Influence of 2,6-Di-*tert*-butyl-4-methylpyridine on the Polymerization of Indene Initiated with Cumyl Chloride/Tin Tetrachloride

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ABSTRACT: The controlled polymerization of indene initiated with cumyl chloride and tin tetrachloride in methylene dichloride solution shows first-order kinetics with respect to $SnCl_4$, which implies the existence of simple equilibria for ionization and dissociation, contrary to the case of $TiCl_4$. Experiments in the presence of a hindered base (2,6-di-*tert*-butyl-4-methylpyridine) allowed to estimate the propagation rate constant for paired and unpaired ions in the range of 5×10^4−10^5 L mol^{-1} s^{-1} at −40 °C. A fast initial polymerization, which takes place in the absence of base, and is suppressed by the base, is attributed to the larger dissociation constant for the $Cum^+,SnCl_5^-$ ion pairs than for the polyindenyl ones, yielding a transitory excess of free ions. The hindered base suppresses the formation of free ions, may act as a proton trap in the case of zero order transfer, and may also be involved in bimolecular termination.

Introduction

In carbocationic polymerizations, the control of molar masses is generally limited by transfer reactions and by the poor stability of the carbocations. With indene, methyl cumyl ether being the initiator and $TiCl_4$ the co-initiator,[1] control of the molar masses ($M_n = M_{nth}$; $M_{nth} = [M]_0 \times$ yield $\times$ molar mass of monomer/$[I]_0$) was obtained at −70 °C (with AMI: all monomer in reactions) up to $M_n = 10^5$ (transfer not detected), but only up to $M_n = 3 \times 10^4$ at −40 °C ($k_{trM}/k_p = 5 \times 10^{-4}$). With cumyl chloride and $TiCl_4$[2] (with added dimethyl sulfoxide in order to reduce $k_{papp} = d(\ln([M]_0/[M]_t)/dt) = k_p[P_n^+]$) $k_{trM}/k_p = 6 \times 10^{-4}$ at −40 °C and 1.4×10^{-3} at +5 °C. These polymerizations with $TiCl_4$ as co-initiator are very fast and completed in 1−30 s according to reagent concentrations. Experiments with incremental monomer addition (IMA) showed however a relative stability of cationic species at −40 °C, and a stopped-flow study[3] of indanyl cations formed with various initiators confirmed their perfect stability at −60 °C and a stability for minutes up to 0 °C. Polymerization of indene initiated by cumyl chloride and $SnCl_4$ in CH_2Cl_2 has been studied in order to examine the variation of M_n and M_w/M_n with conversion for reactions with reduced polymerization rates. This allowed to control the M_n up to 20 000 at −15 °C.[4] However, a decrease of the molar mass was observed for high initial monomer concentrations at complete conversion. This led us to consider the possibility of various transfer reactions and the existence of a zero-order transfer reaction (transfer to the counterion) was shown to happen in media of low dielectric constant. To further elucidate this point, the influence of a hindered pyridine, 2,6-di-*tert*-butyl-4-methylpyridine (DBMP), on the kinetics of the polymerization of indene initiated with CumCl/$SnCl_4$ has been investigated.

Although they have been widely used by a number of authors since their first mention in carbocationic polymerization,[5] the mechanistic role of substituted pyridines is not yet completely understood.

Substituted pyridines such as 2,6-di-*tert*-butyl-pyridine and 2,6-di-*tert*-butyl-4-methylpyridine were first considered to act as proton scavengers which have two main effects.[5,6] They suppress initiation by adventitious protic initiators such as water and hydrogen chloride without interacting with the carbocations due to steric hindrance. Furthermore, in the case of a zero-order transfer (e.g., transfer to the counterion) they would turn the transfer reaction into a termination[7] (terminative chain transfer). Moreover, the formation of a pyridinium salt with protic impurities creates a common ion effect which suppresses the free ions or at least decreases their concentration,[8] thus allowing kinetic measurements related to ion pairs.

Besides, pyridines may be considered as electron donors which may stabilize the carbocation and possibly decrease the propagation rate, thus allowing a higher ratio of initiation to propagation rate and consequently a quantitative initiation and a better control. 2,6-Dimethylpyridine[9] and even unsubstituted pyridine[10] have been used as electron donors, in the last case with a control of the molar mass of polyisobutylene up to M_n = 25 000 at −50 °C, a low polydispersity, and a linear semilogarithmic conversion plot up to 80% yield.

Up to now, it has not been possible to distinguish between the various modes of action,[11] and the role of substituted pyridines is still under discussion.[12] Furthermore, the hindered bases can in some cases interact with the Lewis acid (e.g., with $AlCl_3$[13]), and a comparative investigation of chain-end decay of living polyisobutylene in the presence of 2,6-di-*tert*-butylpyridine and 2,6-dimethylpyridine suggested in the former case the occurrence of a bimolecular β-proton abstraction by the base.[14] On the other hand, Higashimura et al.[15] found that 2,6-dimethylpyridine allowed control of the polymerization of isobutyl vinyl ether, assumedly through stabilization of the carbocation, while 2,6-di-*tert*-butylpyridine had no effect due to steric hindrance.

