

# "Living" Cationic Polymerization of Indene. 1. Polymerization Initiated with Cumyl Methyl Ether/Titanium Tetrachloride and Cumyl Methyl Ether/*n*-Butoxytrichlorotitanium Initiating Systems

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Received February 10, 1992; Revised Manuscript Received May 5, 1992

**ABSTRACT:** Polymerization of indene using cumyl methyl ether as initiator and titanium tetrachloride as coinitiator in methylene chloride solution has been examined, and apparently living polymerizations (called "living") have been observed. At  $-40$  and  $-75$  °C, there is a linear relationship between the  $\bar{M}_n$  and the amount of monomer polymerized, with a number of macromolecules near to that of the initiator. These features were generally attributed for various monomers to the absence of transfer and termination. However, it was shown that at  $-40$  °C significant transfer reactions occur, the same transfer constant being found for polymerizations which were and were not apparently living. At  $-75$  °C, transfer could no longer be detected and the linear increase of the  $\bar{M}_n$  was observed up to  $10^5$ . With butoxytrichlorotitanium as coinitiator, the transfer constant was near zero at  $-40$  °C, and  $\bar{M}_w/\bar{M}_n = 1.7$  instead of 2.2. There was no important effect of solvent polarity and of the addition of dimethyl sulfoxide. These results do not suggest special "stabilized" carbocationic species and are explained by quantitative initiation resulting from high  $R_i/R_p$  ratios and suppression of transfer at a sufficiently low temperature. Reversible termination has been shown by initiating a new polymerization from an isolated polymer, but it is uncertain whether reversibility occurs during a polymerization.

## I. Introduction

Faust and Kennedy recently reported that, under certain experimental conditions and in the presence of various additives, the polymerization of isobutylene,<sup>1</sup> styrene,<sup>2</sup> methylstyrenes,<sup>3,4</sup> and chlorostyrene<sup>5</sup> exhibits features of living polymerizations, namely: (1) The  $\bar{M}_n$ 's of the polymers are proportional to the amount of monomer polymerized. The reactions are generally rapid and in most cases it is impossible to stop the polymerization before complete monomer conversion. The  $\bar{M}_n$ 's obtained in these cases are in most cases those of polymerizations carried out to complete conversion ("all monomer in" reactions—AMI). (2) The concentration of macromolecules is constant and independent of conversion (which is a consequence of the first feature) and, in many cases, equal to the concentration of the initiator. (3) Addition of monomer to a solution in which a polymerization has been carried out to completion causes new polymerization resulting in a proportional increase of the molecular weight ("incremental monomer addition"—IMA).

A monomer which might lead to similar observations is indene. This monomer gives high molecular weight polymers with conventional initiating systems and does not give much transfer at low temperatures.<sup>6</sup> The preparation of triblock copolymers of isobutylene and indene at  $-80$  °C, with polyindene end blocks of  $\bar{M}_n \approx 10\,000$ , has been reported.<sup>7</sup> The growing polyindene end should not undergo chain transfer by formation of indanyl end groups, which occurs during the polymerization of other arylalkyl monomers. In a really living system termination and transfer should be absent or negligible. In a recent review,<sup>8</sup> it was suggested by one of us that a polymerization should still be considered living if reversible termination occurs (presence of active and dormant sites). It was also concluded that, for most cationic systems described as living, the apparent livingness was limited to conditions giving polymers of relatively low molecular weights, because transfer did occur under the conditions used.

Table I  
Polymerization of Indene<sup>a</sup>

expt no.	[indene] (mol·L <sup>-1</sup> )	$10^3 \times$ [CumOMe] (mol·L <sup>-1</sup> )	$10^3 \times$ [DMSO] (mol·L <sup>-1</sup> )	$\bar{M}_n$	$10^3$ [N] (mol·L <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1	0.43	0	0	87 000	0.6	2.3
2	0.43	0	2.5	65 600	0.8	2.4
3	0.43	4.5	2.5	10 100	4.9	2.0

<sup>a</sup> Influence of various additives on the polymerization. [TiCl<sub>4</sub>],  $2 \times 10^{-2}$  mol·L<sup>-1</sup>; temperature,  $-40$  °C; solvent, CH<sub>2</sub>Cl<sub>2</sub>/C<sub>6</sub>H<sub>14</sub> (60/40 vol). Complete conversion is obtained in all cases.

