Influence of Monomer Concentration and Dielectric Constant on Transfer Reactions in the Carbocationic Polymerization of Indene

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Received August 4, 1999; Revised Manuscript Received November 24, 1999

ABSTRACT: The cationic polymerization of indene initiated with cumyl chloride and stannic chloride in solution in methylene chloride at −15 °C is controlled up to $M_n = 20\,000$, with a low transfer to monomer constant ($k_{trM}/k_p = 9 \times 10^{-4}$). Experiments carried out in compensated media allowed kinetic measurements and showed that the sharp decrease of the M_n at high indene concentrations results from zero order transfer due to the change of dielectric constant ($k_{tr}/k_p = 1.5 \times 10^{-3}$ for a dielectric constant of 5.4). In methylene chloride, for indene concentrations higher than 2 mol·L^{-1}, the heat release of the fast reaction adds up to the zero order transfer to lower the molar masses. Bimodal distributions result from propagation on free ions and ion pairs.

Introduction

The control of cationic polymerizations has been achieved in the last 20 years for a variety of systems, the pioneering work being done by Higashimura[1] and Kennedy.[2] Several reviews have been published on this topic,[3−5] and the possibilities and limitations of these systems have been discussed.[6−8] The control generally realized is that of the M_n which corresponds to the theoretical DP$_n$ (DP$_n = \Delta\,[M]_0/[I]_0$) and grows linearly with monomer conversion up to values which may vary with the initiating system and with temperature (e. g. M_n linear ($M_{n\ lin}$) up to 2×10^4). Most experiments were made with all the monomer added at the beginning (all monomer in, AMI), others with incremental monomer additions (IMA). In this last case, this shows the near absence of chain-breaking reactions (transfer and termination) in this range of M_n, and during the synthesis time, the system may be considered to be living.

Control of the M_n results from quantitative and preferably fast reaction of an initiator (e.g., an alkyl halide) with a Lewis acid activator and from absent or negligible irreversible termination. Termination is reversible and involves the establishment of an equilibrium between active and dormant end groups. In these reactions, transfer is not suppressed, which limits the range of molar masses for which the process is controlled.[8,9]

Among the various Lewis acids used as activators, titanium tetrachloride is one of the most frequently employed, particularly for the polymerization of isobutylene and arylalkenyl monomers. In the case of the polymerization of indene, Kennedy observed partial initiation of the polymerization with this Lewis acid and 2-chloro-2,4,4-trimethylpentane[10] ($M_n > M_{n\ theor}$). Controlled polymerization of indene was obtained for M_n up to 100 000 with methyl cumyl ether as initiator at low temperature.[11] With cumyl chloride (CumCl), satisfactory control was obtained at −40 °C in the presence of additives.[12] However, the polymerizations were very fast, completed in a few seconds even in the presence of very low concentrations of initiating species, which did not allow us to monitor the evolution of the molar masses during the reaction.[13] Besides, the slow exchange between active and dormant forms was the cause of the rather broad molecular weight distributions (MWD) observed ($M_w/M_n = 2$).

Consequently, it seemed interesting to check whether other initiating systems would yield lower polymerization rates which would permit to follow the variation of the M_n with conversion and eventually to lower the M_w/M_n. Stannic chloride, which has a long history as a an initiator/co-initiator for a large number of cationic polymerizations, has recently been used for the controlled polymerization of styrene. Controlled polymerization of styrene (with $M_{n\ lin}$ up to 10 000) has been achieved at −15 °C in methylene chloride solution, with phenylethyl chloride as initiator.[14] Addition of tetra-*n*-butylammonium chloride was necessary to avoid bimodal distributions, which were attributed either to the participation of free ions or to competitive initiation by residual water, which was assumed to yield high molar masses. The role of the salt has been investigated.[15] Less satisfactory results were obtained with methanesulfonic acid as an initiator,[16] but control was achieved ($M_{n\ lin}$ up to $M_n = 10.000$), in the absence of salt, by operating in a solvent of lower dielectric constant ($CHCl_3$; $\epsilon = 4.8$).[17,18] The molecular weight distribution was bimodal in pure CH_2Cl_2 and became narrower as the proportion of CH_2Cl_2 in a CH_2Cl_2/ $CHCl_3$ mixture was decreased. The same observation was made with 4-methylstyrene.[19] It should be noted that in all cases, the range of molar masses was lower than 10 000 ($[M]_0/[C]_0 = 100$) and that, under these conditions, a transfer constant to the monomer equal to 10^{-3} would yield a value of the molar mass less than 10% lower than the theoretical value. On the other hand, the polymerization rates were rather low, and it could be expected that indene would also yield controlled polymerizations with lower reaction rates with the CumCl/$SnCl_4$ initiating system.