In the case of initiation in the presence of $TiCl_4$ as activator, an ionization reaction of second order with respect to $TiCl_4$ has been found in the case of the

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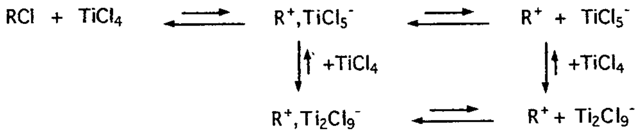
Table 1. Kinetics of the Polymerization of Indene in the Presence of DBMP at −15 °C[a]

expt no.	reaction time (s)	conv	M_n(expt)	M_n(calc)	I_p
1	30	0.08	2700	1900	1.26
2	45	0.11	3200	2700	1.25
3	60	0.14	4200	3500	1.24
4	120	0.22	5700	5400	1.28
5	360	0.39	8700	9600	1.40
6	900	0.57	11300	14000	1.69

[a] [Indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; [DtBMP] = 2 × 10^{-4} mol L^{-1}; Solvent = CH_2Cl_2.

polymerization of isobutylene[16] and styrene,[17] which has been accounted for assuming two successive equilibria involving active species with $TiCl_4^-$ and $Ti_2Cl_9^-$ counterions:



It seemed necessary to check whether similar equilibria take place in the present case and consequently to measure the reaction order with respect to $SnCl_4$.

Experimental Section

Indene (Aldrich), dichloromethane (SDS Pestipur), and tin tetrachloride (Aldrich) were purified under vacuum as previously described[4] and stored under vacuum. DBMP (Aldrich), a white solid, was sublimated under vacuum, and dichloromethane solutions were prepared under vacuum. Cumyl chloride was prepared by addition of hydrogen chloride to α-methylstyrene. The hydrogen chloride content in some $SnCl_4$ solutions was titrated by ^1H NMR in the presence of DBMP (δ 1.35 ppm, *t*-Bu base; δ 1.63 ppm, *t*-Bu pyridinium salt).

The polymerizations were carried out under vacuum in sealed tubes and terminated at variable times by introduction of cooled mixtures of methanol and methylene chloride. The polymers were precipitated in methanol, and the yields were calculated from the weight of recovered polyindene. The molar masses were measured by size exclusion chromatography in tetrahydrofuran with a set of 10^5, 10^4, 10^3, 500, and 100 Å microstyragel columns, using a polystyrene calibration, which has been found to be valid for polyindenes.[1] MALDI TOF measurements of low molar mass samples using a Perceptive Biosystem Voyager Elite apparatus (Framingham, MA) with a nitrogen laser (λ = 337 nm) showed excellent agreement with the values derived from size exclusion chromatography (e.g., for experiment 1 of Table 1: $M_{n\ SEC}$ = 2700; $M_{n\ MALDI}$ = 2750). However, the spectra showed the presence of an unsaturation as the main end group (with a minor amount of hydroxide groups). This was assumed to result from dehydrochlorination of the chlorinated end groups during measurement.

Results

The semilogarithmic plots for the consumption of indene ($\ln([M]_0/[M]_t)$ versus reaction time) for polymerizations carried out at 10^{-3}, 2 × 10^{-3}, and 4 × 10^{-3} mol L^{-1} $SnCl_4$ concentrations ($[\text{indene}]_0$ = 0.21 mol L^{-1}; $[\text{CumCl}]_0$ = 10^{-3} mol L^{-1}) at −15 °C are reported in Figure 1. The plot $\ln(k_1)$ versus $\ln([SnCl_4]_0)$ is a straight line with a slope equal to 1.22 (Figure 2). Although the range of $SnCl_4$ concentrations investigated is rather narrow, the polymerization being too fast to allow measurement at higher $SnCl_4$ concentrations, the results are in approximate agreement with a first order in $SnCl_4$. This suggests that in the present case there is only one type of equilibrium and that the counterion present is $SnCl_5^-$.

