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"Living" Cationic Polymerization of Indene. 3. Kinetic Investigation of the Polymerization of Indene Initiated with Cumyl Methyl Ether and Cumyl Chloride in the Presence of Titanium Derivatives

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ABSTRACT: The kinetics of the polymerization of indene in dichloromethane solution, initiated with cumyl methyl ether and cumyl chloride, in the presence of titanium derivatives ($TiCl_4$ and $TiCl_3OBu$), at variable temperatures (0 to −62 °C), have been investigated by adiabatic calorimetry under vacuum. At −40 °C, with cumyl methyl ether as an initiator, an internal first-order plot with respect to the monomer is observed after 60% yield, and initiation is completed before the end of the polymerization. The polymerization is apparently living or "living", which means only that the molecular weight increases linearly with polymer yield. With the CumCl/$TiCl_4$ initiating system, complete initiation is obtained only in the presence of dimethyl sulfoxide (DMSO). Addition of DMSO increases the initiation rate, decreases the apparent propagation rate constant, and allows the observation of a first-order plot and an apparently living process. The use of a common ion salt (tetra-*n*-butylammonium pentachlorotitanate) has a similar effect. With the CumCl/$TiCl_3OBu$ initiating system, an apparently living polymer is obtained without additive. These data, and the negative apparent activation energies observed, imply that several types of chain ends are present in variable concentrations in the solution (covalent inactive species, ions pairs, and free ions), involving a reversible termination. These results, as well as the occurrence of transfer reactions, may be explained, as in conventional carbocationic polymerization, by a propagation involving ionic active centers.

I. Introduction

A linear increase of the molecular weight of the polymer with conversion has been described in many carbocationic polymerizations, the first cases being reported with vinyl ethers[1] and isobutylene.[2] These investigations were later extended to styrene and substituted styrenes,[3−6] and recently to indene.[7−9] In some cases, polymerization resumed with a further increase of molecular weight after new monomer addition, and narrow molecular weight distributions could be obtained. These polymerizations were described as "truly living", and the absence of transfer and termination was assumed.[10] Since we gave various reasons why we do not agree that these assumptions are correct in most of the examples given,[11] many of these polymerizations cannot be called living. We have described polymerizations for which the proportional increase of $\bar{M}_n$ versus yield was observed as "apparently living" or more shortly "living". This explains the quotation marks (to living) in our previous papers[7,8] and in the present one describing the "living" polymerization of indene.

The assumption of the absence of transfer and termination made by various authors led them to the conclusion that this should result from a difference in the nature of the active species[12] since transfer and termination usually occur in carbocationic polymerizations. Besides, addition of electron-donating compounds, such as dimethyl sulfoxide (DMSO),[13] was in some cases necessary in order to obtain these results. It has been proposed that these compounds participate in the formation of the propagating center,[14] suppressing transfer and termination.

Transfer reactions have been shown to occur in many cases,[7,15] and this is better explained by a "conventional" carbocationic mechanism of propagation. However, some of these results—for instance the narrow molecular weight distributions—may be explained only with the assumption of the occurrence of "reversible termination", as was first proposed by Kennedy,[16] permitting a large number of exchanges between inactive "dormant" end groups and ionic active species.

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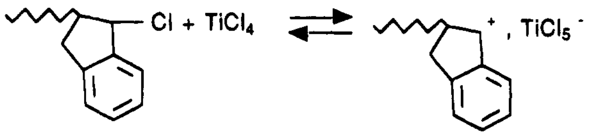
In our previous papers concerning the "living" polymerization of indene initiated with the title compounds,[7,8] it had been tentatively concluded that the results could be accounted for by assuming a conventional carbocationic mechanism, without the formation of any special type of active species. The main parameter allowing the observation of an "apparently living" process was the ratio of initiation to propagation rates, which should be high enough to ensure complete initiation before the end of the polymerization and the formation of a constant number of macromolecules if transfer may be neglected. There may be a limited range of the initial monomer to initiator ratio for which transfer, although present, cannot be detected, thus making the polymer "apparently living" (e.g. cumyl methyl ether/$TiCl_4$ initiating system). In some cases (initiation with the cumyl chloride/$TiCl_4$ system), addition of DMSO is necessary to obtain "apparently living" character, and this has been explained by assuming that the additive permits complete initiation, by decreasing the propagation rate and/or increasing the initiation rate.

Besides, the results obtained led to the assumption that reversible termination is operative in these cases and that the concentration of active species at a given time, which is only a fraction of the added initiator, is determined by an equilibrium, e.g. in the case of the CumCl/$TiCl_4$ initiating system:



(1)

However, kinetic evidence supporting this hypothesis had not been obtained because the reactions were very fast, complete conversion being obtained in a few seconds with the concentrations used, and sampling or kinetic measurements during the polymerization had not been possible. Consequently, kinetic investigations had to be carried out by adiabatic calorimetry under vacuum, at concentrations low enough to allow quantitative measurements.