Experimental Section

The reagents were purified under vacuum on sodium films according to procedures previously reported,[20] and stored in a vacuum line fitted with “Rotaflo” stopcocks. 2,6-Di-*tert*-butyl-4-methylpyridine (DBMP) was sublimed under vacuum before use. The polymerizations were carried out in sealed tubes and terminated by introduction of cooled mixtures of methanol and methylene dichloride. A few experiments were made in a

10.1021/ma9913010 CCC: $19.00

Table 1. Initiation of the Polymerization of Indene by Various Initiators at −15 °C[a]

initiator	T (°C)	M_n	M_w/M_n
CumOMe	−70	45 400	1.90
CumOMe	−40	26 400	2.39
CumOMe	−15	20 900	2.41
CumCl	−70	21 000	1.70
CumCl	−40	20 500	1.65
CumCl	−15	20 800	1.54
1-chloro-1-phenylethane	−15	23 400	2.18

[a] [indene] = 0.43 M; [initiator] = 2.5×10^{-3} mol·L^{-1}; [SnCl$_4$] = 2×10^{-2} mol·L^{-1}. Reaction time: 6 min (complete conversion; calculated M_n = 20 000).

drybox and yielded similar results. The polyindenes were recovered by precipitation in methanol and dried overnight under vacuum. The conversions were determined from the weight of polymer. The molar masses were measured by size exclusion chromatography, with a set of 10^5, 10^4, 10^3, 500, and 100 Å Waters microstyragel columns using a polystyrene calibration. Comparative measurements by osmotic pressure and matrix assisted laser diffusion spectrometry (in the low molar mass range) confirmed the validity of the values derived from SEC.

Results and Discussion

Quantitative initiation is the first prerequisite for the control of a polymerization. Cumyl derivatives have been used as initiators for a large number of systems, in particular cumyl chloride and cumylmethyl ether which proved efficient in the case of the controlled polymerization of indene with TiCl$_4$ and TiCl$_3$OBu.[11−13] To check the efficiency of these compounds, a series of polymerizations have been carried out with these two initiators (2.5×10^{-3} M) in the presence of SnCl$_4$ (2×10^{-2} M) at variable temperature. In all cases, the reactions were fast and complete conversion was reached after 30 s. CumOMe is not an efficient initiator with SnCl$_4$ at −70 °C; the molar mass of the polymer is about twice the calculated value for a controlled process (Table 1). The molar mass decreases when the temperature is increased and corresponds to the expected value at −15 °C, which is in agreement with a quantitative initiation at this temperature. With cumyl chloride, the molar masses have the expected value over the whole range of temperature, which shows that initiator efficiency is 100% even at −70 °C, contrary to the case of ionization by TiCl$_4$, and that initiation is fast enough compared to propagation. This initiator has been used in the following experiments. 1-phenylethyl chloride, which has been used as an initiator for the polymerization of styrene, is also efficient at −15 °C for indene, but initiation is apparently slower ($M_{n\,\mathrm{exptl}}$ are slightly higher than $M_{n\,\mathrm{theor}}$).

(1) Polymerizations in Dichloromethane Solution. To check the range of $[M]_0/[I]_0$ ratios for which control is effective, a series of polymerizations has been carried out at variable initial indene concentrations ([SnCl$_4$] = 2×10^{-2} M; [CumCl] = 2.5×10^{-3} M) at −15 °C. Polymerizations were stopped after 6 min, but complete conversion was reached already after 30 s. Consequently, the only mass measurements which could be done were on polyindenes resulting from polymerizations at complete conversion. The results are reported in Figure 1 and Table 2. A linear increase of the molar masses, corresponding to the expected values, is observed for indene concentrations lower than 0.5 M ($[M]_0/[I]_0$ = 200). In the case of the polymerization of styrene, the domain of control is restricted to monomer-to-initiator ratios lower than 100.[17] In the present case, control is still effective for a molar ratio of about 200. In this range of concentrations, a plot of 1/DP$_n$ vs 1/DP$_o$ (DP$_n$ and DP$_o$: experimental and theoretical degrees of polymerization) yields a straight line with an intercept of 9×10^{-4} (Figure 2), which is the value of the transfer constant ($C_M = k_{trM}/k_p$) to indene under these conditions.

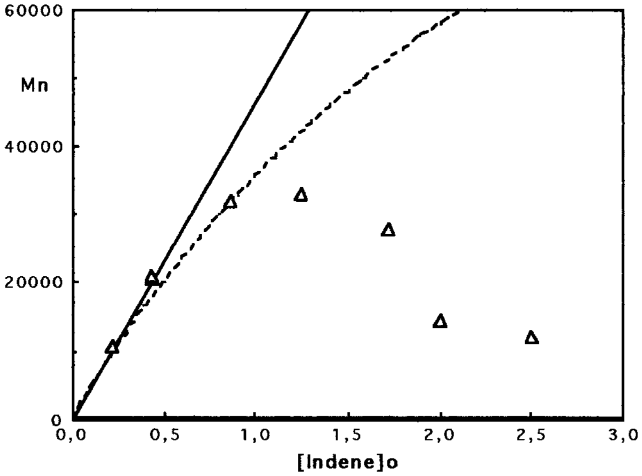

Figure 1. Polymerization of indene initiated with CumCl/SnCl$_4$. Evolution of the molar masses with the initial indene concentration. Reaction time: 6 min, complete conversion. [CumCl] = 2.5×10^{-3} mol·L^{-1}; [SnCl$_4$] = 2×10^{-2} mol·L^{-1}; solvent, CH$_2$Cl$_2$. T: −15 °C. Key (−) controlled process; (- -) calculated values for $C_M = 9 \times 10^{-4}$; (Δ) experimental points.

Table 2. Polymerization of Indene Initiated with Cumyl Chloride at −15 °C, Showing the Influence of the Monomer Concentration on the Molar Masses[a]

expt no.	[indene]$_o$ (mol·L^{-1})	$M_{n\,\mathrm{exptl}}$	$M_{n\,\mathrm{calcd}}$	M_w/M_n
1	0.215	10 500	10 000	1.52
2	0.43	20 800	19 900	1.54
3	0.43	21 000	19 900	1.74
4	0.86	31 900	39 900	1.74
5	1.25	33 000	58 100	2.24
6	1.72	27 900	79 900	2.02
7	2.0	14 500	92 900	3.46
8	2.5	12 100	116 100	2.96

[a] [CumCl] = 2.5×10^{-3} mol·L^{-1}; [SnCl$_4$] = 2×10^{-2} mol·L^{-1}; solvent = CH$_2$Cl$_2$. Reaction time: 6 min (complete conversion).