The aim of this work is to elucidate the conditions under which a "conventional" polymerization becomes an apparently living one and eventually a really living one and to find out what makes a system "living". Preliminary results on this topic have been communicated at the Balatonfüred symposium (1991). In the following, a system will be said to be "living" if the molecular weights of the polymers are proportional to the amount of monomer converted and if the number of macromolecules formed is near that of the initiator added.

Kennedy's definitions of initiator and coinitiator<sup>9</sup> will be used, and the term initiator will be extended to cases in which initiation is attributed to an undefined compound assumed to be present (previously called cocatalyst, e.g. water) and to be responsible of the formation of the initiating cation.

## II. Experimental Section

The polymerizations have been carried out in sealed tubes, with reagents purified under vacuum using the usual techniques.<sup>6</sup> Indene was purified as described<sup>10</sup> and contained less than 0.1 % coumarone. Cumyl methyl ether (CumOMe) was prepared by reacting methanol with  $\alpha$ -methylstyrene. TiCl<sub>3</sub>OBu was prepared by reacting equimolar amounts of *n*-butanol and TiCl<sub>4</sub> (Aldrich) and was recrystallized five times from CH<sub>2</sub>Cl<sub>2</sub> under vacuum. The reagents were introduced using a vacuum line fitted with Teflon stopcocks. The polymerizations were started by breaking a coinitiator bulb (TiCl<sub>4</sub> or TiCl<sub>3</sub>OBu). The conversion was complete in nearly all cases. Most of the experiments reported have been arbitrarily stopped 6 min after the start of the reaction

Table II  
Polymerization of Indene with the  $\text{TiCl}_4/\text{CumOMe}/\text{DMSO}$  Initiating System<sup>a</sup>

temp (°C)	$\bar{M}_n$	$10^3[\text{N}]$ (mol·L <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
0	7 100	7.5	1.9
-20	7 400	6.7	2.2
-30	7 750	6.4	2.3
-40	10 100	4.9	2.0

<sup>a</sup> Influence of the reaction temperature on the "livingness" of the system. [Indene], 0.43 M;  $[\text{TiCl}_4]$ ,  $2 \times 10^{-2}$  M;  $[\text{CumOMe}]$ ,  $4.5 \times 10^{-3}$  M;  $[\text{DMSO}]$ ,  $2.5 \times 10^{-3}$  M; solvent,  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$  (60/40 vol); calculated  $\bar{M}_n$ , 11 100.

by introducing methanol. Calorimetric measurements showed that, in the presence of added initiators, complete conversion is generally obtained in less than 5 s. The polymers have been recovered by evaporating the solvent and dried under vacuum overnight. The molecular weights were measured by size exclusion chromatography, using Waters microstysragel columns ( $10^5$ ,  $10^4$ ,  $10^3$ , 500, and 100 Å), with a polystyrene calibration. The  $\bar{M}_n$  measured by SEC was in good agreement with the results of osmotic measurements for  $\bar{M}_n$  ranging from 30 000 and 80 000. For values lower than 20 000, the  $\bar{M}_n$  obtained by SEC was systematically lower than those derived from osmometry. It was assumed that the shorter chains of the samples went through the membrane of the osmometer and were not taken into account in the calculation of the osmotic  $\bar{M}_n$ . The agreement between SEC and osmometry are shown by the following figures:

$\bar{M}_n$ (osmometry)	$\bar{M}_n$ (SEC)
33 000	27 000
59 000	59 000
90 000	95 000

The discrepancy does not seem to be higher than 5%, except for the lower molecular weights.