II. Experimental Section

The preparation and purification of the reagents used, as well as the recovery of the polymers, and the measurements of the molecular weights by gel permeation chromatography have been described.[7,8]

The adiabatic calorimeter used is derived from that built by Cheradame and Vairon,[17] and has also been described.[18] The removable lower part of the reaction vessel was fitted with a ground glass joint. Airtightness was obtained with an indium wire washer which was crushed under vacuum. The upper part of the apparatus was sealed to a vacuum line and the reagents were introduced through Teflon stopcocks.

The polymerizations were initiated by breaking a bulb containing the $TiCl_4$ or $TiCl_3OBu$ solution, in a mixture of indene, solvent (CH_2Cl_2), and initiator (CumOMe or CumCl) with magnetic stirring. Conversion was complete in all cases. The heat release, which is proportional to the amount of monomer polymerized, was measured with a calibrated resistance and was electrically recorded. The concentration of the monomer at any reaction time could be deduced from the temperature versus time plot. From these data are deduced the plots of $\ln([M]_0/[M]_t)$ shown in the figures. Given the small amount of monomer polymerized in most experiments, the increase of temperature caused by the polymerization was lower than 2 °C and should not affect significantly the values of the kinetic constants measured. Even at the low concentrations of reagents used, the polymerizations were generally complete in less than 10 s. In most cases, the maximum rate was obtained after a short induction period of 1−2 s. As the lag time of the recording device is about 1 s, reactions taking place in more than 3 s can be treated. However, this lag time hinders the obtention of quantitative initiation data. The only qualitative data available are of the time span necessary to observe the linearity of the internal first-order plot for monomer consumption. Since the concentration of macromolecules formed is approximately equal to that of the initiator, this means that at this stage the initiator has quantitatively reacted and that all the potential chains have been formed. Because of the assumed equilibrium between active and dormant species, the concentration of active species $[M^+]$ at a given time is unknown. Consequently, the apparent rate constant k'_p reported in the tables is linked to the rate constant of propagation k_p and to the concentration of M^+ by the relationship

$$k'_p\ (\mathrm{L\ mol^{-1}\ s^{-1}}) = k_p[M^+]/[N]_0 \qquad (2)$$

$[N]_0$ being the concentration of initiator (and of the macromolecules formed, assuming complete initiation and no transfer).

Table 1. Influence of Cumyl Methyl Ether on the Polymerization of Indene at −40 °C[a]

10^3[CumOMe] (mol L^{-1})	polymerization time (s)	$\bar{M}_{n\,calc}$	$\bar{M}_{n\,expt}$	$\bar{M}_w/\bar{M}_n$	$10^3[N]^b$ (mol L^{-1})
0	21		58 000	3.11	0.3
1.5	4	13 300	11 600	2.01	1.7

[a] [indene] 0.179 mol L^{-1}; [$TiCl_4$] 2 × 10^{-2} mol L^{-1}; solvent CH_2Cl_2; yield 100% in both cases. [b] Concentration of macromolecules formed during the polymerization.

III. Results

Table 1 shows a comparison between two polymerizations carried out at −40 °C in the absence of added initiator and in the presence of cumyl methyl ether, with titanium tetrachloride coinitiator. In the first system, the reaction reaches completion in about 20 s and yields a polymer with $\bar{M}_n$ = 58 000, which corresponds to a final concentration of macromolecules equal to 3×10^{-4} mol L^{-1} (which might be compatible with the estimated amount of residual water in the medium). Consequently, if transfer is neglected, one might assume that every molecule of residual water initiated one macromolecule. In the presence of methyl cumyl ether, the concentration of potentially active centers is 5-fold higher (1.5×10^{-3} mol L^{-1} of CumOMe), and the reaction time is reduced in proportion (~4 s instead of ~21 s). This suggests that the reactivity of active centers formed during a "conventional" carbocationic polymerization (i.e. assumedly from initiation by residual water and $TiCl_4$, as in the former experiment) might not be very different from that of the growing species involved in the "living" polymerization initiated with cumyl methyl ether.

The results of other polymerizations initiated with the CumOMe/$TiCl_4$ initiating system are reported in Table 2. Experiments 1−3 show the influence of the reaction temperature between −62 and 0 °C. The $\bar{M}_n$ at −62 °C is slightly higher than the calculated value, assuming complete initiation by the cumyl methyl ether (21 500 instead of 20 000), but the difference remains within the experimental error of $\bar{M}_n$ measurement (10%).[7] However, the $\bar{M}_n$ decreases (to 16 000 at 0 °C) as the temperature increases, due to transfer at higher temperatures. The value of k_{trM}/k_p at −40 °C calculated using the data of experiment 2 is 4.7×10^{-4}, in good agreement with that reported at this temperature.[7]