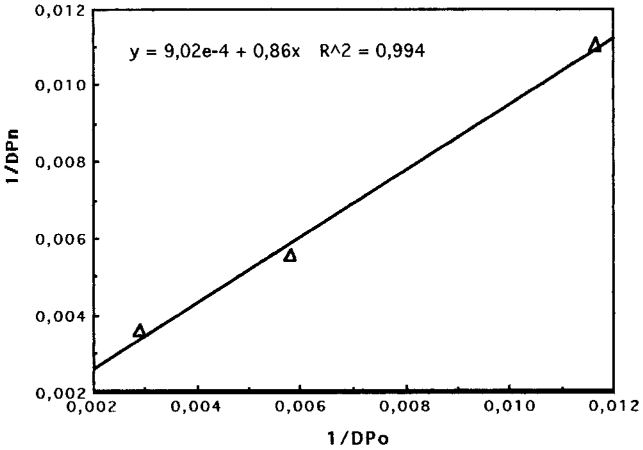

Figure 2. Polymerization of indene initiated with CumCl/SnCl$_4$. [CumCl] = 2.5×10^{-3} mol·L^{-1}; [SnCl$_4$] = 2×10^{-2} mol·L^{-1}; solvent, CH$_2$Cl$_2$. T: −15 °C. Transfer constant to indene.

Between 0.43 and 0.86 M, the experimental masses are in agreement with those calculated taking this

Table 3. Polymerization of Indene at a Fixed Dielectric Constant (Indene + Methylcyclohexane, 30% v/v; CH_2Cl_2, 70% v/v; $\epsilon = 7.2$), Showing the Evolution of the Molar Mass with the Initial Monomer Concentration[a]

expt no.	[indene] ($mol\cdot L^{-1}$)	$M_{n\ exptl}$	$M_{n\ calcd}$	M_w/M_n
1	0.21	9 400	9 750	2.23
2	0.43	10 000	20 000	2.24
3	0.85	14 000	39 500	2.11
4	1.50	16 300	69 700	2.16
5	2.20	19 100	102 200	2.47

[a] $[SnCl_4] = 2.10 \times 10^{-2}$ $mol\cdot L^{-1}$; $[CumCl] = 2.5 \times 10^{-3}$ $mol\cdot L^{-1}$; $T = -15$ °C. Reaction time: 6 min (complete conversion).

transfer into account (Figure 1). However, for higher indene concentrations a decrease from $M_n = 33\ 000$ for 1.25 M indene down to $M_n = 12\ 000$ for 2.5 M indene is observed which cannot be accounted for by classic transfer to monomer alone, since if this transfer were preponderant, the molar masses should remain practically constant.

To investigate the existence of transfer, a polymerization has been carried out at high indene concentration under the same conditions as in experiment 8 of Table 2 ([indene] = 2.5 M; $[CumCl] = 2.5 \times 10^{-3}$ M; $[SnCl_4] = 2 \times 10^{-2}$ M), but in the presence of 2,6-di-*tert*-butyl-4-methylpyridine (4×10^{-3} M). The reaction stops at 11% yield; the molar mass of the polyindene ($M_n = 11\ 300$; $I_p = 2.05$) corresponds to a concentration of macromolecules of 2.6×10^{-3} M, equivalent within experimental error to the concentration of the initiator. This molar mass corresponds to that of experiment 8 of Table 2 (without hindered pyridine) which went to completion ($M_{n\ exptl} = 12\ 100$). This suggests that, in the former case, the polymerization had stopped, either by capture by the hindered pyridine of a proton resulting from transfer or by termination of the active centers by the pyridine. The similar values of the M_n in the two experiments suggests that the former explanation is the most probable. Assuming the transfer constant to monomer determined above (9×10^{-4}), the molar mass for $[indene]_0 = 2.5$ M should have been 61 000 at complete conversion. This implies that some other type of transfer takes place at high monomer concentration.

(2) Polymerizations in Media of Fixed Dielectric Constant. The main change at high indene concentration is the decrease of the dielectric constant of the medium as the proportion of indene ($\epsilon = 2$) with respect to CH_2Cl_2 ($\epsilon = 9$) increases. To check whether a similar evolution of the molar masses would be observed in media of constant polarity, experiments have been carried out at constant volumes of CH_2Cl_2 and of indene + methylcyclohexane (MeCH). In the case of the polymerization of styrene, a medium of lower dielectric constant ($CHCl_3$ instead of CH_2Cl_2) allowed control of the molar masses up to $M_n = 10\ 000$ without addition of salt.[19]

For a dielectric constant equal to 7.2 at 20 °C (30% v/v of indene + methylcyclohexane in CH_2Cl_2) the reaction is still rapid and the molar masses reported are from reactions carried out to completion. The molar masses increase with the initial indene concentration (Table 3), but are much lower than the calculated values for a controlled process (Figure 3) and than those obtained in pure CH_2Cl_2. However, there is no decrease of the M_n at high indene concentration (2.2 M), as was the case previously.

