Transfer and Termination Reactions in "Living" Carbocationic Polymerizations

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ABSTRACT

The available data concerning the polymerization of three classes of monomers deemed to yield living polymers, vinyl ethers, styrenic monomers and isobutylene, are discussed from the point of view of transfer and termination reaction. In the case of vinylethers, linearity of $\overline{M}_n$ with a yield up to 30,000 has been obtained, but when higher $\overline{M}_n$ are planned, there is evidence for the occurrence of transfer reactions. In the case of isobutylene, indene, and p-Me-styrene, the linearity (up to $\overline{M}_n \sim 10^5$) of $\overline{M}_n$ with the amount of monomer polymerized which has been observed (but only at low temperature) is compatible with values of transfer constants to monomer measured in "conventional" systems. In these living systems, irreversible terminations are often not very important but may become significant toward the end of monomer consumption. The main termination process is reversible termination which may lead to narrow molecular weight distributions. The linearity of $\overline{M}_n$ with yield is not conclusive evidence for the absence of transfer and termination and for the presence of particular active centers. The control of the polymerizations achieved up to now can be accounted for by the mechanisms of conventional cationic polymerizations, transfer reactions included.

INTRODUCTION

What may be considered as the first important theoretical breakthrough toward the achievement of living carbocationic polymerizations was made in 1982 by Kennedy, Kelen, and Tüdös [1]. This was the hypothesis of the occurrence of reversible termination in some carbocationic polymerizations in order to explain the linear growth of the molecular weight with the polymer yield observed. The various polymerizations described were called "quasi-living." There was some ambiguity about the meaning of this expression, since in all the examples given the very slow addition of monomer was assumed to be necessary to observe this variation in order to have not only *reversible termination* but also *reversible transfer*.

One of the present authors [2] expressed disagreement about the possible occurrence of reversible transfer in these experimental conditions, but readily accepted the concept of reversible termination because it could also explain many other data observed in so-called "classical" carbocationic polymerizations.

The polymerizations described in 1982, mainly with isobutylene and styrenic compounds, were still imperfect since the $\overline{M}_n$ did not grow linearly from the beginning of the reaction and the data showed that transfer and termination were not completely suppressed. Further developments in the work of Kennedy, Higashimura, and their associates showed that linearity from the origin of $\overline{M}_n$ with yield was observed in a variety of systems [3, 4]. It has been generally assumed by the two groups that this observation resulted from the suppression of transfer and termination reactions in these polymerizations [3, 4], which could also explain the observation of very narrow molecular weight distributions for polyisobutylene and poly(vinylether)s. This suppression was believed to result from the presence in these systems of active species different from those occurring in former "classical" systems, such as active covalent bonds [3, 4] (as in "pseudocationic" polymerizations), special stabilized carbenium ions, or active onium ions [5].

The aim of the present article is to show by a few examples that there is not at the present time conclusive evidence for the occurrence of different reaction mechanisms in "living" and many "classical" carbocationic polymerizations, and that the apparent differences between them may only result from experimental changes which may lead to kinetic control of the reaction. If this is true, it means that reversible termination may also occur in various "classical" systems and that transfer reactions occur to a similar extent in those and in various "living" systems. This is the reason why we prefer to call such systems "apparently living" [6] or, more briefly, "living" [7]. This mode of writing means only that in these polymerizations the control of the molecular weight (through controlled rates of initiation and propagation) is such that $\overline{DP}_n = [M]_{cons.}/[I]_{cons.}$, leading to a linearity of $\overline{M}_n$ with polymer yield if initiation is completed at the beginning of polymerization. In the favorable conditions of reversible termination and slow propagation, very narrow molecular weight distributions may also be achieved. A fuller comparison, in a unified approach to living and nonliving carbocationic polymerization of ethylenic monomers, has been made recently [8].

Before we discuss definite examples, it may be observed that most recent developments are in agreement with these conclusions. Recent studies by different groups [7–12] have shown the involvement of ionic species in the polymerization mechanisms of several monomers. Polymerizations which had been found not to be

living near room temperature could approach livingness (e.g., observation of "living" polymerization up to $\overline{M}_n \geq 10^5$) [7, 13] by lowering the temperature, which strongly decreases the transfer and termination reactions, as is the case for "classical" systems.

POLYMERIZATION OF VINYL ETHERS

The first examples of polymerizations (see Table 1) showing a constancy of the number N of macromolecules during the reaction were observed with these monomers (mainly with isobutyl vinyl ether, IBVE), this being deduced from the linearity of $\overline{M}_n$ with the polymer yield, which we shall symbolize as "$\overline{M}_n$ lin." But the $\overline{M}_n$ were limited to 7.5×10^3 for polymerizations initiated with I_2 alone in CH_2Cl_2 at $-60°C$ [14] ($\overline{M}_w/\overline{M}_n \approx 1.5$) or initiated by IH/I_2 in hexane at $-25°C$ [3] ($\overline{M}_w/\overline{M}_n < 1.1$). We shall see that this might be compatible with transfer constant to monomer k_{trM}/k_p larger than 10^{-3}. Moreover, the low $\overline{M}_w/\overline{M}_n$ values in the second case showed that termination reactions were small or absent.