### III. Results

(1) **Polymerizations Initiated with Cumyl Methyl Ether and Titanium Derivatives.** (A) **Influence of Additives.** The results of conventional polymerizations of indene initiated with titanium tetrachloride in a mixture of methylene chloride and hexane (60/40 vol/vol) without initiator, at -40 °C, are shown in Table I. The polymerization of indene (0.43 M), initiated with  $\text{TiCl}_4$  ( $2 \times 10^{-2}$  M), yields a polymer having a molecular weight of 87 000. Consequently, this result suggests initiation by  $5.7 \times 10^{-4}$  mol·L<sup>-1</sup> residual water, not necessarily in contradiction with the formation of a living polymer. It has been reported<sup>11</sup> that addition of electron-donating compounds, such as dimethyl sulfoxide (DMSO), favors the formation of living polymers. However, addition of DMSO does not drastically affect the results (cf. experiments 1 and 2 of Table I). As has already been reported by Kennedy for isobutylene,<sup>12</sup> in the presence of cumyl methyl ether, the  $\bar{M}_n$  of the polymer is much lower (experiment 3,  $\bar{M}_n = 10\,100$ ) and the concentration of macromolecules derived from this figure approximately corresponds to that of the ether. Consequently, the polymerizations initiated with this system may be "living".

(B) **Influence of Temperature.** Table II shows the influence of the temperature on polymerizations carried out with cumyl methyl ether (CumOMe) initiator. At 0 °C, the  $\bar{M}_n$  of the polymer ( $\bar{M}_n = 7100$ ) is lower than the theoretical value ( $\bar{M}_n = 11\,000$ ) calculated by assuming quantitative initiation by the ether yielding a living polymer. The concentration of macromolecules at the end of the reaction is higher than that of the cumyl methyl ether, and this may be the result of transfer reactions. When the temperature is decreased, the  $\bar{M}_n$  approaches

Table III  
Polymerization of Indene Initiated with the  $\text{TiCl}_4/\text{CumOMe}$  Initiating System<sup>a</sup>

expt no.	[indene] (mol·L <sup>-1</sup> )	$10^3 \times$ [CumOMe] (mol·L <sup>-1</sup> )	$10^3 \times$ [DMSO] (mol·L <sup>-1</sup> )	sol- vent	$\bar{M}_n$	$10^3[\text{N}]$ (mol·L <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1	0.06	4.5	2.5	A	1 550	3.6	1.90
2	0.43	4.5	2.5	A	10 100	4.9	2.28
3 <sup>b</sup>	0.97	4.5	2.5	A	20 100	5.6	1.77
4	1.88	4.5	2.5	A	43 200	5.0	2.30
5	0.43	4.5	0	A	9 900	5.0	2.23
6 <sup>b</sup>	0.79	4.5	0	A	17 000	5.4	2.60
7	0.43	4.5	2.5	B	10 600	4.7	2.30
8	0.43	2.5	2.5	B	21 800	2.3	2.10
9	0.129	4.5	0	B	3 150	4.8	1.87
10	0.43	4.5	0	B	10 800	4.6	2.20
11	0.86	4.5	0	B	21 000	4.8	2.10
12	0.43	3.0	0	B	15 000	3.3	2.20
13	0.215	1.0	0	B	23 700	1.0	2.10
14	0.733	1.0	0	B	65 900	1.3	2.18
15	1.07	1.0	0	B	82 000	1.5	2.35

<sup>a</sup>  $[\text{TiCl}_4]$ ,  $2 \times 10^{-2}$  mol·L<sup>-1</sup>; temperature, -40 °C; solvent A,  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$  (60/40 vol); solvent B,  $\text{CH}_2\text{Cl}_2$ ; reaction time, 6 min. Complete conversion in all cases. <sup>b</sup> Experiments with incremental monomer addition (IMA). First polymerization:  $[\text{M}]_0 = 0.43$  mol·L<sup>-1</sup>.