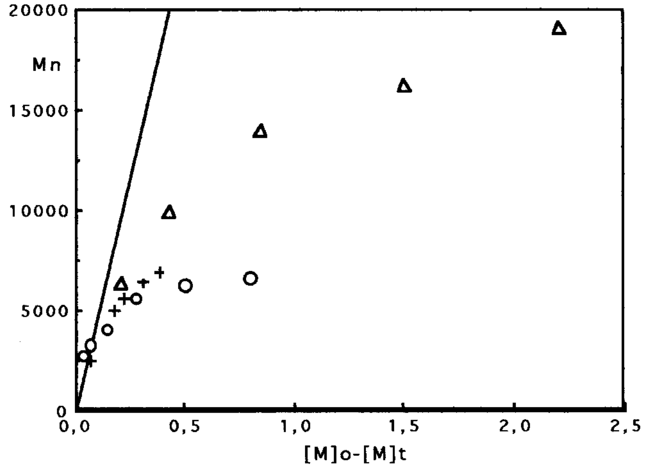

Figure 3. Polymerization of indene initiated with CumCl/$SnCl_4$ in compensated media. $[CumCl] = 2.5 \times 10^{-3}$ $mol\cdot L^{-1}$; $[SnCl_4] = 2 \times 10^{-2}$ $mol\cdot L^{-1}$. *T*: −15 °C. Key: (Δ) $\epsilon = 7.2$ (indene + MeCH, 30% v/v in CH_2Cl_2); variable initial indene concentration; reaction time, 6 min; complete conversion. (○) $\epsilon = 5.4$ (indene + MeCH: 50% v/v in CH_2Cl_2); [indene] = 0.43 M; variable conversion. (+) $\epsilon = 5.4$ (indene + MeCH: 50% v/v in CH_2Cl_2); variable initial indene concentration; reaction time, 6 min; conversion, 36%; (−) calculated M_n for a controlled process.

Table 4. Polymerization of Indene at a Fixed Dielectric Constant (Indene + Methylcyclohexane, 50% v/v; CH_2Cl_2, 50% v/v; $\epsilon = 5.4$), Showing the Evolution of the Molar Mass with Conversion[a]

expt no.	reacn time (min)	convn	global M_n	high M_n	low M_n	M_w/M_n high M_n	M_w/M_n low M_n	calcd M_n
1	2	0.15	2500	39 700	2100	1.55	1.24	3000
2	10	0.42	5000	20 500	5000	2.02	1.49	8400
3	15	0.52	5600	19 900	5900	1.96	1.56	10400
4	30	0.72	6400		6400		2.20	14400
5	55	0.89	6900		6900		2.28	18000

[a] $[indene]_0 = 0.43$ $mol\cdot L^{-1}$; $[SnCl_4] = 2.10^{-2}$ $mol\cdot L^{-1}$; $[CumCl] = 2.5\ 10^{-3}$ $mol\cdot L^{-1}$; $T = -15$ °C.

In a medium of lower dielectric constant (50% v/v of indene + methylcyclohexane in CH_2Cl_2; $\epsilon = 5.4$), the polymerization is slow enough to allow monitoring the evolution of the molar masses with conversion. The results of a polymerization ([indene] = 0.43 M; $[CumCl] = 2.5 \times 10^{-3}$ M; $[SnCl_4] = 2 \times 10^{-2}$ M) are reported in Table 4. The consumption of indene follows a first-order law (Figure 4). However, up to 52% yield, the molecular weight distribution (MWD) is bimodal, with a small peak of high M_n and a main peak of low M_n (Figure 5). The ratio of the two peaks, which can be measured up to 52% yield by integration of the SEC traces, remains constant (18% of high M_n polymer). For higher conversions, the bimodality is no longer visible, but the two peaks merge, as is shown by the broadening of the MWD (Table 4; Figure 5). The molar masses are much lower than those obtained in pure CH_2Cl_2 and in a medium of dielectric constant = 7.2.

A polymerization carried out under the same conditions ($[indene]_0 = 0.43$ M), but in the presence of 1.6×10^{-3} M 2,6-ditertbutyl-4-methylpyridine (yield, 9% in 2 min; $M_n = 2700$; $M_{n\ theor} = 1800$) yielded a polymer having a unimodal distribution with a narrow polydispersity ($M_w/M_n = 1.22$) with no visible trace of high molar mass polymer (Figure 5).

In the same medium ($\epsilon = 5.4$), for polymerizations at variable initial indene concentration, the yield in 6 min was 36% in all cases independently of $[M]_0$, which is in agreement with a first-order internal law for the

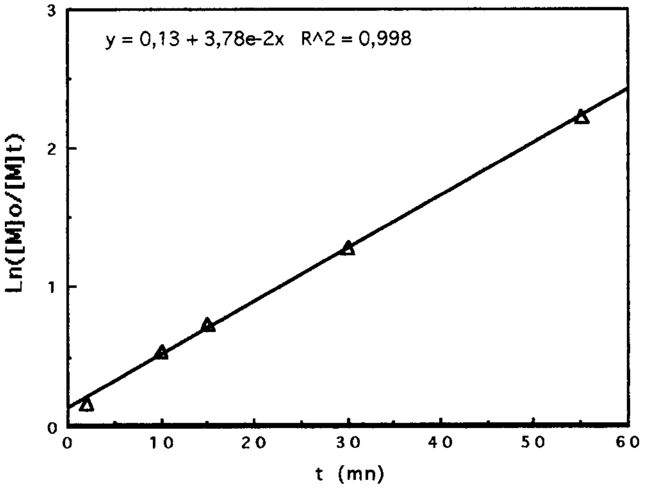

Figure 4. Polymerization of indene initiated with CumCl/$SnCl_4$ in a compensated medium ($\epsilon = 5.4$; indene + MeCH, 50% v/v in CH_2Cl_2). [indene] = 0.43 $\text{mol}\cdot\text{L}^{-1}$; [CumCl] = 2.5×10^{-3} $\text{mol}\cdot\text{L}^{-1}$; [$SnCl_4$] = 2×10^{-2} $\text{mol}\cdot\text{L}^{-1}$. *T*: −15 °C. First-order plot for the comsumption of indene.