Figure 1 shows the first-order plots for monomer consumption at variable temperature. In all cases, a

Table 2. Kinetic Investigation of the Polymerization of Indene Initiated with the Cumyl Methyl Ether/TiCl$_4$ Initiating System[a]

expt no.	1	2	3	4
reacn temp (°C)	−62	−40	0	−40
10^3[TiCl$_4$] (mol L^{-1})	2	2	2	4
$\bar{M}_n$	21 500	18 500	16 100	19 900
$\bar{M}_w/\bar{M}_n$	2.30	2.08	1.70	1.90
10^4[N]^b (mol L^{-1})	4.6	5.4	6.2	5.0
k'_p (L mol^{-1} s^{-1})	3300	1500	540	3600

[a] [indene] 8.6×10^{-2} mol L^{-1}; [CumOMe] 5×10^{-4} mol L^{-1}; calculated M_n 20 000. [b] Concentration of macromolecules formed during the polymerization.

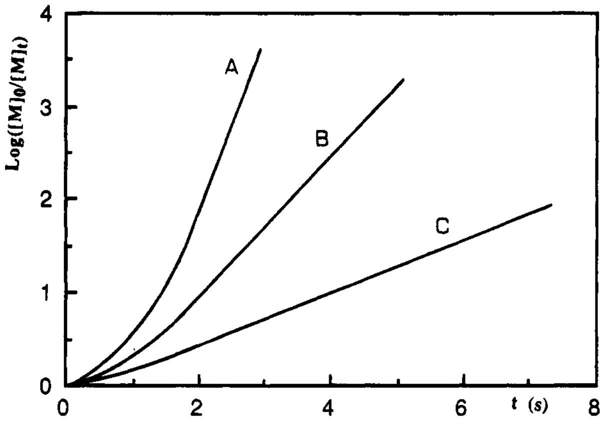


Figure 1. Polymerization of indene initiated with the CumOMe/TiCl$_4$ initiating system at variable temperatures. Conditions: solvent CH$_2$Cl$_2$; [TiCl$_4$] 2×10^{-3} M; [CumOMe] 5×10^{-4} M; [indene] 8.6×10^{-2} M; temperatures (A) −60 °C, (B) −40 °C, (C) 0 °C.

straight line is obtained in less than 1.5 s. This shows that, after this time, the concentration of the active centers is constant; that is to say initiation is complete (if a "living" process is assumed). In this case, the slope of the straight line yields the value of the apparent propagation rate constant k'_p ($k'_p = k_p[M^+]/[N]_0$, see eq 2).

As mentioned,[8] the apparent propagation rate constant increases as the reaction temperature decreases. The corresponding apparent activation energy for propagation is 13.7 kJ/mol. Since initiation is quantitative and the concentration of cumyl methyl ether is the same, this variation of k'_p implies the existence of temperature dependent equilibria between species having different reactivities, such as inactive covalent species and ion pairs according to eq 1, and possibly between free ions and ion pairs. A negative apparent activation energy had previously been found for the polymerization of indene initiated with TiCl$_4$ (without added initiator),[19] and recently by Storey[20] in the case of the "living" polymerization of isobutylene.

Comparison of experiments 2 and 4 of Table 2 shows that the apparent propagation rate increases proportionally to the concentration of TiCl$_4$ at constant initiator (CumOMe) concentration. This is in accordance with the existence of an equilibrium of ionization for the formation of the active species.

Initiation with the CumCl/TiCl$_4$ initiating system yields quite different results (Table 3). Without DMSO (experiment 1 of Table 3) the first-order internal law for the disappearance of the monomer is never observed, even at high yields (see Figure 2). The curvature of the plots of log([M]$_0$/[M]$_t$) vs time in Figure 2 (curve A) shows a continuous increase of the polymerization rate during the whole polymerization, which is due to a continuous increase of the concentration of growing macromolecules during the reaction. The value k'_p = 6500 L mol^{-1} s^{-1} is estimated from the slope of the tangent to the curve at the end of the polymerization. The $\bar{M}_n$ of the polyindene recovered (31 000) is significantly higher than that calculated by assuming quantitative initiation by CumCl and the absence of transfer (20 000). This shows that initiation is incomplete and that the efficiency of initiation is about 65%.

Under similar conditions, but in the presence of DMSO (5×10^{-4} mol L^{-1}) the polymer has the expected value for a living polymer when complete initiation is assumed ($\bar{M}_n$ = 20 000). A straight line is obtained after an induction period of about 2 s, i.e. at about 50% yield (Figure 2, curve B). Consequently, at this time, initiation is quantitative, and the concentration of macromolecules is equal to that of the initiator. The apparent propagation rate constant (k'_p = 1700 L mol^{-1} s^{-1}) is significantly lower than that in the absence of DMSO. A polymerization carried out in the presence of tetra-n-butylammonium pentachlorotitanate (without DMSO) yielded a polyindene with nearly the calculated $\bar{M}_n$, but k'_p was much lower than that in the presence of DMSO (400 instead of 1700 L mol^{-1} s^{-1}) (cf. experiment 3 and curve C of Figure 2).