Better results were obtained with HI and ZnI_2 as initiators at $0°C$ in toluene, $\overline{M}_n$ lin being observed up to 15,000 [15] (8000 in CH_2Cl_2 [16], and also with AlEtCl$_2$ in the presence of polar additives. With AlEtCl$_2$ in toluene with 10%/volume of

TABLE 1. "Living" Polymerization of Vinyl Ethers

Monomer	Initiator	Solvent	Temperature, (°C)	$\overline{M}_n$ lin up to	Ref.
n-Butyl vinyl ether	I_2	CH_2Cl_2	-60	7×10^3	14
Isobutyl vinyl ether	$HI + I_2$	Hexane	-25	7×10^3	3
Isobutyl vinyl ether	$HI + ZnI_2$	Toluene	0	1.5×10^3	15
Isobutyl vinyl ether	AlEtCl$_2$	Toluene + 10% EtOAc[a]	0	20×10^3	17
Isobutyl vinyl ether	CH$_3$CH(OiBu)-OCOCH$_3$	Toluene + 10% EtOAc[a]	0	18×10^3	5
Isobutyl vinyl ether	CH$_3$CH(OiBu)I + nBu$_4$N$^+$, ClO4$^-$	CH_2Cl_2	-25	33×10^3	22

[a]EtOAc: Ethyl acetate.

ethyl acetate (EtOAc), water was assumed to be the initiator, with $\overline{M}_n$ lin observed up to 20,000 [17] (see Fig. 1, Curve 1). Similar results were obtained ($\overline{M}_n$ lin up to 18,000) when the ester $CH_3CH(OiBu)OCOCH_3$ was used as initiator [5]. In the absence of added initiator, it was found later with the same system that higher molecular weights could be obtained (up to 40,000) in conditions of higher purity [18], but that deviation from linearity occurred for $\overline{M}_n \approx$ 20,000, indicative of transfer reactions (see Fig. 1, Curve 2). Polymers prepared in the presence of $AlCl_3$ as coinitiator [19] (see Fig. 1, Curve 3) have higher $\overline{M}_n$ (up to 8×10^4) than those obtained with $AlEtCl_2$ (Curve 2), but there was still a deviation from linearity above $\overline{M}_n \approx$ 30,000. Since the two series of experiments were carried out under similar experimental conditions, the concentration of adventitious initiator, although poorly reproducible, may be assumed to be roughly the same in both cases. The higher $\overline{M}_n$ would then result from a lower transfer constant for the active species derived from $AlCl_3$. The results obtained in the presence of $CH_3CH(OiBu)Cl$ (IBCE) as initiator were similar [19]; linear variation up to 2×10^4 for [IBCE] = 2×10^{-3} mol·L^{-1}; deviation from linearity for [IBCE] = 10^{-3} mol·L^{-1} (see Fig. 2).

From experiments at variable initiator concentrations [19], it could be seen that the amount [N] of macromolecules increased linearly with time, which is indicative of a zero-order transfer in monomer, for which

$$[N] = [N]_{0.} + k_{tr}[N]_0 t$$

$[N]_0$ is equal to the initiator concentration (for a quantitative initiation).

This zero-order transfer involves ethyl acetate, since a transfer constant of zero order in monomer, k_{tr}/k_p, has been found to be proportional to ethyl acetate concentration [20]. A strong decrease of the transfer constant k_{tr} occurred when the temperature varied from 20 to $-18°C$ (in toluene, initiation with $AlCl_3$) [19].

This polymerization has been assumed to propagate through ionic species formed according to an ionization equilibrium involving an inactive dormant covalent halide end-group, similar to the initiator, and ion pairs:
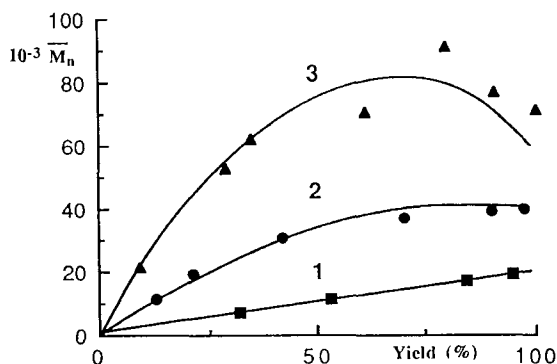

FIG. 1. Polymerization of isobutyl vinyl ether in the presence of ethyl acetate, initiated with adventitious initiator and aluminum derivatives. Variation of $\overline{M}_n$ with yield. [IBVE]$_0$, 0.76 M; [EtOAc], 0.5 M; temperature, 0°C; solvent, toluene. (1) Lewis acid: $AlEtCl_2$ (2×10^{-2} M), data from Higashimura et al. (17). (2) Lewis acid: $AlEtCl_2$ (2×10^{-2} M), data from Granier et al. (6, 18). (3) Lewis acid: $AlCl_3$ (10^{-2} M), Sigwalt et al. (19).
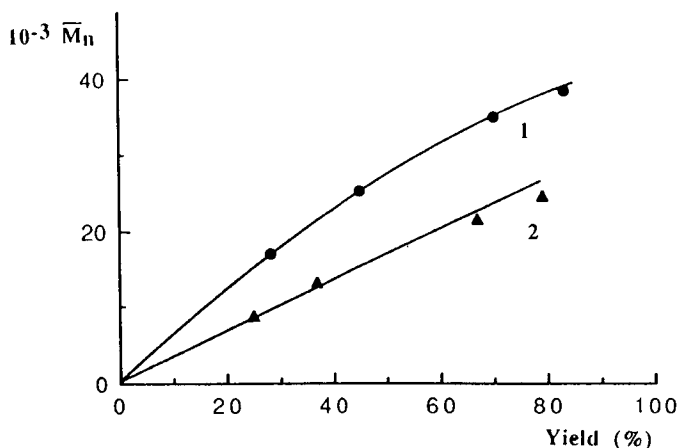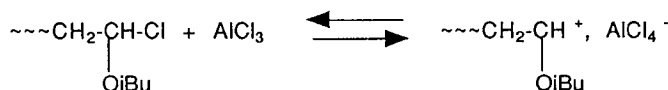
FIG. 2. Polymerization of isobutyl ether initiated with isobutyl-1-chloroethyl ether (IBCE) and AlCl$_3$ in the presence of ethyl acetate. Variation of $\overline{M}_n$ with yield for various IBCE concentrations. [IBVE]$_0$, 0.76 M; [AlCl3], 10^{-2} M; [EtOAc], 0.5 M; temperature, 0°C; solvent, toluene. [IBCE]: (1), 10^{-3} M; (2), 2 × 10^{-3} M.