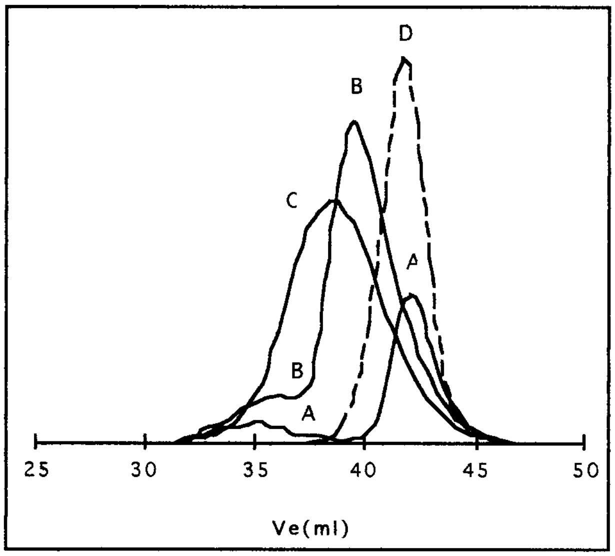

Figure 5. Polymerization of indene initiated with CumCl/$SnCl_4$ in a compensated medium ($\epsilon = 5.4$; indene + MeCH, 50% v/v in CH_2Cl_2). [indene] = 0.43 $\text{mol}\cdot\text{L}^{-1}$; [CumCl] = 2.5×10^{-3} $\text{mol}\cdot\text{L}^{-1}$; [$SnCl_4$] = 2×10^{-2} $\text{mol}\cdot\text{L}^{-1}$. *T*: −15 °C. Evolution of the SEC traces with conversion. Conversion: (A) 15%; (B) 42%; (C) 89%; (D) [2,6-di-*tert*- butyl-4-methylpyridine] = 1.6×10^{-3} $\text{mol}\cdot\text{L}^{-1}$, conversion 9%.

Table 5. Polymerization of Indene at a Fixed Dielectric Constant (Indene + methylcyclohexane, 50% v/v; CH_2Cl_2, 50% v/v; $\epsilon = 5.4$), Showing the Evolution of the Molar Mass with the Initial Monomer Concentration[a]

expt no.	[indene]$_0$ ($\text{mol}\cdot\text{L}^{-1}$)	convn	global M_n	M_n high mass	M_n low mass	M_w/M_n high mass	M_w/M_n low mass	calcd M_n
1	0.11	0.38	2700	16 300	1900	1.67	1.16	1900
2	0.21	0.36	3200	19 000	3300	1.58	1.21	3600
3	0.43	0.35	4000	29 100	3700	1.65	1.46	7000
4	0.85	0.33	5600		5600		2.43	12600
5	1.49	0.34	6200		6200		2.26	23100
6	2.00	0.40	6600		6600		2.21	37200

[a] [$SnCl_4$] = 2×10^{-2} $\text{mol}\cdot\text{L}^{-1}$; [CumCl] = 2.5×10^{-3} $\text{mol}\cdot\text{L}^{-1}$; *T* = −15 °C. Reaction time: 6 min.

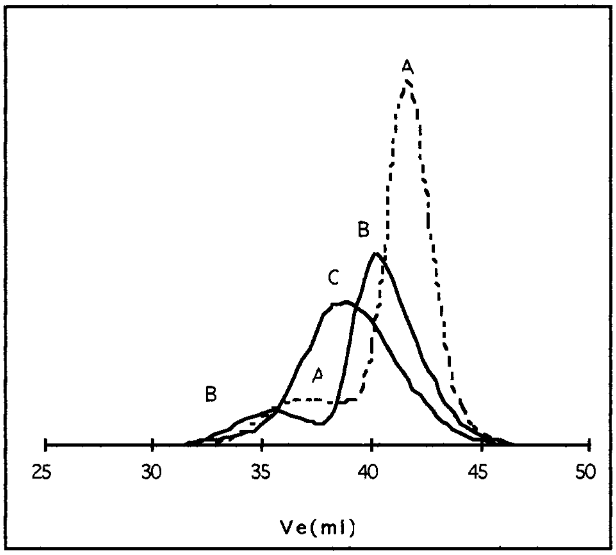

Figure 6. Polymerization of indene initiated with CumCl/$SnCl_4$ in a compensated medium ($\epsilon = 5.4$; indene + MeCH, 50% v/v in CH_2Cl_2). [CumCl] = 2.5×10^{-3} $\text{mol}\cdot^{-1}$; [$SnCl_4$] = 2×10^{-2} $\text{mol}\cdot\text{L}^{-1}$. *T*: −15 °C. Reaction time: 6 min. Conversion: 35%. Evolution of the SEC traces with the initial indene concentration. [indene]$_0$: (A) 0.21 $\text{mol}\cdot\text{L}^{-1}$; (B) 0.43 $\text{mol}\cdot\text{L}^{-1}$; (C) 1.5 $\text{mol}\cdot\text{L}^{-1}$.