Also, experiments 2 and 4 of Table 2 show that k'_p increases when the temperature decreases, as in the previous system.

Experiment 5 of Table 3 shows the results of a polymerization initiated with CumCl in the presence of TiCl$_3$OBu as a Lewis acid, and without DMSO. The apparent rate constant is the lowest of the series of initiating systems.

$$k'_p(\text{CumCl/TiCl}_4) = 6500 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$k'_p(\text{CumOMe/TiCl}_4) = 1500 \text{ L mol}^{-1} \text{ s}^{-1}$$

$$k'_p(\text{CumCl/TiCl}_3\text{OBu}) = 340 \text{ L mol}^{-1} \text{ s}^{-1}$$

The corresponding plots of log([M]$_0$/[M]$_t$) vs time for the three systems are reported in Figure 3. That of the CumCl/TiCl$_3$OBu pair is linear over the whole reaction, after a short induction period.

IV. Discussion

The differences between the initiating systems containing an alkoxy group (CumOMe/TiCl$_4$ and CumCl/TiCl$_3$OMe) and the CumCl/TiCl$_4$ system have already been underlined.[7,8] The former systems yield "living" polymers without additive (i.e. with theoretical $\bar{M}_n$ assuming quantitative initiation) with molecular weight distributions from 1.9 to 2.4. With the CumCl/TiCl$_4$ initiating system in the absence of DMSO, the $\bar{M}_n$'s are higher than calculated values and the molecular weight distributions are broad ($\bar{M}_w/\bar{M}_n \approx 4-5$). "Living" polymers with $\bar{M}_w/\bar{M}_n \approx 2$ can be obtained either in the presence of DMSO or of a common ion salt, such as tetra-n-butylammonium pentachlorotitanate (see Table 3).

A similar difference is found by kinetic investigation. The initiating systems having a methoxy group in the counterion yield lower propagation rates, and initiation is complete before the end of the reaction, which is the first requirement for the observation of a living process. With the CumCl/TiCl$_4$ initiating system this condition is not fullfilled and complete initiation is not achieved in the absence of DMSO. It appears from Figure 2 that

Table 3. Kinetic Investigation of the Polymerization of Indene Initiated with the Cumyl Chloride/TiCl$_4$ Initiating System[a]

expt no.	1	2	3	4	5
initiating system	TiCl$_4$/CumCl	TiCl$_4$/CumCl/DMSO	TiCl$_4$/CumCl/Bu$_4$N$^+$TiCl$_5^-$	TiCl$_4$/CumCl/DMSO	TiCl$_3$OBu/CumCl
reacn temp (°C)	−40	−40	−40	−20	−40
$\bar{M}_{n\ \mathrm{expt}}$	31 000	20 000	19 200	18 500	18 500
$\bar{M}_w/\bar{M}_n$	4.7	2.0	2.2	2.3	2.3
10^4[N][b] (mol L^{-1})	3.2	4.9	5.2	5.4	5.4
k'_p (L mol^{-1} s^{-1})	6500[c]	1700	400	900	340

[a] Solvent CH$_2$Cl$_2$; calculated $\bar{M}_n$ for complete initiation 20,000. [indene] 8.6×10^{-2} mol L^{-1}; [CumCl] 5×10^{-4} mol L^{-1}; [TiCl$_4$] 2×10^{-3} mol L^{-1}; [TiCl$_3$OBu] 2×10^{-3} mol L^{-1}; [DMSO] 5×10^{-4} mol L^{-1}; [nBu$_4$N$^+$, TiCl$_5^-$] 5×10^{-4} mol L^{-1}. [b] Concentration of macromolecules formed during the polymerization. [c] Maximum slope of the curve log([M]$_0$/[M]$_t$) = *f(t)*.

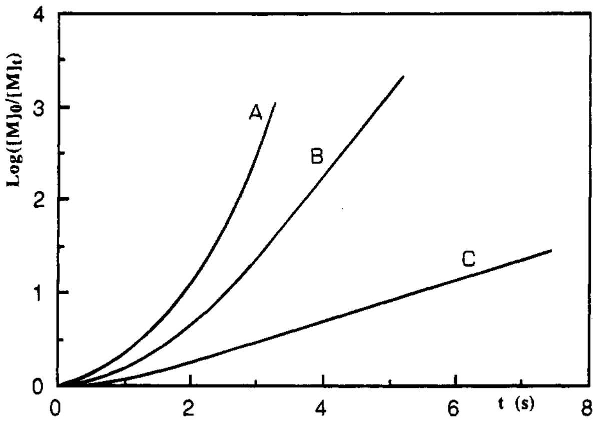


Figure 2. Polymerization of indene initiated with the CumCl/TiCl$_4$ initiating system. Influence of additives on the reaction rate: (A) without additive; (B) with [DMSO] 5×10^{-4} M; (C) with [nBu$_4$N$^+$, TiCl$_5^-$] 5×10^{-4} M. Conditions: temperature −40 °C; solvent CH$_2$Cl$_2$; [TiCl$_4$] 2×10^{-3} M; [CumCl] 5×10^{-4} M; [indene] 8.6×10^{-2} M.