There is a linear increase of the rate with [AlCl$_3$], with k_{tr}/k_p remaining constant.

The strong lowering of the rate observed when [EtOAc] increased indicated either a displacement of the equilibrium toward the left or a deactivating solvation of the ion pairs, or both.

The presence of ionic species is difficult to prove in the solvent used (toluene). But for polymerizations carried out in CH$_2$Cl$_2$, various results are in agreement with their presence [21]. For the polymerization of IBVE in the absence of a polar additive, using CH$_3$CH(OiBu)I as initiator in CH$_2$Cl$_2$ and various ammonium salts as coinitiators (such as ClO$_4^-$, NBu$_4^+$), Nuyken [22] observed that the rate was higher in a polar solvent such as CH$_2$Cl$_2$, and the results were explained by a special salt effect resulting from an equilibrium ionization of the iodide:
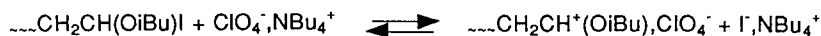
The rate is still very low (polymerizations lasting several hours) because the equilibrium is displaced toward the left. In CH$_2$Cl$_2$ at -25°C, $\overline{M}_n$ lin was observed up to $\overline{M}_n$ = 32,000 with a narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$ < 1.1). It was stated that linearity could be observed up to an $\overline{M}_n$ of at least 10^5. This shows that the presence of an electron donor is not necessary to observe $\overline{M}_n$ lin up to these values. It seems that the salt effect resulting from the presence of excess ClO$_4$NBu$_4$ also suppresses the presence of free ions with a longer lifetime than the ion pairs, thus explaining, together with the large number of exchanges between dormant and ionic species, the narrow molecular weight distributions. When the

iodide initiator was associated with $AgClO_4$, the ionic species was formed in a large amount and the reaction was finished in a few seconds.

Other data showing that transfer constants for IBVE are low, even at higher temperatures, have been observed in several laboratories, since $\overline{M}_n$ of 10^5 to 2×10^5 could be obtained with classical initiators such as $\Phi_3C^+, AlCl_4^-$ in toluene at 0°C [20] or $\Phi_3C^+, SbCl_6^-$ in CH_2Cl_2 [23]. However, the $\overline{M}_n$ were two or three times lower than the theoretical ones.

It was shown earlier (see Fig. 1 in Ref. 6) that for molecular weights of the order of 20,000, perfect linearity was observed for $k_{trM}/k_p = 5 \times 10^{-4}$ and near linearity for 10^{-3}. It may be seen in Fig. 3 that for $k_{trM}/k_p = 10^{-4}$, it is difficult to detect experimentally the occurrence of transfer from the variation of $\overline{M}_n$ with yield, even with a maximum $\overline{M}_n$ larger than 10^5.

In conclusion, the assumption that transfer is absent in "living" polymerizations and present in "nonliving" reactions has never been really substantiated. The reason why a linear increase of $\overline{M}_n$ with polymer yield is not observed in the "nonliving" polymerization may result from the high theoretical $\overline{DP}_n$ $(= [M]_0/[I]_0)$ which cannot be reached for low $[I]_0$ on account of transfer reactions. We shall now see that this is even truer for the case of monomers of the styrene family.

POLYMERIZATION OF STYRENE DERIVATIVES

The results obtained with these monomers have been generally much less spectacular than those with vinyl ethers. The $\overline{M}_n$ lin reached are of the same order of magnitude (10^4 to 2×10^4), but the linearity is less good and the molecular weight distribution is generally much broader. This was particularly the case ($\overline{M}_w/\overline{M}_n \sim 5$–6) for styrene [24] and p-Me-styrene initiated by 1(4-Me phenyl)ethyl
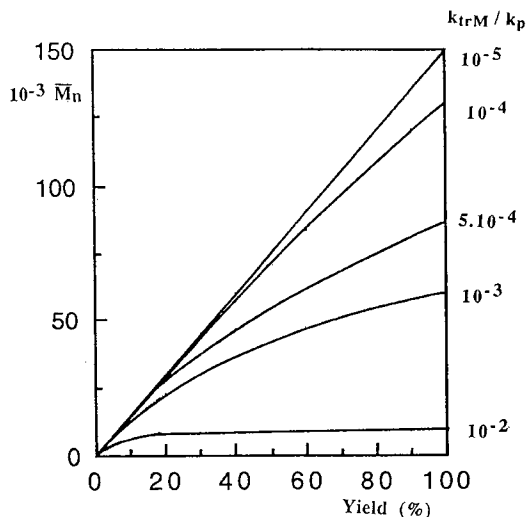