Table 6. Incremental Monomer Addition in the Polymerization of Indene in CH_2Cl_2 Solution, Showing the Influence of the Temperature on the Stability of the Active Centers[a]

temp (°C)	1st addition ($\text{mol}\cdot\text{L}^{-1}$)	2nd addition ($\text{mol}\cdot\text{L}^{-1}$)	$M_{n\,\text{exptl}}$	$M_{n\,\text{theor}}$	M_w/M_n
−15	0.215	0	10 500	10 000	1.5
−15	0.215	0.215	14 300	20 000	1.9
−15	0.430	0	20 800	20 000	1.5
−75	0.215	0	10 500	10 000	2.5
−75	0.215	0.215	21 250	20 000	1.5

[a] [$SnCl_4$] = 2×10^{-2} $\text{mol}\cdot\text{L}^{-1}$; [CumCl] = 2.5×10^{-3} $\text{mol}\cdot\text{L}^{-1}$.

consumption of indene, (Table 5). For initial indene concentrations lower than 0.85 M, a bimodal MWD is observed (Figure 6), with a small peak of high molar mass and a main peak of low M_n. For higher concentrations, the two peaks merge, as is shown by the broadening of the MWD. The M_n of the low molar mass peak increases with the amount of monomer consumed, but are lower than the calculated values (Figure 3). The M_n of the high molar masses peak also increase (Table 5).

Successful IMA is the best proof for livingness. IMA have been carried out at −15 and −75 °C (Table 6). The second monomer addition was made 6 min after the first polymerization, long after the polymerization time (30 s). At −75 °C the M_n of the final polymer had the expected value for a living process, the polydispersity decreases after the second addition, and the dormant species could be reactivated. At −15 °C, the M_n is lower (14 300 instead of 20 000). This shows that at least a fraction of the end groups has been destroyed after 6 min. This destruction probably takes place after the polymerization through ionization of chlorinated chains by $SnCl_4$, followed by proton abstraction from the β-carbon in the absence of monomer. This would ultimately yield unsaturated dead chains, HCl and $SnCl_4$, which would initiate new chains upon a second addition of monomer.

However, the polyindene of an AMI (all monomer in) addition carried out at −15 °C with twice the concentration of the IMA had the expected value. At −15 °C, addition at a shorter time, immediately after the first

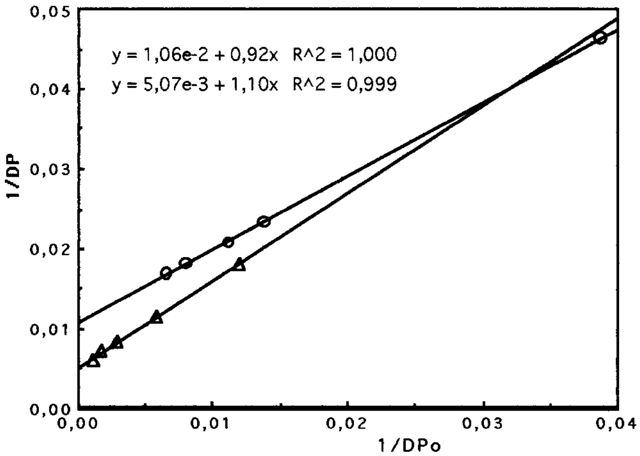

Figure 7. Polymerization of indene initiated with CumCl/SnCl$_4$ in compensated media. [CumCl] = 2.5 × 10^{-3} mol·L^{-1}; [SnCl$_4$] = 2 × 10^{-2} mol·L^{-1}. *T*: −15 °C. Apparent transfer constants to monomer: (Δ) $\epsilon = 7.2$ (indene + MeCH, 30% v/v in CH$_2$Cl$_2$); variable initial indene concentration; reaction time, 6 min; complete conversion. (○) $\epsilon = 5.4$ (indene + MeCH, 50% v/v in CH$_2$Cl$_2$); [indene] = 0.43 mol·L^{-1}; variable conversion.

reaction, might have yielded the expected value. Anyway, under these conditions, the polymerization is controlled, but not living.

(3) Discussion. Polyindenes with controlled molar masses up to M_n = 20 000 ([M]$_0$/[I]$_0$ = 200; M_w/M_n = from 1.57 to 1.74) have been obtained with the SnCl$_4$/CumCl initiating system at −15 °C, which is better than that for styrene at the same temperature.[17] This is probably due to the absence of indanyl-type termination, which imparts a better stability to the cation. Slightly better control of M_w/M_n than with indene and TiCl$_4$ may result from a lower polymerization rate, from a smaller ionization of the end groups, and from more frequent exchanges with the dormant species. Up to [indene]$_0$ = 0.8 M ([M]$_0$/[I]$_0$ = 350), the evolution of the M_n with indene concentration is in agreement with a transfer constant to indene equal to 9 × 10^{-4}. Control is lost at higher [M]$_0$/[I]$_0$ ratios and the M_n actually decreases in the range of high indene concentrations. The domain of high monomer concentrations has rarely been investigated in controlled polymerization mainly because control is lost on account of transfer reactions, but the observation of a decrease of M_n at high indene concentrations was made by Sigwalt[21] and Maréchal[22] for noncontrolled polymerizations.