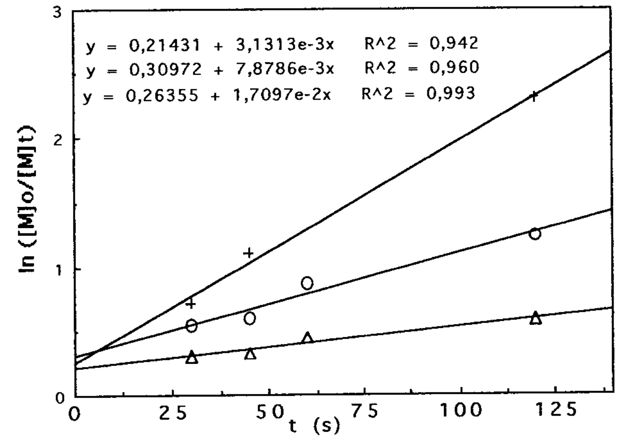


Figure 1. Polymerization of indene initiated with $SnCl_4$/CumCl; semilogarithmic plots for indene consumption: [indene] = 0.21 mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −15 °C; solvent = CH_2Cl_2; [$SnCl_4$]: (△) 10^{-3} mol L^{-1}; (○) 2 × 10^{-3} mol L^{-1}; (+) 4 × 10^{-3} mol L^{-1}.

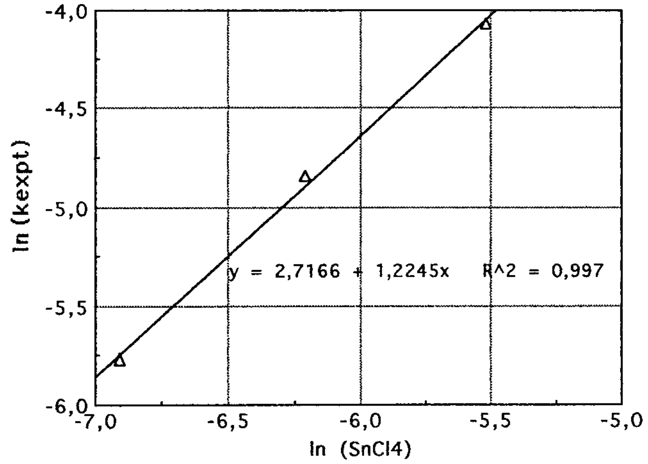


Figure 2. Reaction order with respect to $SnCl_4$: [indene] = 0.21 mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −15 °C; solvent = CH_2Cl_2.

However, it can be seen in Figure 1 that the extrapolations of the plots at zero time have positive intercepts, which suggests that a fast polymerization takes place at the beginning of the reaction, before a stationary state of the concentration of active species is achieved. Such a phenomenon has recently been reported in the case of the polymerization of isobutylene.[18] In all cases the molar masses are in good agreement with the calculated values for a living process ($DP_{n,calc} = [M]_0 \times \text{yield}/[I]_0$) (Figure 3), the slight deviation at high yields resulting from transfer. The plot of $1/DP_n$ versus $[I]_0/([M]_0 \times \text{yield} = 1/DP_0)$ is a straight line (Figure 4), the intercept of which gives the value of the transfer constant to the monomer ($C_M = 1.9 \times 10^{-3}$), in rather good agreement with that previously reported for higher concentrations of reagents ($C_M = 10^{-3}$).[4]

To investigate the influence of hindered bases, a first series of experiments have been carried out at −15 °C in CH_2Cl_2 solution in the presence of DBMP ([DBMP] = 2 × 10^{-4} mol L^{-1}; [indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}) (Table 1) and have been compared with a polymerization carried out in the absence of base (Table 2).

In the presence of base, the polymerization is slow (57% yield in 900 s, Table 1). The semilogarithmic plot for the consumption of indene is not linear (Figure 5),

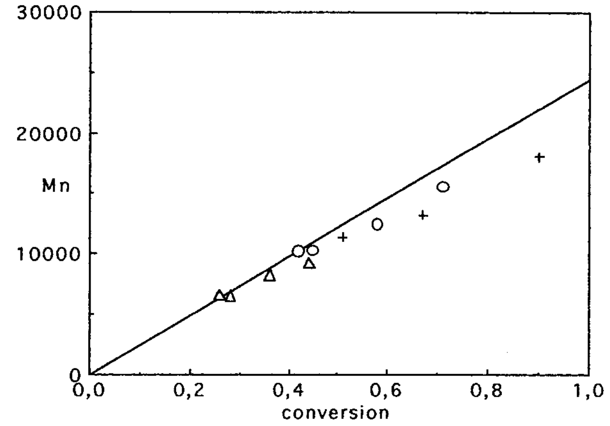


Figure 3. Polymerization of indene initiated with $SnCl_4$/CumCl; evolution of the molar masses with monomer conversion: [indene] = 0.21 mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −15 °C; solvent = CH_2Cl_2; [$SnCl_4$]: (△) 10^{-3} mol L^{-1}; (○) 2 × 10^{-3} mol L^{-1}; (+) 4 × 10^{-3} mol L^{-1}.

