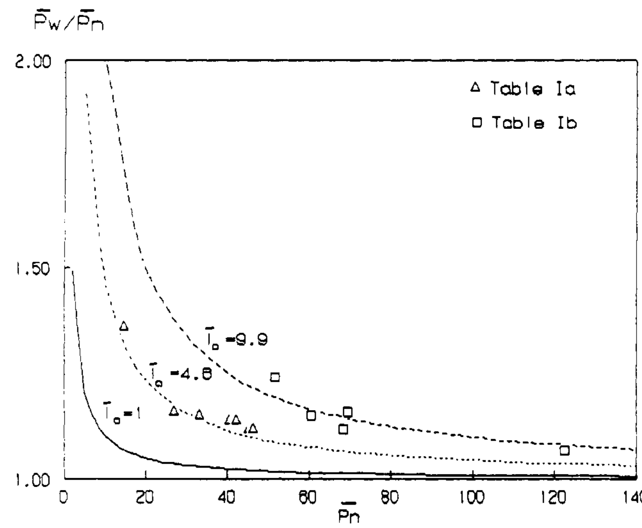



**Figure 2.** $\bar{P}_\mathrm{w}/\bar{P}_\mathrm{n}$ vs $\bar{P}_\mathrm{n}$ plots for $\bar{l}_0$ = 4.6 and 9.9 calculated from eq 14. Experimental points: (Δ) data in Table Ia; (□) data in Table Ib.

## D. Evaluation of MWDs Measured in Living IB Polymerizations in the Presence of Certain Electron-Pair Donors

Table Ia shows $\bar{l}$ and $\bar{l}_0$ values calculated by using eqs 14 and 15 for a living batch isobutylene polymerization. Assuming free-ion chain carriers, the active center concentration was calculated to be on the order of $10^{-8}$ mol/L (see section B.1). These active centers would add several thousand units before interacting with the counteranion. This means that no center would react more than once at the relatively low monomer/initiator ratio (Table Ia). We would then expect a high $\bar{P}_\mathrm{n}$ initially, which would decrease as the monomer was used up and the chains formed became shorter. The data in Table Ia show that exactly the opposite was found. $\bar{l}$ values are reasonably constant, as expected in the case of living polymerizations. A gradual rise of $\bar{l}_0$ with conversion in Table Ia may be due to the rise of the dielectric constant of the medium as isobutylene is used up. Table Ib shows living IB batch polymerizations by incremental monomer addition. $\bar{l}_0$ values calculated using eq 14 are reasonably constant for the same initial monomer concentration ($[\mathrm{M}]_0$ = 0.6 mol/L).

Figure 2 shows $\bar{P}_\mathrm{w}/\bar{P}_\mathrm{n}$ vs $\bar{P}_\mathrm{n}$ plots calculated for $\bar{l}_0$ = 4.6 and 9.9 using eq 14. The experimental data points (Table

I) in Figure 2 are in good agreement with the calculated values. In addition, the data in Table Ib reveal that $\bar{l}_0$ has no dependence on the initiator concentration, confirming ion-pair chain carriers.

Table II shows that $\bar{l}_0$ increases dramatically with increasing solvent polarity, which is characteristic of ion pairs,[22] and reaches $\bar{l}_0 = 54$ for the $TiCl_4$-coinitiated polymerization in $CH_3Cl$. This suggests a higher degree of ion-pair stabilization or a lower collapse rate compared to $BCl_3$-coinitiated polymerizations in the same solvent ($\bar{l}_0 = 4.6$; Table Ia).

## E. Summary and Conclusions

Several hypotheses were discussed regarding the nature of the active centers in living isobutylene polymerizations in the presence of electron-pair donors. The first was that unpaired ("free") ions participated in the polymerization. On the basis of the observed polymerization rate, the free ion concentration would be on the order of $10^{-8}$ mol/L and would polymerize several thousand units before interacting with the counteranion. This means that no center would react more than once at the low monomer/initiator ratios used in the isobutylene polymerizations discussed above. We would then expect a high $\bar{P}_n$ initially, which would decrease as the monomer was used up and the chains formed became shorter. Table I shows that exactly the opposite was found.

Even if a small fraction of the polymerization were due to free ions, a different molecular weight distribution would be found; a few percent of high molecular weight polymer would give a very broad distribution. Thus, the narrow MWD and a degree of polymerization that is proportional to conversion under the conditions described in this paper imply that only one species is active and that is has a low-propagation rate constant. Since the covalent species has earlier been shown to be inactive, the active species can only be the ion pair. The lack of dependence of $\bar{l}_0$ on initiator concentration, Table Ib, verifies that the collapse is a first-order process, and thus the propagation proceeds only through solvated ion pairs.

A gradual rise of $\bar{l}_0$ with conversion is noted in Table Ia. This could be due to the rise of the dielectric constant of the medium as isobutylene is used up. Table II shows the drastic changes in $\bar{l}_0$ with the dielectric constant for the $CumCl/TiCl_4$ initiating system, which is characteristic of ion pairs. The change in volume due to polymerization of isobutylene will raise the dielectric constant from 11.0 to 11.6. This might raise $\bar{l}$ sufficiently to compensate for the decreasing monomer concentration and raise the calculated value of $\bar{l}_0$.

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## References and Notes

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**Registry No.** Isobutylene, 115-11-7; isobutylene (homopolymer), 9003-27-4.