However, the polymerizations are fast, and complete conversion is obtained in less than 30 s. The reactions are still relatively fast in a compensated medium of slightly lower polarity ($\epsilon = 7.2$). Under these conditions, the M_n values increase with the [M]$_0$/[I]$_0$ ratio over the whole range of indene concentrations (up to 2.2 M) but are much lower than those obtained in pure CH$_2$Cl$_2$. A lower polarity ($\epsilon = 5.4$) makes kinetics measurements possible. There is still an increase of the M_n values, both with conversion and with initial indene concentration at a given conversion, but they tend to level off. Transfer increases at low dielectric constant. In all cases, the plots of 1/DP$_n$ vs 1/DP$_o$ yield straight lines which might be at first sight in agreement with a transfer to monomer. The apparent value of C_M increases when the dielectric constant of the medium decreases from $\epsilon = 9$ ($C_M = 9 \times 10^{-4}$ in pure CH$_2$Cl$_2$, Figure 2) to $\epsilon = 7.2$ ($C_M = 5 \times 10^{-3}$) and to $\epsilon = 3.5$ ($C_M = 1 \times 10^{-2}$, Figure 7).

The main difference between the polymerization in pure CH$_2$Cl$_2$ and in the compensated media is the evolution of the molar mass which decreases with increasing concentration of indene in CH$_2$Cl$_2$ above 1 mol·L^{-1} while they still increase up to [M]$_0$ = 2.2 mol·L^{-1} even for a relatively high polarity ($\epsilon = 7.2$) and tend to level off for $\epsilon = 5.4$. In all cases, lowering the dielectric constant decreases the molar masses, indicating an increase of the transfer reactions.

The influence of the dielectric constant on the various reactions which may take place during a polymerization has been discussed.[23] A decrease of the dielectric constant has a negative effect on the ionization rate (dipole−dipole reaction leading to ionic species). It increases the rate of ion−ion reactions such as deactivation of the ion pairs and transfer to the counterion, and has little influence on ion−dipole reactions such as propagation and transfer to the monomer. Slower activation and faster deactivation account for the drop of overall polymerization rate at low dielectric constant by shifting the equilibrium toward the dormant species. Although the 1/DP$_n$ vs 1/DP$_o$ plots for transfer to monomer yield straight lines, this transfer should not be as strongly affected as it is here by a change of dielectric constant. However, transfer to the counterion has to be considered under these conditions. Incidence of zero order transfer with respect to the monomer has been shown in the case of the polymerization of α-methylstyrene in a mixed solvent (CH$_2$Cl$_2$−methylcyclohexane 50/50 v/v)[24] and in the polymerization of isobutylvinyl ether in toluene.[25] Recently, transfers to the counterion have been measured in the case of the polymerization of isobutylene in mixed solvents.[26] Transfer decreases at low temperatures and at high dielectric constant.

Assuming the existence of transfer to the counterion and to the monomer (which is still operative), the DP$_n$ can be calculated according to the following relationship:

$$\mathrm{DP_n} = \frac{[\mathrm{M}]_\mathrm{O} Y}{[\mathrm{I}]_\mathrm{o} + C_\mathrm{M}[\mathrm{M}]_\mathrm{O} Y + C_\mathrm{tr} \ln[1/(1 - Y)]}$$

Hence:

$$\frac{[\mathrm{M}]_\mathrm{O} Y}{\mathrm{DP_n}} - C_\mathrm{M}[\mathrm{M}]_\mathrm{O} Y = [\mathrm{I}]_\mathrm{o} + C_\mathrm{tr} \ln[1/(1 - Y)]$$

$C_\mathrm{M} = k_\mathrm{trM}/k_\mathrm{p}$ (transfer constant to monomer assumed to be that measured in CH$_2$Cl$_2$ (9 × 10^{-4}))

$C_\mathrm{tr} = k_\mathrm{tr}/k_\mathrm{p}$ (transfer constant to counterion)

Y = yield

The corresponding graph is shown in Figure 8. The intercept, 3.1 × 10^{-3}, is slightly higher than the concentration of cumyl chloride (2.5 × 10^{-3} M), and the value of the transfer constant to the counterion is 1.47 × 10^{-3}. Because of the logarithmic term, this relationship can only be used for partial conversions. However, Figure 9 shows the calculated values for the evolution of the molar mass with conversion for a given value of the zero order transfer rate constant (C_tr = 10^{-3}) and of initiator (2.5 × 10^{-3} M) at variable initial monomer concentration. For any given yield lower than one, the molar mass of the polymer increases with the initial

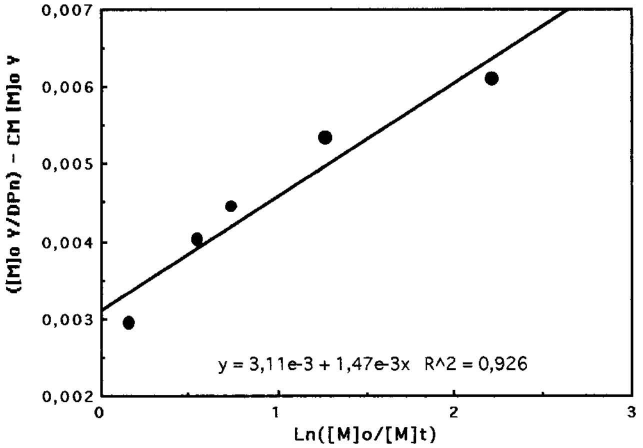

Figure 8. Measurement of the zero order transfer constant in a compensated medium ($\epsilon = 5.4$). [indene] = 0.43 mol·L^{-1}; [SnCl$_4$] = 2 × 10^{-2} mol·L^{-1}; [CumCl] = 2.5 × 10^{-3} mol·L^{-1}. Temperature: −15 °C.