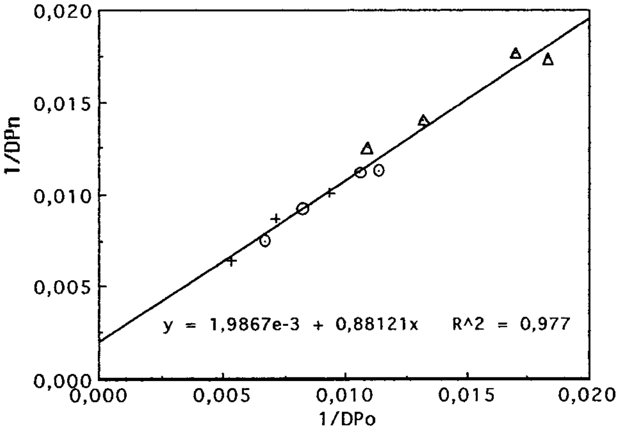


Figure 4. Polymerization of indene initiated with $SnCl_4$/CumCl; transfer constant to the monomer: [indene] = 0.21 mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −15 °C; solvent = CH_2Cl_2; [$SnCl_4$]: (△) 10^{-3} mol L^{-1}; (○) 2 × 10^{-3} mol L^{-1}; (+) 4 × 10^{-3} mol L^{-1}.

Table 2. Kinetics of the Polymerization of Indene at −15 °C[a]

expt no.	reaction time (s)	conv	M_n(expt)	M_n(calc)	I_p
1	30	0.42	10 300	10 200	1.55
2	45	0.45	10 400	11 000	1.51
3	60	0.58	12 600	14 200	1.52
4	120	0.71	15 600	17 100	1.47

[a] [Indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; [DBMP] = 0; solvent: CH_2Cl_2.

which should result from termination reactions. However, it is approximately linear during the first 120 s of reaction, and extrapolation at zero time is practically nil (Figure 6). Assuming that in this time span the incidence of termination is negligible, the value of the first-order rate constant is 1.8 × 10^{-3} s^{-1}. The molar masses are well controlled up to 60% yield but are slightly lower than the theoretical value at 60% yield (Figure 7). The polydispersity regularly increases with conversion from 1.26 at 8% yield to 1.69 at 57% yield (Table 1), which shows the occurrence of transfer reactions at −15 °C.

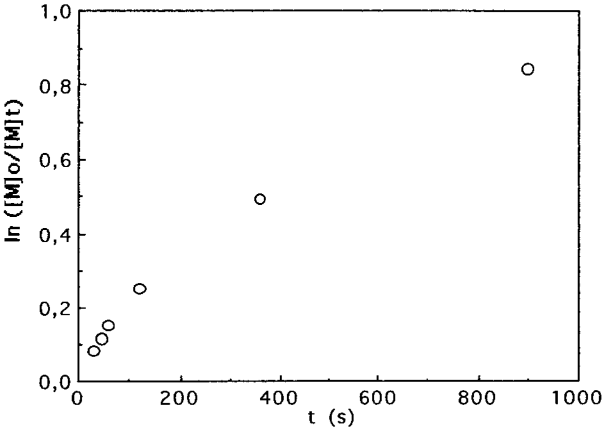


Figure 5. Polymerization of indene initiated with $SnCl_4$/CumCl; influence of 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) on the kinetics. Semilogarithmic plot for monomer conversion: [indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; [DBMP] = 2 × 10^{-4} mol L^{-1}; temperature = −15 °C; solvent = CH_2Cl_2.

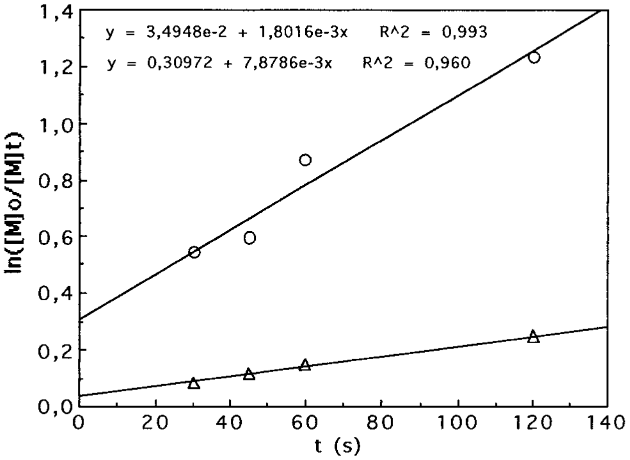


Figure 6. Polymerization of indene initiated with $SnCl_4$/CumCl with and without 2,6-di-*tert*-butyl-4-methylpyridine (DBMP). Partial semilogarithmic plots for monomer conversion: [indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −15 °C; solvent = CH_2Cl_2; (△) [DBMP] = 2 × 10^{-4} mol L^{-1} ; (○) [DBMP] = 0.