FIG. 3.   Theoretical evolution of $\overline{M}_n$ with yield for exclusive transfer to monomer, for variable values of k_{trM}/k_p. Isobutyl vinyl ether: $[M]_0$, 0.76 M; $[I]_0$, 5×10^{-4} M.

acetate [25] in CH_2Cl_2 at -30 and at $-50°C$, without much difference according to temperature. The linearity was better (up to $\overline{M}_n = 30,000$) and the $\overline{M}_w/\overline{M}_n$ lower (1.1 to 1.2) for 1,3,5-trimethylstyrene [26], which was indicative of a possible suppression of some termination and transfer through the crowding of the ortho position in the monomer, which might inhibit the formation of an indanic end-group.

The data are compatible with k_{trM}/k_p values of about 5×10^{-4}, and this is not different from what has been observed for a "nonliving" system ($TiCl_4$ in CH_2Cl_2) which has given $k_{trM}/k_p = 4 \times 10^{-4}$ at $-60°C$ for styrene [27].

Much more satisfactory results have been obtained with indene. Several initiating systems were used with CH_2Cl_2 as solvent: $CumCl/TiCl_4$, $CumCl/TiCl_3OBu$, $CumOMe/TiCl_4$, $CumOMe/TiCl_3OBu$.

With $CumOMe/TiCl_4$ at $-40°C$ for example [7], good linearity of $\overline{DP}_n$ versus $[M]_0$ for complete yields was observed up to $\overline{M}_n = 40,000$, but the plot showed a strong curvature for higher molecular weights (see Fig. 4). A plot of $1/\overline{DP}_n$ versus $1/\overline{DP}_{n0}$ ($= [N_0]/[M]_0$) was linear up to $\overline{M}_n$ 80,000, with an ordinate intersection of $k_{trM}/k_p = 5 \times 10^{-4}$ (see Fig. 5). This value is of the same order of magnitude as that measured previously (7.5×10^{-4}) for an assumed "nonliving" system: polymerization by $PhCH_2Cl/AlEt_2Cl$ in CH_2Cl_2 methyl cyclohexane (50/50 by volume) at $-50°C$ [28].

Initiation at $-40°C$ with $CumCl/TiCl_4$ was incomplete (and the molecular weights higher than theoretical), but became complete with the addition of DMSO with a "living" behavior. This permitted us to draw a Mayo plot which gave $k_{trM}/k_p = 6 \times 10^{-4}$ (in CH_2Cl_2 at $-40°C$), which is similar to the former case [9]. At $+5°C$ with the same initiator, but without DMSO, initiation was complete and the $\overline{M}_n$ plot was linear up to $\overline{M}_n = 17,000$ (but it strongly deviated above this value) (see Fig. 6). The k_{trM}/k_p derived from the Mayo plot was equal to 1.4×10^{-3}. This again clearly shows that for molecular weights in this range, the observation of $\overline{M}_n$ lin is compatible with the existence of rather extensive transfer reactions. The

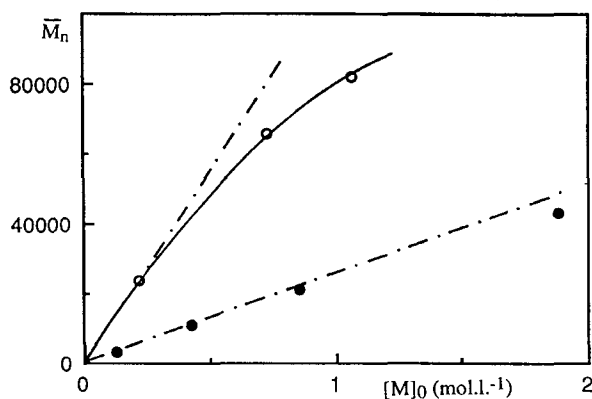FIG. 4.   Polymerization of indene initiated with the $CumOMe/TiCl_4$ initiating system at $-40°C$. Variation of $\overline{M}_n$ with initial monomer concentration. Solvent, CH_2Cl_2; reaction time, 6 minutes; yield, 100%; $[TiCl_4]$, 2×10^{-2} M. (●) [CumOMe]: 4.5×10^{-3} M. (○) [CumOMe]: 10^{-3} M, without DMSO. ($- \cdot$) Theoretical line for $\overline{DP}_n = [M]_0/[I]_0$.
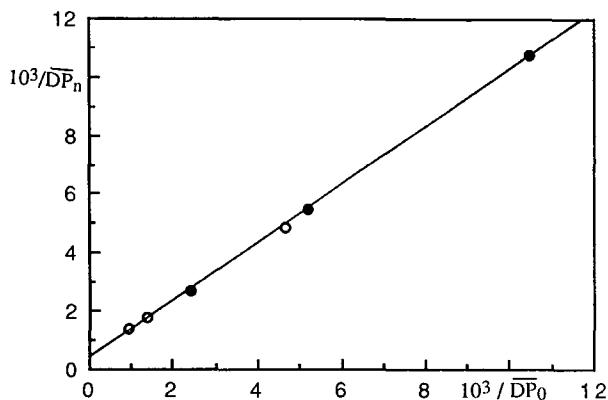
FIG. 5. Polymerization of indene initiated with the CumOMe/TiCl$_4$ initiating system at $-40°C$. Measurement of the transfer constant to monomer: $k_{trM}/k_p = 5 \times 10^{-4}$. Conditions as in Fig. 4.

unexpectedly very good agreement between theoretical and experimental values of the $\overline{M}_n$ up to 17,000 probably results from incomplete initiation.