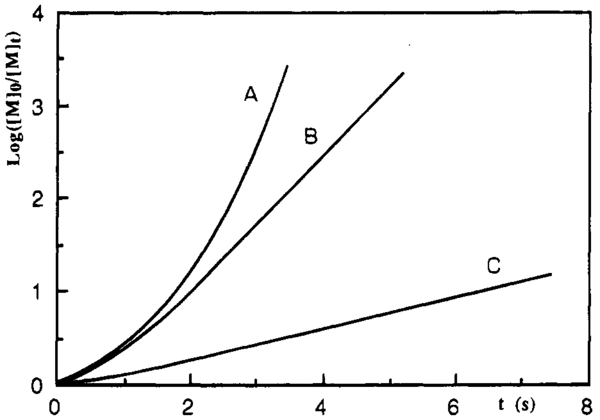


Figure 3. Influence of the initiating system on the kinetics of the polymerization of indene in dichloromethane at −40 °C: (A) CumCl/TiCl$_4$, [TiCl$_4$] 2×10^{-3} M, [CumCl] 5×10^{-4} M; (B) CumOMe/TiCl$_4$, [TiCl$_4$] 2×10^{-3} M, [CumOMe] 5×10^{-4} M; (C) CumCl/TiCl$_3$OBu, [TiCl$_3$OBu] 2×10^{-3} M, [CumCl] 5×10^{-4} M.

DMSO decreases the propagation rate constant and at the same time increases the rate of initiation, which is completed in 2 s. Thus, the role of DMSO can be accounted for on purely kinetic grounds.

A living polymerization implies the absence of termination and transfer reactions. The existence of transfer to monomer at −40 °C with similar constants ($k_{trM}/k_p = (5-6) \times 10^{-4}$) has been established in both systems. Transfer is decreased at low temperatures, but so is the initiation rate, and for the CumCl/TiCl$_4$/DMSO initiating system, it was not possible to find a temperature at which initiation is complete and transfer negligible.

Transfer did not decrease in the presence of DMSO with the CumOMe/TiCl$_4$ initiating system at −40 °C (see Table 3 in ref 7) or with the CumCl/TiCl$_4$ system at +5 °C (see Table 9 and Figure 6 in ref 8). This is not in agreement with the hypothesis of the participation of DMSO in the formation of a special active center which would not transfer.

Termination must also be absent to obtain living polymer. However, a distinction must be made between irreversible termination, which is the termination most often postulated in conventional polymerizations, and reversible termination, which has already been mentioned. A moderate extent of irreversible termination which would allow complete conversion would still yield polymers with the expected $\bar{M}_n$, but with broader molecular weight distributions. Such a termination cannot be ruled out. However, if irreversible termination was important, conversion would not be complete, or at least one should observe a curvature of log([M]$_0$/[M]$_t$) vs time plots. Since this is not the case, it is assumed that irreversible termination is negligible during the time of the reaction. Reversible termination is apparently involved in the formation of many "living" polymers.

In experiments carried out with incremental monomer addition (initiating system: CumOMe/TiCl$_4$), the second monomer addition was made 6 min after the start of the polymerization, which is completed in a few seconds. The polymers still have the expected $\bar{M}_n$ with unimodal molecular weight distributions, which implies that the macromolecules formed in the first polymerization have resumed growth. This suggests that reinitiation involves dormant reactivable end groups rather than long lived carbocations, which are not stable for such a long time at −40 °C.