In the absence of base, the polymerization is faster (71% yield in 120 s; Table 2). The value of the first-order rate constant derived from the semilogarithmic plot for monomer consumption is 7.8 × 10^{-3} s^{-1} (Figure 6), a 4-fold increase with respect to that observed in the absence of base. Extrapolation of this plot at zero time gives an intercept (intercept = 0.26, which corresponds to 22% yield). This indicates that a fast polymerization has taken place before a stationary state of the concentration of active centers is established. The molar masses are satisfactorily controlled up to about 70% conversion (Figure 7). The polydispersity remains practically constant with a slight decreasing trend (1.55 at 30% yield, 1.47 at 71% yield; Table 2), which implies that first-order transfer (to the monomer) is negligible under these conditions.

Another series of experiments has been carried out at −40 °C in the same conditions with and without base (Tables 3 and 4). In the presence of base the semilogarithmic plot is linear for a longer time than at −15 °C (900 s; Figure 8), a slight deviation being observed at 1800 s (not reported in Figure 8; see Table 3), but there is the same 4-fold difference between the first-order rate constants for monomer consumption with and without base (1.4 × 10^{-3} vs 5.9 × 10^{-3} s^{-1}). In the absence of

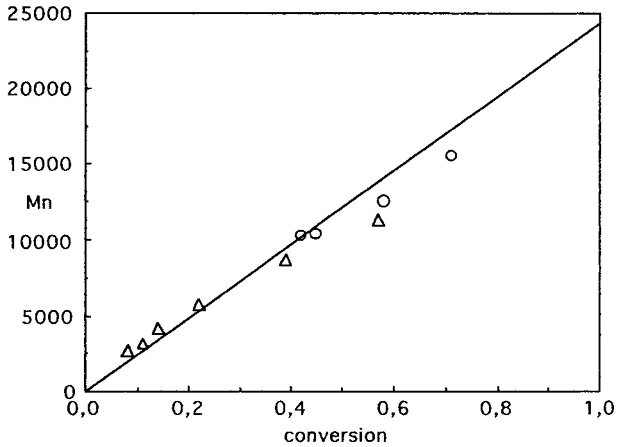


Figure 7. Polymerization of indene initiated with $SnCl_4$/CumCl; influence of 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) on the kinetics. Dependence of molar mass on monomer conversion. [indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −15 °C; solvent = CH_2Cl_2; (△) [DBMP] = 2 × 10^{-4} mol L^{-1}; (○) [DBMP] = 0.

Table 3. Kinetics of the Polymerization of Indene in the Presence of DtBMP at −40 °C[a]

expt no.	reaction time (s)	conv	M_n(expt)	M_n(calc)	I_p
1	30	0.10	3900	2440	1.26
2	45	0.13	3200	3170	1.28
3	60	0.19	5000	4640	1.34
4	120	0.23	6200	5610	1.40
5	120	0.25	6400	6100	1.33
6	360	0.46	11300	11200	1.40
7	900	0.75	17700	18300	1.57
8	1800	0.85	15400	21000	1.58

[a] [Indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; [DBMP] = 2 × 10^{-4} mol L^{-1}; solvent = CH_2Cl_2.

Table 4. Kinetics of the Polymerization of Indene at −40 °C[a]

expt no.	reaction time (s)	conv	M_n(expt)	M_n(calc)	I_p
1	30	0.48	10 300	11 700	1.86
2	45	0.55	11 500	13 400	1.86
3	60	0.56	13 700	13 700	1.68
4	120	0.70	14 800	17 100	1.49

[a] [Indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; solvent = CH_2Cl_2; [DBMP] = 0.

base, the intercept of the semilogarithmic plot is higher than at −15 °C (intercept = 0.5, corresponding to 40% yield). The molar masses are in good agreement with the calculated values for a controlled process in both cases (Figure 9), and the evolution of the polydispersities is similar to that at −15 °C. In the presence of base, I_p continuously increases from 1.26 to 1.58 at 85% yield (Table 3) while in the absence of base it decreases from 1.86 to 1.49 at 70% yield (Table 4). The control of the molar masses together with the decrease of I_p with conversion shows that at −40 °C in the absence of base the polymerization is controlled.

The incidence of increasing concentrations of base is shown in Table 5. The yield in 15 min decreases when the concentration of base is increased, but even for a concentration higher than that of initiator (1.2 × 10^{-3} mol L^{-1}) the polymerization still takes place and goes on for at least 45 min (expt 4 of Table 5). However, conversion hardly increases between 15 and 45 min, and the polymerization may stop before complete conversion at this concentration.