However, transfer reactions were strongly reduced when the temperature was lowered. With CumOMe/TiCl$_4$ at $-75°C$, $\overline{M}_n$ lin was observed up to $\overline{M}_n = 10^5$ (see Fig. 7), the Mayo plot passing through the origin [7]. But this only shows that $k_{trM}/k_p \leq 10^{-4}$ at this temperature. It might, in fact, be much lower since $\overline{M}_n$ higher than 4×10^5 could be obtained at $-70°C$ with TiCl$_4$ "alone" [29] (initiation mechanism unknown).

An ionic mechanism for the polymerization of indene with these initiators is supported by various observations which point to the existence of an ionization equilibrium between covalent dormant and ionic active species:

FIG. 6. Polymerization of indene initiated with the CumCl/TiCl$_4$ initiating system at $5°C$. Variation of $\overline{M}_n$ with initial monomer concentration. Solvent, CH$_2$Cl$_2$; reaction time, 6 minutes; yield, 100%; [TiCl$_4$], 2×10^{-2} M. (■) [CumCl]: 3×10^{-3} M, without DMSO. (○) [CumCl]: 10^{-3} M, without DMSO. (△) [CumCl]: 10^{-3} M; [DMSO]: 2.5×10^{-3} M. (— ·) Theoretical line.
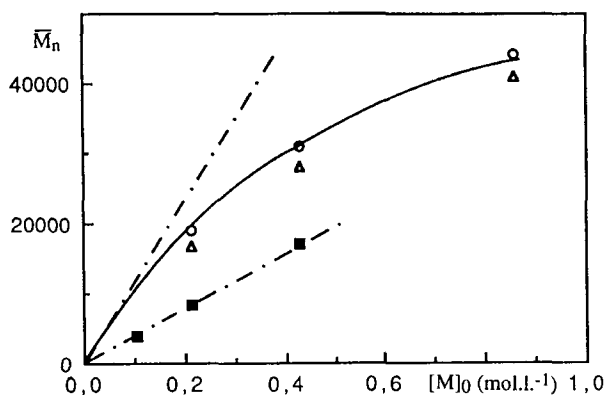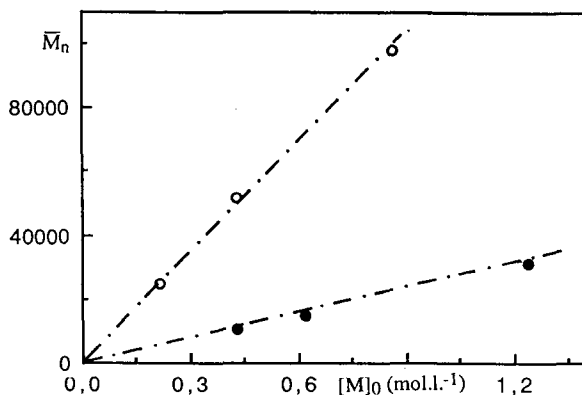
FIG. 7. Polymerization of indene initiated with the CumOMe/TiCl$_4$ initiating system at $-75°C$. Variation of $\overline{M}_n$ with initial monomer concentration. Solvent, CH$_2$Cl$_2$; reaction time, 6 minutes; yield, 100%, [TiCl$_4$], 2 × 10^{-2} M. (●) [CumOMe]: 4.5 × 10^{-3} M. (○) [CumOMe]: 10^{-3} M. (— ·) Theoretical line.

$$\text{---CX + TiCl}_4 \rightleftharpoons \text{---C}^+, \text{TiCl}_4\text{X}^- \rightleftharpoons \text{---C}^\bullet + \text{TiCl}_4\text{X}^-$$

With CumCl/TiCl$_4$ as initiator, the addition of tetra-n-butylammonium chloride or of tetra-n-butylammonium pentachlorotitanate causes a lowering of the $\overline{M}_n$ which becomes nearly theoretical, and a narrowing of the molecular weight distribution (see Table 2). This results from the suppression by a salt effect of free ions which have longer lifetimes than ion pairs and which lead to a broadening of the molecular weight [21], as is well known in anionic polymerization [30]. The global rate is also reduced, permitting more exchanges between dormant species and ion pairs during propagation [21]. A similar effect (see Table 2) is observed when DMSO instead of a salt is added to the solution, without observing a significant change in the k_{trM}/k_p.

Kinetic data [31] led to a negative apparent activation energy (-13.7 kJ· mol^{-1}), in agreement with an increased ionization at lower temperatures. They also showed clearly that for initiating systems or experimental conditions leading to

TABLE 2. Influence of DMSO and Tetra-n-butyl Ammonium Pentachlorotitanate on the $\overline{M}_n$ and Molecular Weight Distribution of Polyindene[a]

Additive	$\overline{M}_n$(calc)	$\overline{M}_n$(expt)	$\overline{M}_w/\overline{M}_n$
0	16,600	25,900	4.9
DMSO, 2.5 × 10^{-3} M	16,600	15,500	3.1
nBu$_4$N$^+$TiCl$_5^-$, 8 × 10^{-3} M	16,600	14,450	2.4