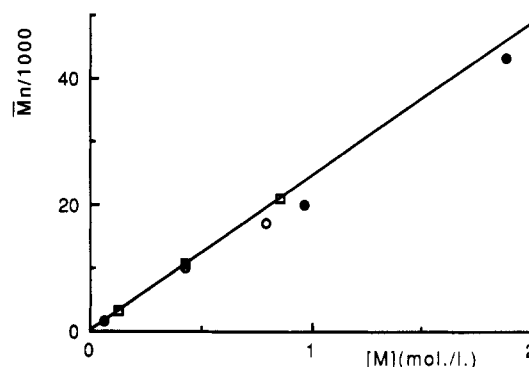
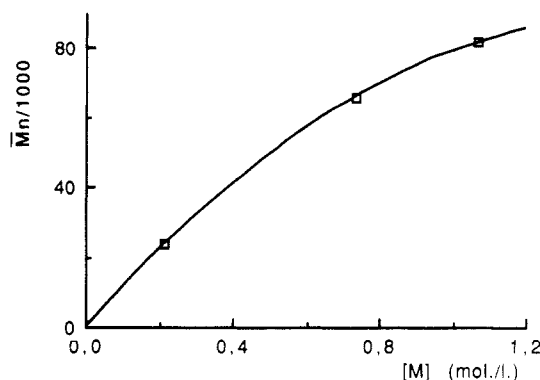


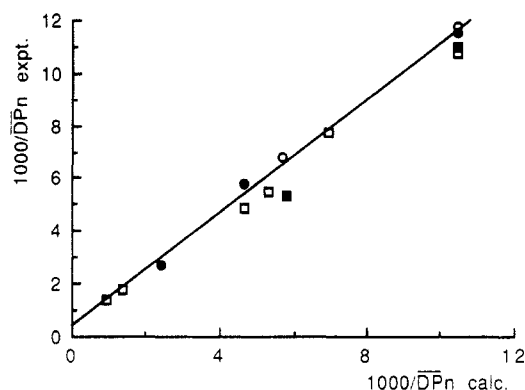
Figure 1. Polymerization of indene initiated with the CumOMe/ $\text{TiCl}_4$  initiating system. Variation of the  $\bar{M}_n$  with the amount of monomer polymerized. Conditions:  $[\text{TiCl}_4]$ ,  $2 \times 10^{-2}$  mol·L<sup>-1</sup>; temperature, -40 °C;  $[\text{CumOMe}]$ ,  $4.5 \times 10^{-3}$  mol·L<sup>-1</sup>. Key: for solvent  $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$  (60/40 vol), (●)  $[\text{DMSO}]$ :  $2.5 \times 10^{-3}$  mol·L<sup>-1</sup>, (○)  $[\text{DMSO}]$ : 0 mol·L<sup>-1</sup>; for solvent  $\text{CH}_2\text{Cl}_2$ , (■)  $[\text{DMSO}]$ :  $2.5 \times 10^{-3}$  mol·L<sup>-1</sup>, (□)  $[\text{DMSO}]$ : 0 mol·L<sup>-1</sup>.

the theoretical value, which is obtained at -40 °C. This temperature was chosen for most of our following experiments.

(C) **Polymerizations Initiated with CumOMe/ $\text{TiCl}_4$  at -40 °C.** The results of polymerizations of indene initiated with cumyl methyl ether are shown in Table III and Figure 1. Experiments 1–4 have been carried out in a mixture of methylene chloride and hexane (60/40 vol) in the presence of DMSO. The  $\bar{M}_n$  of the polyindenes increase linearly with the amount of monomer polymerized and are very near the values calculated by assuming quantitative initiation by CumOMe, even for experiments involving addition of new monomer 6 min after the first polymerization (cf. experiments 3 and 6). The same results are obtained in the absence of DMSO (cf. experiments 5 and 6). The remaining experiments of this table have been carried out in pure methylene chloride, and experiments 7 and 9–11 show a linear increase of the  $\bar{M}_n$  with the quantity of monomer converted, and the concentration of macromolecules formed is only slightly higher than that of the cumyl methyl ether. However, linear growth of  $\bar{M}_n$  with the weight of monomer polymerized is not a sufficient criterion for the existence of a living polymerization.<sup>13–15</sup> It has been shown<sup>8</sup> that, for a monomer to initiator ratio of 200, an apparently linear relationship is observed for  $k_{trM}/k_p$  lower than  $10^{-3}$ . Indeed, experiments 13–15, carried