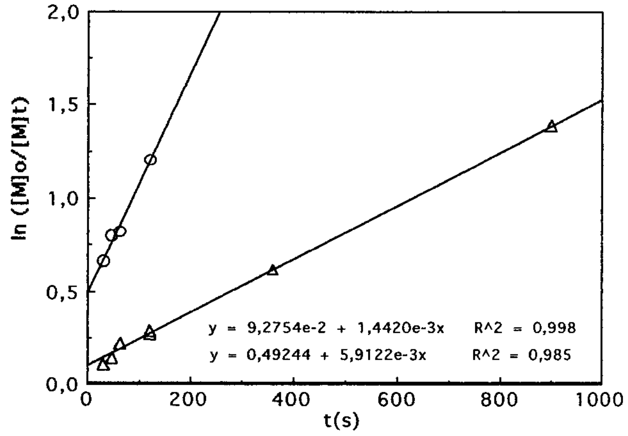


Figure 8. Polymerization of indene initiated with $SnCl_4$/CumCl; influence of 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) on the kinetics. Partial semilogarithmic plots for monomer conversion. [indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −40 °C; solvent = CH_2Cl_2; (△) [DBMP] = 2 × 10^{-4} mol L^{-1}; (○) [DBMP] = 0.

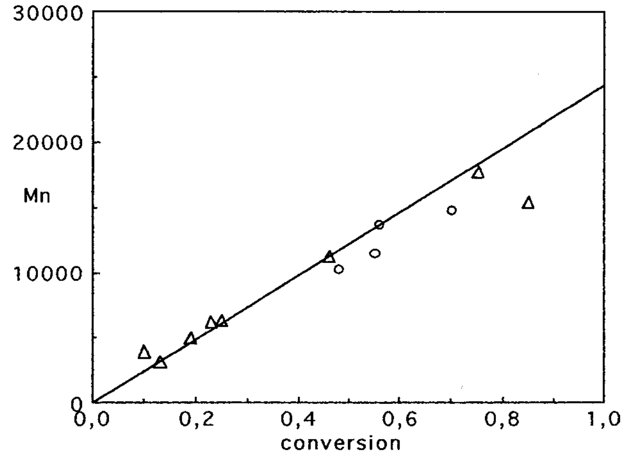


Figure 9. Polymerization of indene initiated with $SnCl_4$/CumCl; influence of 2,6-di-*tert*-butyl-4-methylpyridine (DBMP) on the kinetics. Dependence of molar mass on monomer conversion. [indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −40 °C; solvent = CH_2Cl_2; (△) [DBMP] = 2 × 10^{-4} mol L^{-1}; (○) [DBMP] = 0.

Table 5. Influence of 2,6-Di-*tert*-butyl-4-methylpyridine on the Polymerization of Indene[a]

expt no.	[DBMP] × 10^3 (mol L^{-1})	reaction time (min)	conv	M_n (expt)	M_n (calc)	I_p
1	0.20	15	0.57	12 400	14 000	1.71
2	0.44	15	0.50	10 600	12 000	1.66
3	1.20	15	0.40	10 000	9 700	1.69
4	1.20	45	0.45	12600	14 000	1.61

[a] [Indene] = 0.21 mol L^{-1}; [$SnCl_4$] = 2 × 10^{-3} mol L^{-1}; [CumCl] = 10^{-3} mol L^{-1}; temperature = −15 °C; solvent = CH_2Cl_2.

Discussion

$SnCl_4$ may yield $SnCl_6^{2-}$ anions when the $SnCl_4$/initiator ratio is lower than 0.5,[19] which is not the case here, or in the presence of salts,[20] but there is no mention of a complex $Sn_2Cl_9^-$ counterion in the literature. This allows to discard the possibility of complex counterions such as those formed with $TiCl_4$. The first order in $SnCl_4$ implies the existence of simple equilibria for ionization and dissociation:

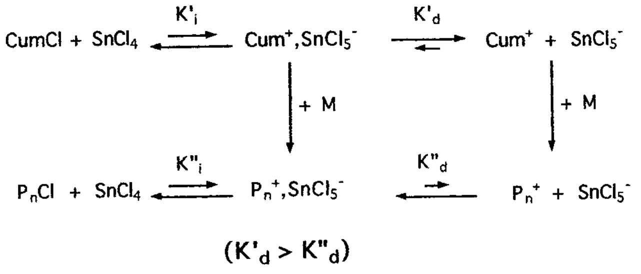
$$\mathrm{CumCl} + \mathrm{SnCl_4} \overset{K_i}{\rightleftharpoons} \mathrm{Cum^+,SnCl_5^-} \overset{K_d}{\rightleftharpoons} \mathrm{Cum^+} + \mathrm{SnCl_5^-}$$

The two main observations are the fast initial polymerization in the absence of base and the steep decrease of the first-order rate constant in the presence of base.