[a]Initiating system: CumCl/TiCl$_4$; [TiCl$_4$], 2 × 10^{-2} mol·L^{-1}; [indene], 0.43 mol·L^{-1}; temperature, $-40°C$.
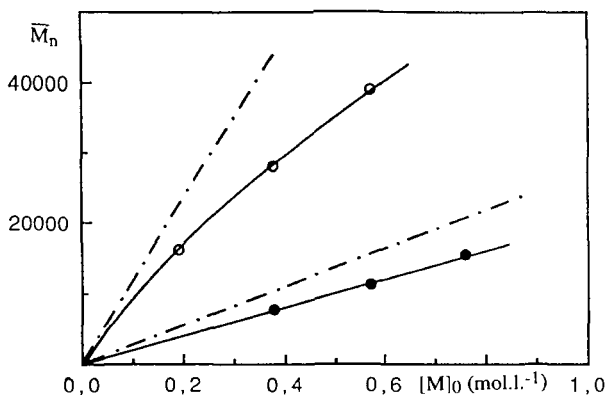
FIG. 8.   Polymerization of p-methyl styrene initiated with the CumOMe/TiCl$_4$ initiating system at $-40°C$. Variation of $\overline{M}_n$ with initial monomer concentration. Solvent, CH$_2$Cl$_2$; reaction time, 6 minutes; yield, 100%; [TiCl$_4$], 2×10^{-2} M. ($\bullet$) [CumOMe]: 4.5×10^{-3} M. ($\bigcirc$) [CumOMe]: 10^{-3} M. ($-\cdot$) Theoretical line.

slower propagation, a significant reduction of $\overline{M}_w/\overline{M}_n$ occurred (between 4 and 1.7) [9].

A comparison of the behavior of p-methylstyrene with that of indene using the same initiators was made. If one looks only at the $\overline{M}_n$ lin plots, the results are very similar.

With CumOMe/TiCl$_4$ in CH$_2$Cl$_2$ at $-40°C$, $\overline{M}_n$ lin is observed for high ratios of [M]$_0$/[I]$_0$ up to $\overline{M}_n = 16,000$, but a deviation from linearity occurs for higher ratios (see Fig. 8). A Mayo plot including all the experimental data (with "living" and "nonliving" behavior) gave $k_{trM}/k_p = 10^{-3}$ at $-40°C$ (see Fig. 9).

At $-75°C$, $\overline{M}_n$ lin was observed up to $\overline{M}_n = 80,000$ (Fig. 10) and the Mayo line passed through the origin (Fig. 11), as for indene. However, the $\overline{M}_w/\overline{M}_n$ ratios are rather high (2.3 to 3.4) and are larger for higher molecular weights.
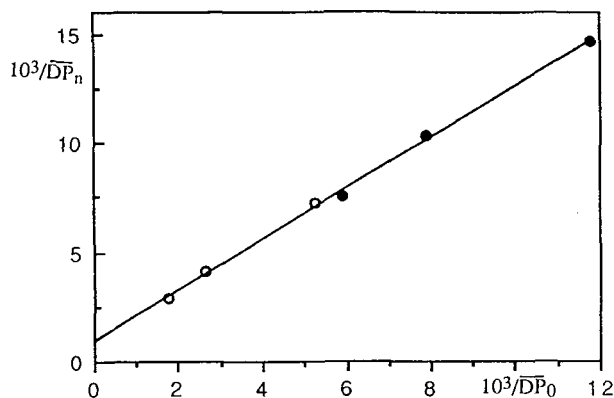

FIG. 9.   Polymerization of p-methyl styrene initiated with the CumOMe/TiCl$_4$ initiating system at $-40°C$. Measurement of the transfer constant to monomer: $k_{trM}/k_p = 1 \times 10^{-3}$. Conditions as in Fig. 8.

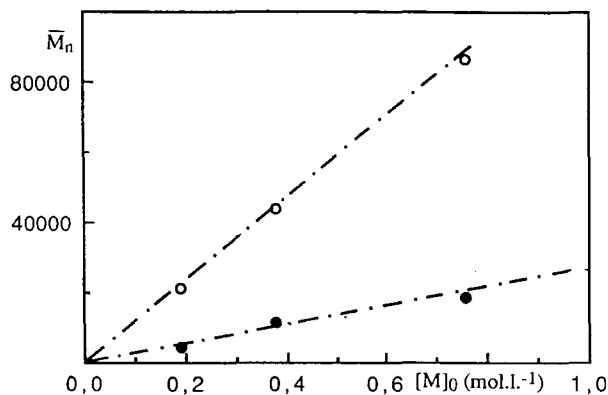FIG. 10. Polymerization of p-methyl styrene initiated with the CumOMe/TiCl$_4$ initiating system at $-75°C$. Variation of $\overline{M}_n$ with the initial monomer concentration. Solvent, CH$_2$Cl$_2$; reaction time, 6 minutes; yield, 100%; [TiCl$_4$], 2×10^{-2} M. (●) [CumOMe]: 4.5 $\times$ 10^{-3} M. (○) [CumOMe]: 10^{-3} M. $(- \cdot)$ Theoretical line.

Quite different results were observed when a new monomer batch was added at the end of a first polymerization (see Fig. 12). For a second addition after 49 seconds (see Fig. 12a), the final polymer was bimodal, with the larger peak corresponding mainly to the first polymerization (only a small increase of M_{peak}) and the smaller peak of the higher molecular weight corresponding to the second polymerization.