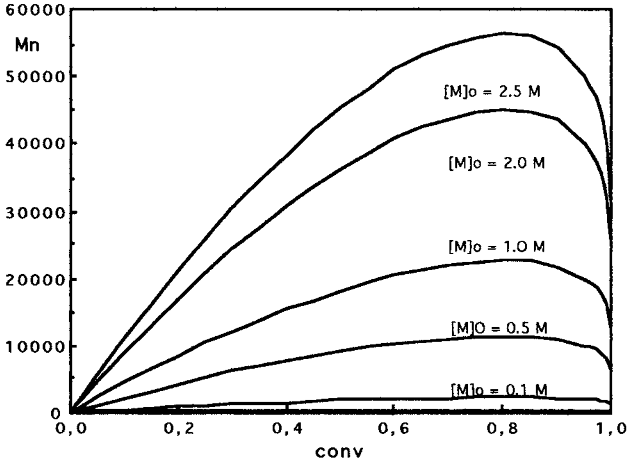

Figure 9. Calculated values for the evolution of the molar mass with conversion at variable initial monomer concentration in the case of a zero order transfer. $[M]_o = 1$ mol·L^{-1}; $[I]_0 = 2.5 \times 10^{-3}$ mol·L^{-1}; $k_{tr}/k_p = 10^{-3}$ s^{-1}.

monomer concentration. This is in agreement with the results of Table 3 ($\epsilon = 7.2$; variable monomer concentration, complete conversion). However, this does not account for the decrease of the molar masses observed in the case of the polymerization of indene in pure CH_2Cl_2.

A possible explanation for this decrease may be the time span of the polymerization. In a medium of low polarity ($\epsilon = 5.4$) the reaction is slow enough, the heat exchange can take place, and the polymerization is isothermal, as we have verified. In CH_2Cl_2, the reaction is very fast and the temperature increase due to the heat of polymerization may favor transfer reactions, if heat exchange between the reaction vessel and the thermostated bath is slow. The heat release (estimated at about 50 °C for adiabatic conditions for $[\text{indene}]_0 = 2.5$ mol·L^{-1}) would enhance transfer reactions, and this effect would add up to the "normal" transfer and decrease the molar masses.

Furthermore, the hypothesis of a zero order transfer is in agreement with the experiment at high indene concentration (2.5 mol·L^{-1}) in the presence of an hindered base. The polymerization stops at 11% yield. The M_n (12 000) corresponds to that of a polymerization at 0.25 mol·L^{-1} initial indene concentration carried out to complete conversion, i.e., in a range in which the M_n is controlled. Transfer to the monomer, even if it takes place to some extent, should not lead to a termination by the base.[26,27] Consequently, the termination observed here should result from a zero order transfer with subsequent proton capture by the base. In the absence of base, the reaction goes to completion to yield a polyindene with the same molar mass.

In a medium of dielectric constant 5.4, bimodal MWDs are observed, both at low conversion and at low initial monomer concentration, and the two peaks merge afterward. In the case of polymerizations in pure CH_2Cl_2 (or for $\epsilon = 7.2$) the same phenomenon might take place but would not be detected because conversion is complete. This bimodality has been attributed to propagations involving two different active centers, with little interconversion during the polymerization. The two possibilities are either separate propagation on free ions and ion pairs or initiation by adventitious protic initiator present in the medium (presumably HCl, which could come from $SnCl_4$ or residual H_2O).

HCl is an efficient initiator with $SnCl_4$.[20] However, initiation by an adventitious HCl would in principle yield the same counterion (assumedly $SnCl_5^-$) than initiation by cumyl chloride, and there should be no difference between the behavior of the two types of initiation. A faster initiation by HCl than with CumCl, which would yield high molar mass polyindene at the beginning of the polymerization, can be ruled out because the ratio of the peaks of high and low molar masses remains constant during the reaction and the two polymers are formed simultaneously. On the other hand, H_2O is not an efficient initiator with $SnCl_4$,[20] and it should be present in very low concentration given the experimental conditions.

In the present case, given the low dielectric constant of the medium ($\epsilon = 5.4$), the contribution of free ions might at first sight appear less likely, unless the equilibrium constant between active and dormant species is low enough to yield a small concentration of ion pairs, leading to important dissociation. On the other hand, theoretical calculations concerning the evolution of the MWD with yield for polymerizations involving ion pairs and free ions yielded bimolar distributions for the polymerization of styrene at −20 °C initiated with phenylethyl chloride and with $SnCl_4$ as activator, in fairly good agreement with experimental results.[28] In the present case, the M_n of the high polymer decreases with yield and that of the low polymer increases (Table 4), which is in agreement with this theoretical model. As initiation with HCl (which could be present in the $SnCl_4$) should not lead to bimodality and H_2O (which should be present in very low concentration given the experimental conditions) is not an efficient initiator with $SnCl_4$, the most likely explanation is a propagation on both free ions and ion pairs. Assuming that the apparent rate constants for the two species have similar values, the bimodality may result from the different lifetimes of the species, the free ions being destroyed through a bimolecular reaction, and the ion pairs, through a unimolecular one.

In the compensated medium ($\epsilon = 5.4$; $[\text{indene}]_0 = 0.43$ M), addition of 2,6-di-*tert*-butyl-4-methylpyridine suppresses the high M_n peak. This may be due to a common ion effect of pyridinium pentachlorostannate resulting from reaction of $SnCl_4$ with a protic impurity which would shift the equilibrium in favor of the ions pairs.

Acknowledgment. We want to thank Professor Krzystof Matyjaszewski for helpful comments and suggestions.

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MA9913010