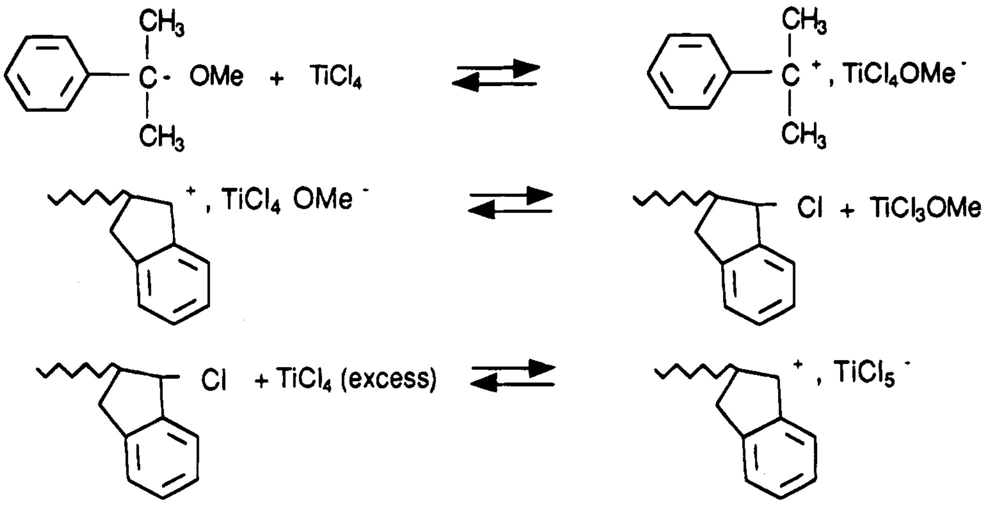
Initiation using 1-chloroindan shows that activated chlorinated end groups initiate the polymerization of indene.[8] Consequently, in polymerizations initiated with the CumCl/TiCl$_4$ initiating system, the most probable termination reaction would be the formation of a reactivable chlorinated end group according to eq 1.

The reactivation reaction might be different in the case of initiation with the CumOMe/TiCl$_4$ initiating system. One might think that, as the concentration of TiCl$_4$ is at least 4 times higher than that of the CumOMe, chlorine exchange might occur during the polymerization (Scheme 1).

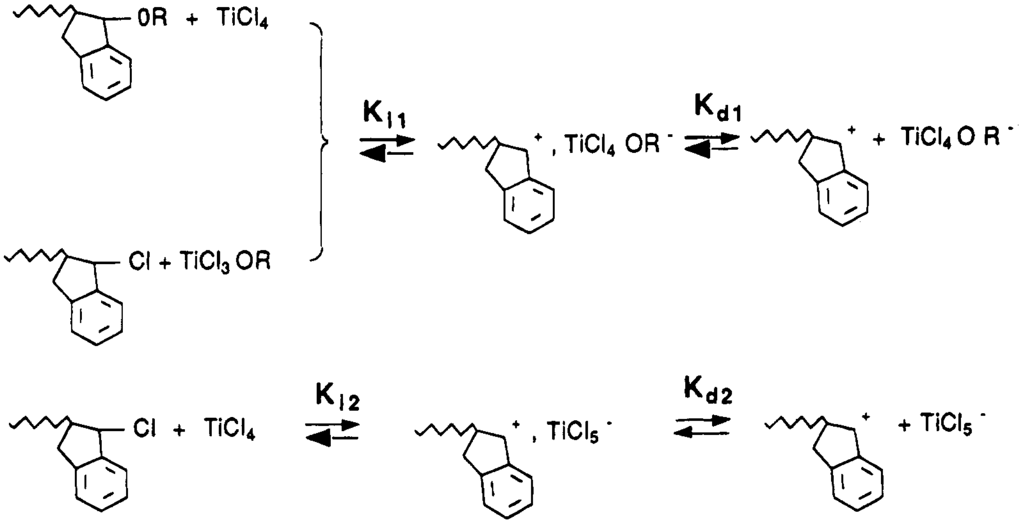
Such an exchange seems to take place in the polymerization of isobutylene[21] initiated with ethers and boron trichloride, at −10 or −30 °C in methylene chloride, but the polymerization was much slower than in the present system.

Fast equilibration does not occur in the case of indene in methylene chloride, since the polymerization rate in the presence of excess TiCl$_4$ (which should mainly yield TiCl$_5^-$ counterions) is much smaller for TiCl$_4$/CumOMe than for TiCl$_4$/CumCl. And if exchange occurred progressively during the reaction, there would be a con-

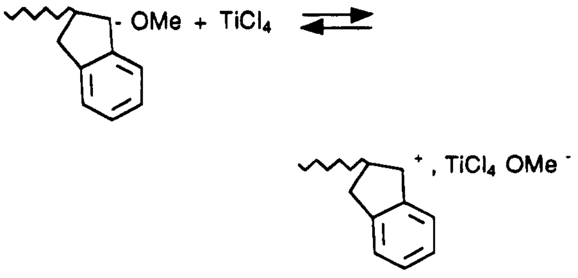
Scheme 1



Scheme 2



tinuous change of the nature of the counterion (from $TiCl_4OMe^-$ to $TiCl_5^-$) during the polymerization, and this would cause a corresponding modification of the kinetics, k'_p varying from 1500 (experiment 2 of Table 2) to 6500 (experiment 1 of Table 3). This is not observed in the polymerization initiated with CumOMe/$TiCl_4$. The first-order plots obtained (Figures 1 and 2) suggest that the main reversible termination reaction during propagation involves the capture of an alkoxy group by the cation and re-formation of the same end group (eq 3).