**Figure 2.** Polymerization of indene initiated with the CumOMe/TiCl<sub>4</sub> initiating system. Variation of the  $\bar{M}_n$  with the amount of monomer polymerized. Evidence for the occurrence of transfer at high  $[M]_0/[I]_0$  ratios. Conditions: [TiCl<sub>4</sub>],  $2 \times 10^{-2}$  mol·L<sup>-1</sup>; temperature, -40 °C; [CumOMe],  $1 \times 10^{-3}$  mol·L<sup>-1</sup>.



**Figure 3.** Measurement of the transfer rate constant to the monomer in the polymerization of indene at -40 °C. Conditions: initiating system, CumOMe/TiCl<sub>4</sub>; solvent, CH<sub>2</sub>Cl<sub>2</sub>;  $k_{trM}/k_p = 5 \times 10^{-4}$ . Concentrations as in Table III.

out with higher monomer to initiator ratios ( $[M]_0/[I]_0 = 215, 730$ , and  $1070$ , respectively) yield polymers with  $\bar{M}_n$  significantly lower than calculated. The discrepancy increases with the initial concentration of indene, and the plot of  $\bar{M}_n$  vs monomer concentration is no longer linear (cf. Figure 2). This, and the fact that in most cases the concentration of macromolecules formed is slightly higher than that of the initiator, show that transfer reactions occur.

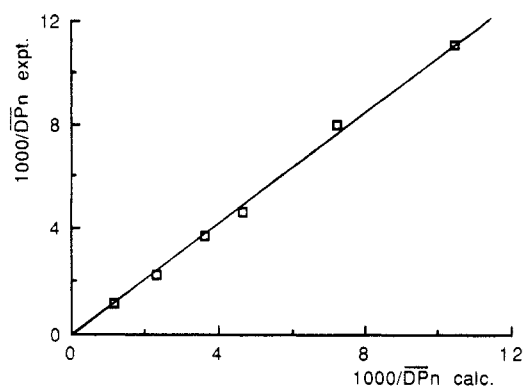
Assuming quantitative initiation by the cumyl methyl ether, absence of termination, and transfer to the monomer, the transfer constant for complete conversion can be obtained by the following relationship:

$$\frac{1}{\overline{DP}_n(\text{expt})} = \frac{[I]_0}{[M]_0} + \frac{k_{trM}}{k_p} = \frac{1}{\overline{DP}_n(\text{calc})} + \frac{k_{trM}}{k_p}$$

The corresponding MAYO plot, which includes all the experiments carried out in methylene chloride (i.e. those giving a linear relationship (Figure 1) and those showing a curvature (Figure 2)), is shown in Figure 3. The resulting straight line has a positive intercept which gives the transfer constant to the monomer at -40 °C ( $5 \times 10^{-4}$ ).

The difference between the calculated and experimental values of the  $\bar{M}_n$  might be due exclusively to extra initiation by adventitious initiator. But in this case a proportionality between these values should have been observed over the whole range of monomer concentrations. The curvature of the  $\bar{M}_n$  vs  $[M]$  plot obtained at higher monomer concentrations (cf. Figure 2) demonstrates the occurrence of transfer.

**(D) Polymerization at -75 °C.** The results of polymerizations at -75 °C are shown in Table IV. There is a



**Figure 4.** Measurement of the transfer rate constant to the monomer in the polymerization of indene at -75 °C. Conditions: initiating system, CumOMe/TiCl<sub>4</sub>; solvent, CH<sub>2</sub>Cl<sub>2</sub>;  $k_{trM}/k_p = 0$ . Concentrations as in Table IV.