The fast initial polymerization in the absence of base might have been explained by protic initiation by adventitious initiator (water or HCl). However, given the experimental conditions (reactions under vacuum), significant fast initiation by adventitious water is unlikely, since water is not an efficient initiator with $SnCl_4$.[21] The most probable initiator would be HCl present in the $SnCl_4$ solutions. In fact, the presence of up to 7% HCl has been found in some $SnCl_4$ solutions by NMR titration in the presence of base. This means that the concentration of adventitious HCl is at most 1.4×10^{-4} mol L^{-1} and hence that the "global" initiator concentration is 1.14×10^{-3} mol L^{-1}. It has been shown[21] that the first-order rate constant for the polymerization of indene initiated with $SnCl_4$/HCl at -30 °C ($[SnCl_4] = 10^{-2}$ mol L^{-1}) is 3.3×10^{-4} s^{-1} for $[HCl] = 6 \times 10^{-5}$ mol L^{-1} and 1.8×10^{-3} s^{-1} for $[HCl] = 4 \times 10^{-4}$ mol L^{-1}. A reasonable value for $[HCl] = 1.4 \times 10^{-4}$ mol L^{-1} HCl would be 1 or 2×10^{-4} s^{-1}. Hence, fast adventitious initiation by 1.4×10^{-4} mol L^{-1} HCl cannot account for the fast initial polymerization in the absence of base for which the first-order rate constant is higher than 5×10^{-3} L mol^{-1} s^{-1} in all cases.

The occurrence of a fast initial polymerization of isobutylene initiated with dicumyl chloride/$TiCl_4$ (in the presence of base, i.e., of ion pairs) has been explained by the larger ionization constant K_i of cumyl chloride compared to that of the chlorinated polyisobutylene,[18] which would create a larger concentration of ion pairs during the initiation period before a steady state of active centers concentration is established. A similar explanation might be considered in the present case. However, recent data on ionization of CumCl and 1-chloroindane by $TiCl_4$ have shown that the K_i's are similar at -65 °C and even somewhat larger for 1-chloroindane.[22,23] The (much lower) K_i's for ionization by $SnCl_4$ should follow the same trend. Besides, this fast initiation is suppressed in the presence of base, which suggests that free ions and not ion pairs are involved in the process.

This implies that at the beginning of the reaction a larger amount of free ions is formed than that present during the stationary state. A possible explanation may be that the cumyl ion pairs have a larger dissociation constant than the polyindanyl ones, due to the greater bulkiness of the cumyl cation compared to the indanyl one. During the initiation period, which stretches at most over a few seconds, the cumyl chloride is practically converted into cumyl free ions which cause fast polymerization before an equilibrium between free ions, ion pairs, and dormant species of the polyindene chains may be established with a lower value of the global concentration of active species, leading to a linear first-order plot:



This initial formation of a large P_n^+ concentration may result from a much larger K_d for $Cum^+,SnCl_5^-$ ion pairs than for $Pn^+,SnCl_5^-$ ion pairs, the former corresponding to a trisubstituted carbenium ion. The data of the literature are the following:

$$Ph_3C^+, SbCl_6^-: \quad K_d = 3.6 \times 10^{-4} \text{ (at } -40\ °C)^{24}$$

$$Ph_3C^+, SnCl_5^-: \quad K_d = 3.6 \times 10^{-4} \text{ (at } -40\ °C)^{25}$$

$$[CH_3OPh)_2CH^+,BCl_4^-: \quad K_d = 2.2 \times 10^{-4} \text{ (at } -40\ °C)^{26}$$

$$(CH_3Ph)_2CH^+,BCl_4^-: \quad K_d = 1.9 \times 10^{-4} \text{ (at } -70\ °C)^{26}$$

This makes quite possible a K_d for $Cum^+,SnCl_5^-$ of about $5 \times 10^{-5}-10^{-4}$ mol L^{-1} at -40 °C.

On the other hand, the results obtained allow to estimate the kinetic constants for the stationary state polymerization. At -40 °C, the first-order rate constants with and without base are respectively equal to 1.44×10^{-3} and 5.91×10^{-3} s^{-1}. Assuming complete suppression of free ions by the base, the former rate constant is related to ion pairs. A preliminary estimation of the ionization equilibrium constant K_i yielded a value in the lower part of the 10^{-2} L mol^{-1} range. Taking 10^{-2} L mol^{-1} as a tentative value for K_i:

$$[P_n^+, SnCl_5^-] = K_i[P_nCl]\,[SnCl_4] = 2 \times 10^{-8} \text{ mol L}^{-1}$$

and

$$k_p^{\pm} = 1.44 \times 10^{-3}/2 \times 10^{-8} = 7.2 \times 10^4 \text{ L mol}^{-1}\text{ s}^{-1}$$

Assuming equal reactivity for free ions and ion pairs ($k_p^+ = k_p^{\pm}$):

$$([P_n^+] + [P_n^+,SnCl_5^-])/[P_n^+,SnCl_5^-] = 5.91 \times 10^{-3}/1.44 \times 10^{-3} \approx 4$$

$$[P_n^+] = 3[P_n^+,SnCl_5^-] \approx 6 \times 10^{-8} \text{ mol L}^{-1}$$

which allows an estimation of the dissociation constant K_d:

$$[P_n^+]^2 = K_iK_d[P_nCl][SnCl_4] \rightarrow K_d \approx 1.8 \times 10^{-7} \text{ mol L}^{-1}$$