If the second addition was made after a longer time (6 min), the first peak corresponded exactly to the $\overline{M}_n$ of the first polymer and the second peak was more clearly separated (see Fig. 12b). These results suggest the existence of rapid termination reactions, the polymerization of the second monomer batch being initi-
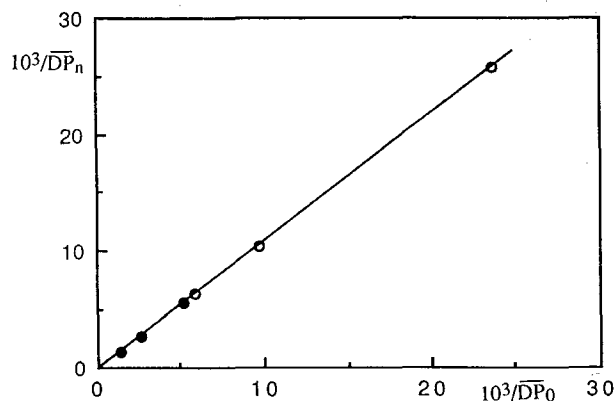

FIG. 11. Polymerization of p-methyl styrene initiated with the CumOMe/TiCl$_4$ initiating system at $-75°C$. Measurement of the transfer constant to monomer. Conditions as in Fig. 10.
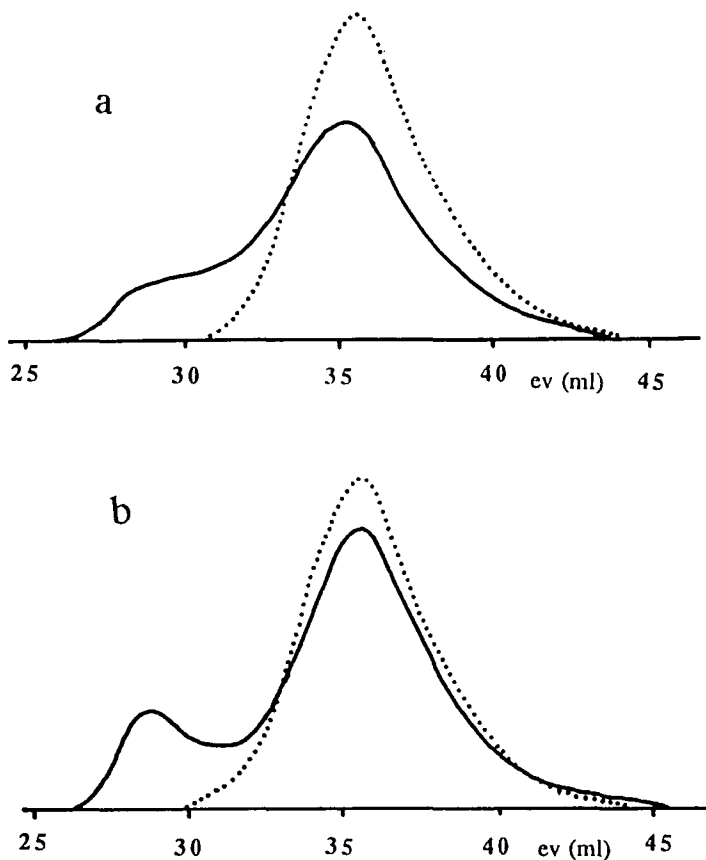
FIG. 12. Polymerization of p-methyl styrene in CH_2Cl_2 initiated with the CumOMe/ $TiCl_4$ initiating system at $-75\,^\circ C$, with incremental monomer addition: GPC chromatograms of the polymers (refractive index). (a) Second addition 49 seconds after the start of the first polymerization. (b) Second addition 6 minutes after the start of the first polymerization. ($\cdots$) Polymer formed during the first polymerization, $[M]_0$: 0.76 M. (——) Polymer recovered after the second polymerization, $[M]$: 0.26 M.

ated by impurities in the monomer or by HCl resulting from a termination reaction by alkylation of a penultimate unit (indanic termination).

POLYMERIZATION OF ISOBUTYLENE

With this monomer initiated by cumyl acetate/BCl_3 in CH_2Cl_2, it was concluded by Kennedy et al. from early experiments showing $\overline{M}_n$ lin that zero-order transfer in monomer occurred at $-10\,^\circ C$ but not at $-30\,^\circ C$, and from Mayo plots that transfer to monomer did not occur [4]. However, the molecular weight range was only up to $\overline{M}_n = 11,000$, which does not permit us to reach a clear conclusion
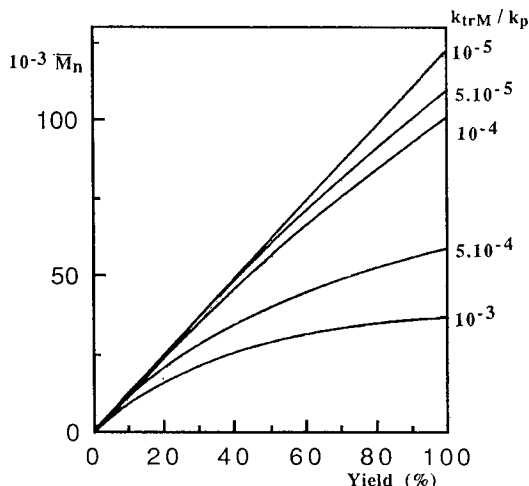
FIG. 13. Polymerization of isobutylene. Evolution of $\overline{M}_n$ with yield in the case of exclusive transfer to the monomer for variable values of k_{trM}/k_p. [M]$_0$: 1 M. [I]$_0$: 4.5 × 10^{-4} M.

since k_{trM}/k_p had been found earlier to be very low and equal to 3×10^{-5} at $-48°C$ for a "classical" initiating system [32] (TiCl$_4$ "alone" in CH$_2$Cl$_2$).