**Table IV**  
Polymerization of Indene Initiated with the TiCl<sub>4</sub>/CumOMe Initiating System at -75 °C<sup>a</sup>

expt no.	[indene] (mol·L <sup>-1</sup> )	$10^3 \times$ [CumOMe] (mol·L <sup>-1</sup> )	$\bar{M}_n(\text{expt})$	$\bar{M}_n(\text{calc})$	[N] (mol·L <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1	0.43	4.5	10 500	11 100	4.7	2.0
2	0.62	4.5	14 600	16 000	4.9	2.1
3	1.24	4.5	31 000	32 000	4.6	2.0
4	0.215	1.0	25 000	25 000	1.0	2.2
5	0.43	1.0	52 000	50 000	1.0	2.2
6	0.86	1.0	98 000	100 000	1.0	2.2

<sup>a</sup> [TiCl<sub>4</sub>],  $2 \times 10^{-2}$  mol·L<sup>-1</sup>; solvent, CH<sub>2</sub>Cl<sub>2</sub>.

**Table V**  
Kinetic Investigation of the Polymerization of Indene by Adiabatic Calorimetry<sup>a</sup>

$10^3 \times$ [CumOMe] (mol·L <sup>-1</sup> )	polym-erization time (s)	$10^2 R_{pmax}$ (mol·L <sup>-1</sup> ·s <sup>-1</sup> )	$\bar{M}_n$	$10^3 [N]$ (mol·L <sup>-1</sup> )	$k_{papp}$ (L·mol <sup>-1</sup> ·s <sup>-1</sup> )
0	24	3.5	62 000	0.3	1100
1.5	4	8.6	11 700	1.7	600

<sup>a</sup> [Indene], 0.172 mol·L<sup>-1</sup>; [TiCl<sub>4</sub>],  $10^{-2}$  mol·L<sup>-1</sup>; solvent, CH<sub>2</sub>Cl<sub>2</sub>; temperature, -40 °C. For definition of  $k_{papp}$  see text.

linear relationship between  $\bar{M}_n$  and the amount of polyindene formed and the corresponding MAYO plot (Figure 4) goes through the origin within experimental error, which means that at this temperature transfer is frozen out or is too small to be detected. In this case, a decrease of temperature has changed a polymerization which was apparently living into a polymerization which cannot be distinguished from a truly living one.

**(E) Kinetic Investigation by Vacuum Calorimetry.** Although all the experiments have been routinely terminated 6 min after the breaking of the initiator bulk, it has been found that quantitative yield is generally obtained in a few seconds. Thus, adiabatic calorimetry under vacuum seemed to be a convenient investigation tool for these polymerizations.

The results of two polymerizations carried out with and without cumyl methyl ether are shown in Table V. In the absence of CumOMe, the time necessary for complete conversion is 24 s. The concentration of macromolecules at the end of the reaction ( $[N] = 3 \times 10^{-4}$  mol·L<sup>-1</sup>) is in fairly good agreement with values from previous experiments carried out in similar conditions, as well as with the assumed concentration of "adventitious initiator". The kinetics of disappearance of indene obeys a first-order internal law after a short induction period (1 s), which may be due either to the lag time of the recording device

Table VI  
Polymerizations Stopped at Partial Conversion<sup>a</sup>

$10^3 \times$ [CumOMe] (mol·L <sup>-1</sup> )	yield (%)	$\bar{M}_n(\text{expt})$	$\bar{M}_n(\text{calc})$	$\bar{M}_n$ (calc for 100% yield)	$\bar{M}_w/\bar{M}_n$
4.5	55	9 200	10 700	19 500	2.2
3.0	80	22 100	24 000	29 200	2.3

<sup>a</sup> [Indene], 0.75 mol·L<sup>-1</sup>; [TiCl<sub>4</sub>],  $2 \times 10^{-2}$  mol·L<sup>-1</sup>; [DMSO],  $2.5 \times 10^{-3}$  mol·L<sup>-1</sup>; solvent, CH<sub>2</sub>Cl<sub>2</sub>; temperature, -40 °C.

or to relatively slow initiation. This implies that the concentration of active centers remains constant during the polymerization but gives no clue for the mechanism.

In the presence of cumyl methyl ether ( $1.5 \times 10^{-3}$  mol·L<sup>-1</sup>), the reaction is completed in about 4 s, and is too fast to allow reliable quantitative assessment of the internal reaction order in the monomer. However, the available data seem to be compatible with a first-order internal law. The concentration of chains is roughly equal to that of the added cumyl methyl ether.