(3)

The existence of reversible termination implies that the macromolecules may be present as dormant species, as ion pairs, and in relatively polar solvents such as methylene chloride, as free ions. These equilibria may be represented as in Scheme 2 for the two types of initiating systems.

The effect of the exchange on the molecular weight distribution has been discussed by Matyjaszewski[22] and Litt.[23] Frequent exchange during the formation of a macromolecule narrows the molecular weight distributions, while slow exchange broadens them. Relationships between the number of exchanges and the MWD have been proposed, when propagation involves exclusively ion pairs.

The situation is still more complicated in the presence of free ions. The two types of propagating species may have different propagation rate constants, and two exchange reactions between the three species should be considered. The difference of reactivity between free ions and ion pairs may not be as important as in anionic polymerization.[24] However, the collapse of an ion pair to a dormant macromolecule is unimolecular, while the recombination of free ions is bimolecular and must be slower. Consequently, free carbocations should have longer lifetimes than ion pairs, the number of monomers added during each period of growth should be higher, and the presence of free ions should broaden the molecular weight distribution.

In all the systems investigated, the ion pairs involved are not fundamentally different and have similar sizes. Consequently, it can be reasonably assumed that the propagation rate constants are similar. The differences in k'_p are mainly due to different values of the concentrations of active centers [M^+]. The values of the ionization equilibrium constants (K_{i1} and K_{i2}) in Scheme 2 determine the concentration of the active centers. The average length of a growth period depends on the value of the ionization rate constant k_i and of the deactivation rate constant k_{-i}, with the following relationship:

$$K_i = k_i/k_{-i}$$

The k'_p values suggest the following order for the equilibrium constants:

$$K_i(\mathrm{PolCl/TiCl_3OBu}) < K_i(\mathrm{PolOMe/TiCl_4}) < K_i(\mathrm{PolCl/TiCl_4})$$

where PolCl and PolMe represent the functionalized end groups.

Besides, since initiation is slower for CumCl/$TiCl_4$ than for CumOMe/$TiCl_4$, the ionization rate constants k'_i of the initiators should vary in the reverse order, assuming that ionization is the rate-determining step in initiation:

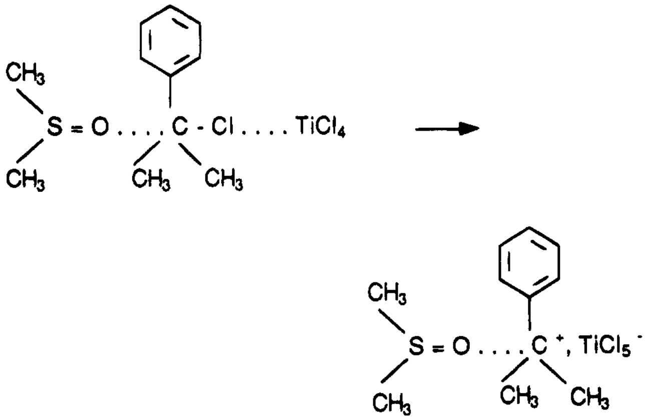
$$k'_i(\mathrm{CumCl/TiCl_3OBu}) > k'_i(\mathrm{CumOMe/TiCl_4}) > k'_i(\mathrm{CumCl/TiCl_4})$$

Hence, in the case of the CumCl/$TiCl_3OBu$ initiating system, the equilibrium constant K_i would be low and the polymerization would be slow, but the ionization rate constant k_i (and also the deactivation rate constant k_{-i}) would be high. This would lead to fast initiation, deactivation, and reactivation and would allow several interchanges between active and dormant species during the formation of a macromolecule, which would result in narrower molecular weight distributions. In the case of the CumCl/$TiCl_4$ initiating system, the equilibrium constant would be high, yielding a higher concentration of active species and fast polymerization. But the rate constants for initiation, reinitiation, and deactivation would be smaller than in the previous system, which would cause partial initiation, fewer interchanges between active and dormant species, and broader molecular weight distributions. The reason for the above order for k'_i is not obvious and should be explored by kinetic measurement of the formation of the carbocationic species.