Kennedy et al. [33] later found a good linear $\overline{M}_n$ plot up to $\overline{M}_n \sim 1.2 \times 10^5$ at $-80°C$ (in CH$_2$Cl$_2$/hexane; volume ratio of 40/60), and also a narrow molecular weight distribution with p-(dimethoxyisopropyl) benzene/TiCl$_4$ as initiator. But if k_{trM}/k_p is of the order of 10^{-5}, the corresponding Mayo plot does not permit transfer to be detected. It may be seen in Fig. 13 that a nearly perfect variation of $\overline{DP}_n$ with yield is expected up to $\overline{DP}_n \sim 2200$ (for polyisobutylene, $M_n = 120,000$) for $k_{trM}/k_p = 10^{-5}$. Even for $k_{trM}/k_p = 10^{-4}$, the difference with linearity is not easily detectable experimentally, particularly if the possible errors in $\overline{M}_n$ determination are considered.

On the other hand, the narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n \sim 1.1$) observed by Kennedy [33], even after several monomer additions at $-80°C$, show that definitive termination reactions are negligible up to high yields in this system and that the reversibility of termination is nearly perfect, which is quite different from what was observed with styrene monomers. Polymerization of IB in these conditions permits a control of the polymer similar to that obtained with anionic living polymerizations.

If one compares this with the indene case for which definitive terminations and transfer are also limited since $\overline{M}_n$ lin was also observed after addition of a new monomer, the much better control of molecular weight distribution in the isobutylene case probably results from a slowing down of the reaction in the mixed solvent, which permits many exchanges between active and inactive species during the growth of the macromolecule. With indene in CH$_2$Cl$_2$, polymerization is completed within 1 to 10 seconds, which does not allow as many exchanges.

CONCLUSION

It has been asserted that the linearity of $\overline{M}_n$ with yield as observed in various cationic polymerizations of isobutylene and vinyl ethers, together with narrow molecular weight distributions, proves the absence of transfer and termination, i.e., the occurrence of living polymerizations, and that therefore the nature of the active sites should be different from those involved in the usual carbocationic polymerizations.

We have shown that the results observed were in fact strongly dependent on the range of molecular weights studied and on temperature. For low values of the theoretical molecular weight ($\overline{M}_{nth} = [M]_{consumed} / [II]_{consumed}$), a good linearity of $\overline{M}_n$ from the origin may be observed even at relatively high temperatures [5]. This linearity disappears for higher $\overline{M}_n$, which shows the occurrence of transfer [18]. The molecular weight distribution remains narrow, however. For very low temperatures (e.g., -70 to $-80°C$), transfer may become undetectable up to an $\overline{M}_n$ of about 10^5, but it might become significant for higher $\overline{M}_n$s [7]. In several cases the order of magnitude of the transfer constants measured for usual carbocationic polymerizations are compatible with the variation of $\overline{M}_n$ with polymer yield [6].

The main reason why a "living" behavior is not observed in "classical" polymerizations is linked to the relatively slow or limited initiation which results in a very low concentration of macromolecules. For example, with isobutylene and indene, initiation by $TiCl_4$ "alone" (in fact, initiation either by water or by direct initiation) may give values of $\overline{M}_n$ higher than 10^6 at $-80°C$, showing that transfer is very small (perhaps even smaller than in "living" systems). However, the molecular weights are limited by transfer because the theoretical molecular weight is still higher.

The growth of macromolecules may also be limited by irreversible termination reactions which may be significant only when the theoretical molecular weights are very high but are not important enough to affect the molecular weight distributions when they are relatively low. (The $\overline{M}_n$ is *not* affected.)

In conclusion, it is not necessary to assume the presence of special types of active species to explain the linear increase of $\overline{M}_n$ with yield often observed. In order to obtain narrow molecular weight distributions (e.g., $\overline{M}_w/\overline{M}_n < 1.2$), initiation should be sufficiently fast in comparison with propagation. However, an $\overline{M}_w/\overline{M}_n$ of about 1.3 may be observed even with slow initiation [34], and termination should be either very limited or reversible [1]. In order to obtain low values of $\overline{M}_w/\overline{M}_n$, there should be a sufficient number of exchanges between dormant and active species during the reaction time [21, 35].

There has been no evidence until now that "living" systems may give polymers of higher molecular weight than "nonliving" ones, and this is true even for isobutylvinylether for which molecular weights up to 2×10^5 have been obtained in the second case [20, 22]. However, a possible reduction of transfer reactions linked to the presence of some additives cannot be excluded, even if this reduction has been shown not to occur in various cases: polymerization of isobutylene in the presence of DMSO or of proton traps [36]; polymerization of indene in the presence of DMSO or of $NBu_4^+,TiCl_5^-$ [9]. However, some recent results obtained with vinyl ethers show that while zero-order transfer in [M] increases in the presence of an additive such as ethyl acetate [19], first-order transfer in monomer may decrease [37]. This might result from a particular type of propagation involving acetate-

complexed or monomer-complexed carbenium ions [6]. However, the decrease of stability of dormant polymers at high yields (low monomer concentrations) in the case of vinyl ethers [38] and of isobutylene [39] still remains to be explained.

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