Given the high reaction rates in the presence of cumyl methyl ether, it is difficult to stop the polymerization at partial conversions. Nevertheless, two polymerizations have been terminated after a few seconds, partial conversions have been obtained, and it has been found that the  $\bar{M}_n$  of the polymer is proportional to the reaction yield within an AMI reaction (Table VI).

These facts, and the increase of the  $\bar{M}_n$  with the amount of monomer polymerized shown before, confirm that initiation is rapid and produces a number of macromolecules which remain constant throughout the reaction. This implies that there is no quasistationary state (continuous initiation and irreversible termination). Either the active sites are stable during the whole reaction or they are formed by another type of quasistationary state involving reversible termination and reactivation.

Another point worth noting is that the value of the apparent propagation rate constant  $k_{\text{papp}}$  is higher for the polymerization carried out without cumyl methyl ether (1100 instead of 600). These constants have been calculated using the following relationship:

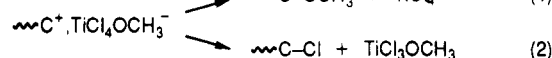
$$k_{\text{papp}} = \frac{R_{\text{pmax}}}{[M]_0[N]_f}$$

[M]<sub>0</sub> being the initial monomer concentration, [N]<sub>f</sub> the final concentration of macromolecules, and  $R_{\text{pmax}}$  the maximum rate deduced from the conversion vs time curve. Even if there is some inaccuracy in the case of the estimation of  $R_{\text{pmax}}$  in the presence of cumyl methyl ether, the difference may be due to the nature of the counterions (presumably TiCl<sub>4</sub>OH<sup>-</sup> and TiCl<sub>4</sub>OCH<sub>3</sub><sup>-</sup>).

**(F) Reversible Termination.** The previous results raise the question of the stability, and of the structure, of the active centers. Either the cation is stable enough to ensure complete conversion or the active species undergoes a reversible termination.

In the presence of CumOMe, complete conversion is achieved in a few seconds, and addition of monomer 6 min later causes a growth of the chains formed during the first polymerization. This might suggest that the active centers retain their propagating ability long after polymerization.

A possible structure for the counterion in the case of the polymerization initiated with the CumOMe/TiCl<sub>4</sub> system is the methoxytetrachlorotitanium anion. The most probable termination reaction is a collapse of the ion pair according to one of the two following reactions:



Termination by introduction of methanol may produce the same end group as in (1), which should be able to initiate the polymerization. To check the hypothesis of reversible termination, a polyindene has been prepared using the TiCl<sub>4</sub>/CumOMe initiating system (without DMSO). The polymer has been precipitated, characterized (Table VII; experiment 1;  $\bar{M}_n(\text{calc})$  16 600,  $\bar{M}_n(\text{expt})$  14 800), and used as an initiator for a second polymerization, in the presence of DMSO since we shall see in the next paper that chloroindan end groups formed in (2) give quantitative initiation only in the presence of DMSO as an electron donor. The increase of  $\bar{M}_n$  observed corresponds to the calculated value, assuming quantitative initiation by the prepolymer ( $\bar{M}_n(\text{calc})/31\,800$ ,  $\bar{M}_n(\text{expt})$  32 700). The SEC traces of the polymers confirm chain extension during the second polymerization (Figure 4 and Table VII) even if it seems likely that a fraction of the original polymer did not initiate the second polymerization. The shoulder observed in the second chromatogram represents the polymer from the first polymerization which has not been reactivated. This shoulder amounts to 14% of the final polymer and 30% of the first one. Nevertheless, this confirms that a large part of the end groups resulting from termination, which may occur either by addition of a terminating agent or spontaneously, can be reactivated.