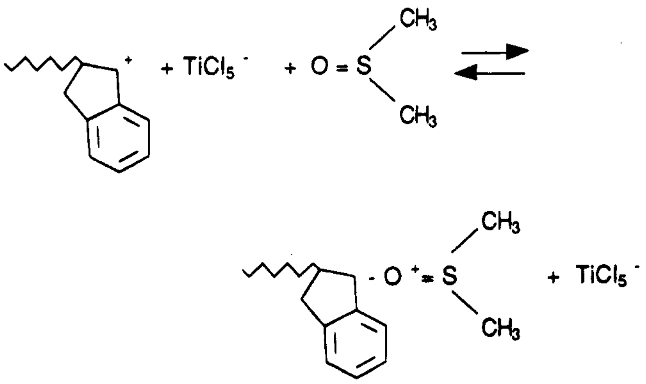
With this system, addition of DMSO yields "living" polymer. The role of electron-donating compounds in cationic polymerizations is not fully understood. DMSO and dimethylacetamide (DMA) were first used by Kennedy and colleagues to control the polymerization of isobutylene.[14] According to these authors, these compounds are included in the active end group and yield stabilized active centers. Storey and colleagues[20] agree with this interpretation in the case of the polymerization of isobutylene in the presence of pyridine as additive. Di-*tert*-butyl pyridine (DTBP), however, which cannot interact with bulky cations, may act as a scavenger and prevent adventitious protic initiation.[25] Using both DTBP and DMA, Kennedy obtained "living" polystyrenes ($\bar{M}_n$ proportional to yield up to 40 000 at −80 °C; Figure 6 of ref 26). However, Faust and colleagues conclude that, in the case of the polymerization of isobutylene[27] and styrene,[28] DTBP and DMSO are just proton scavengers and do not stabilize the active centers.

In the systems investigated here, DMSO does not seem to affect transfer,[7,8] and the kinetic data reported here show that in increases the initiation rate and decreases the propagation rate.

It is proposed that DMSO increases the initiation rate according to the mechanism proposed by Penzcek,[29] and that it also favors reinitiation of the dormant species, thus narrowing the molecular weight distribution:



The reduction of the propagation rate has been explained by some authors assuming that the DMSO becomes part of the active center,[14] making it less reactive. Another possibility is that it deactivates one type of active species, i.e. the free ions, through formation of an oxonium ion



But since DMSO also gives complexes with $TiCl_4$, its presence may simply modify equilibrium 1.

This implies that the active species present in the solution are "conventional" ions, paired or unpaired. This assumption is in agreement with the observation that the addition of a common ion salt has a similar influence on the molecular weight distribution as that of DMSO, in the initiation with the CumCl/$TiCl_4$ system (see Table 3). Both compounds would suppress free cations, the DMSO by complexation, and the common ion by shifting the dissociation equilibrium.

The results concerning the polymerization of indene initiated with different initiating systems at −40 °C are summarized in Table 4, together with kinetic measurements. It may be seen that there is a decrease of the apparent propagation rate constant and a progressive improvement of the "living" character of the systems from CumCl/$TiCl_4$ to CumOMe/$TiCl_3OBu$ (extended range of linearity for the $\bar{M}_n$, narrower molecular weight distribution).

In conclusion, the data concerning the "living" cationic polymerization of indene reviewed in this paper may be accounted for by the mechanisms generally postulated

Table 4. Summary of the Results Obtained at −40 °C with Different Initiating Systems[7,8,a]

Lewis acid	initiator	linearity of $\bar{M}_n$ vs [M]	$\bar{M}_w/\bar{M}_n$	k_{trM}/k_p	k'_p (L mol^{-1} s^{-1})
$TiCl_4$	CumCl	no linearity	3.6−4.9		6500
$TiCl_4$	CumCl + DMSO	linear up to 40 000	2.1−3.2	6×10^{-4}	1700
$TiCl_4$	CumOMe	linear up to 40 000	1.6−2.4	5×10^{-4}	1500
$TiCl_3OBu$	CumCl	linear up to 70 000	1.6−2.4	not measurable	340
$TiCl_3OBu$	CumOMe	linear up to 80 000	1.6−1.7	not measurable	

[a] Solvent: methylene chloride.

and accepted for "conventional" polymerizations, including transfer reactions.

The only supplementary hypothesis is the occurrence of reversible termination, which may as well take place in some "conventional" systems. This implies the existence of a particular type of stationary state of the concentration of active centers, which results from an equilibrium between covalent dormant species and active ionic species, instead of the quasi stationary state resulting from equal initiation and termination rates, postulated for many "conventional" systems.[30] The molecular weight distributions of the polymers depend on the frequency of the exchanges.

Evidence for the occurrence of transfer has been found in many systems investigated, but transfer is not detectable at low monomer to initiator ratios (low $\bar{M}_n$) and is considerably reduced at low temperatures.[15]

Quantitative initiation, which is necessary to assess the livingness of the polymerizations, may be achieved by choosing initiating systems with high initiation to propagation rate ratios and allowing complete initiation to take place before the end of the polymerization. These ratios may be improved by electron-donating additives.

The complete conversions obtained in all cases, together with the first-order internal law observed for monomer consumption over the whole polymerization, suggest that irreversible termination may be less important than was thought in conventional systems. From this point of view, a reexamination of some nonliving systems assuming reversible termination would be interesting.

There is strong evidence for the presence of ionic chain carriers (salt effect, negative apparent activation energy). However, the exact nature of these active species, such as their possible solvation by monomer, polymer, and solvent, as well as their ionization and dissociation constants, is still unknown.

The observation of "living" polymers results from kinetic control of the polymerization in a range of molecular weights in which the existence of transfer cannot be assessed.

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