Then K_d for the growing chains should lie in the 10^{-7} range. This value of K_d is much lower than those reported above for the trityl and benhydryl ion pairs which should be of the same order of magnitude as that for the dissociation of the $Cum^+,SnCl_5^-$ ion pair. It may seem surprisingly low even if the indanyl carbocation is only disubstituted and less hindered than the diphenyl ones, but it should be noted that higher K_d (e.g., 10^{-6} and 10^{-5} mol L^{-1}) would yield values of k_p^+ respectively equal to 2.9×10^4 and 1.3×10^4, lower than the propagation rate constant derived for the ion pairs, which is unlikely.

For a polymerization at -40 °C stopped after 30 s, the experimental molar mass ($M_{n\ expt} = 10\ 300$) is near the calculated value ($M_{nth} = 11\ 700$), which shows that initiation (CumCl consumption) is approximately quantitative. Extrapolation of the semilogarithmic plot to zero time yields an intercept equal to 0.5, corresponding to 40% conversion. The time necessary to reach this conversion is not known and is probably shorter than 30 s. But

$$\ln([\mathrm{M}]_0/[\mathrm{M}]_t) = k_\mathrm{p}^{+}[\mathrm{P}_\mathrm{n}^{+}]t = 0.5$$

Assuming a propagation rate constant equal to about 7×10^4 L mol^{-1} s^{-1}, the average concentration of (predominant) free ions is $[\mathrm{P}_\mathrm{n}^{+}] \approx 7 \times 10^{-6}$ mol L^{-1} if it is reached in 1 s and 7×10^{-7} mol L^{-1} if it is reached in 10 s. These values are larger than that of $[\mathrm{P}_\mathrm{n}^{+}]$ previously calculated when the equilibrium is established. The larger concentration of initiating free cumyl cations compared to that of the polyindenyl ones would explain the burst of polymerization at the beginning of the reaction.

What is left to account for is the 4-fold decrease of the first-order rate constant in the presence of base.

Although the presence of up to 7% HCl has been found in some $SnCl_4$ solutions, it has been shown that the presence of this amount of HCl as extra initiator cannot account for the 4-fold increase of the first-order rate constant of the polymerization in the absence of base. Furthermore, if HCl contributed to initiation, this would lead to a corresponding increase of the number of macromolecules, but the control of the molar masses with and without base shows that the same number of chains is formed during the polymerizations. This confirms that initiation by HCl is slow compared to that by CumCl and incomplete during the timespan of the reaction. Consequently, the hypothesis of a extra protic initiation by adventitious HCl can be ruled out.

The possibility of a larger ionization constant for CumCl than for the chlorinated polyindene chains has previously been discarded. Thus, the most probable explanation is that, in the presence of base and of HCl, pyridinium pentachlorostannate is formed which immediately shifts the equilibrium toward the ion pairs and dormant species. The concentration of active centers would be lower than in the absence of base, due to the suppression of free ions. This accounts for the decrease of the first-order rate constant in the presence of base.

Furthermore, the DBMP also acts as a terminating agent by turning zero-order transfer into termination (terminative chain transfer). The curvature of the semilogarithmic plot in Figure 1 shows that termination reactions take place in the presence of base. This is also in agreement with the increase of I_p with yield in the presence of DBMP (Table 3). It has been found in a previous paper[4] that a zero-order transfer occurs in media of low dielectric constant, i.e., in media which favors the existence of ion pairs. The increase of I_p with conversion in the presence of DBMP and the better control of the M_n in the absence of base can be accounted for assuming the existence of a zero-order transfer involving the ion pairs which would lead to termination. In the presence of base, i.e., in the exclusive presence of ion pairs, the longer reaction times would allow this transfer to take place to a significant extent, while in the absence of base it could not be detectable either because of the shorter timespan of the polymerization or because zero-order transfer involves preferentially ion pairs.

Although this has not been proved up to now, the hindered base might also participate in a bimolecular proton abstraction from the growing chain. Bimolecular termination by DBMP has been considered by Storey et al.[14] in the case of the polymerization of isobutylene initiated with $CumCl/TiCl_4$. The kinetics of a zero-order transfer should be independent of the concentration of the base if the rate-determining step is the proton transfer to the counterion. On the other hand, the rate of bimolecular proton abstraction should depend on the concentration of base. In the present case, the yield in 15 min decreases from 57% to 40% when the concentration of base increases from 2×10^{-4} to 1.2×10^{-3} mol L^{-1} (Table 5). This suggests that bimolecular termination cannot be ruled out especially in the presence of high concentrations of base.

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