**(G) Polymerizations Initiated with the CumOMe/*n*-Butoxytrichlorotitanium System.** The results obtained with this system at -40 °C are similar to those reported for TiCl<sub>4</sub> (Table VIII). The main difference is that the molecular weight distribution is narrower (1.60–1.75) and that transfer is practically negligible at this temperature for  $\bar{M}_n$  up to 74 000 (cf. Figure 5). With this initiating system, the polymerization could not be distinguished from a living process at -40 °C and the progressive evolution from a "living" to a truly living polymerization cannot be shown. TiCl<sub>3</sub>OBU is insoluble in methylene chloride at -75 °C at the concentrations used here ( $2 \times 10^{-2}$  mol·L<sup>-1</sup>).

**(2) Polymerizations Initiated with Water and HCl in the Presence of TiCl<sub>4</sub> and TiCl<sub>3</sub>OBU.** In the absence of added initiator, it is generally assumed that the initiating agent is an adventitious compound, generally water or possibly hydrogen chloride from hydrolysis of the Lewis acid. Consequently, some exploratory experiments have been carried out with these compounds. In all cases, complete conversion was obtained. The calculated values of the  $\bar{M}_n$ , reported in Tables IX and X, are computed by assuming quantitative initiation by the added initiator.

Water was introduced first by breaking a bulb at room temperature, and the solution did not turn hazy upon cooling, as would have happened if water had precipitated. The influence of water is shown in Table IX. The polymerization of indene (0.215 M) initiated with TiCl<sub>4</sub> ( $2 \times 10^{-2}$  M) in methylene chloride at -40 °C, in the absence of added water, yields a polymer having a  $\bar{M}_n$  of 106 000. The corresponding concentration of macromolecules is  $2.3 \times 10^{-4}$  M, which is roughly what might be expected from initiation by residual water. However, in the presence of  $10^{-3}$  mol·L<sup>-1</sup> of added water, the  $\bar{M}_n$  of the polymer (130 000) is much higher than the calculated value (25 000), assuming quantitative initiation by water. The difference might be explained if water is an inhibitor decreasing the number of macromolecules formed by another mechanism. Polymerizations carried out with TiCl<sub>3</sub>OBU and added water yield polymers with lower molecular weights, and

Table VII  
Initiation of the Polymerization of Indene with a Functionalized Polyindene<sup>a</sup>

expt no.	[indene] (mol·L <sup>-1</sup> )	10 <sup>3</sup> conc (mol·L <sup>-1</sup> )	10 <sup>-3</sup> [DMSO] (mol·L <sup>-1</sup> )	$\bar{M}_n$ (calc)	$\bar{M}_n$ (expt)	$\bar{M}_w/\bar{M}_n$
first polymerization	0.43	(CumOMe, initiating species)	0	16 600	14 800	2.2
second polymerization <sup>b</sup>	0.43	2.94 (end groups <sup>c</sup> )	2.5	31 800	32 700	2.7

<sup>a</sup> For both experiments: [TiCl<sub>4</sub>],  $2 \times 10^{-2}$  mol·L<sup>-1</sup>; solvent, CH<sub>2</sub>Cl<sub>2</sub>; temperature, -40 °C. <sup>b</sup> The initiating polymer prepared as indicated in the first experiment of the table has been precipitated in methanol, vacuum-dried, and characterized before being used as an initiator for the second polymerization. <sup>c</sup> Calculated by assuming one initiating group per macromolecule.

Table VIII  
Polymerization of Indene Initiated with the TiCl<sub>3</sub>OBu/  
CumOMe Initiating System<sup>a</sup>

expt no.	[indene] (mol·L <sup>-1</sup> )	10 <sup>3</sup> × [CumOMe] (mol·L <sup>-1</sup> )	$\bar{M}_n$ (expt)	$\bar{M}_n$ (calc)	10 <sup>3</sup> [N] (mol·L <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
1	0.215	4.5	5 000	5 540	4.9	1.72
2	0.43	4.5	10 000	11 080	4.9	1.71
3	0.86	4.5	19 900	22 170	5.0	1.75
4	0.69	1.0	74 300	80 000	1.1	1.61

<sup>a</sup> [TiCl<sub>3</sub>OBu],  $2 \times 10^{-2}$  mol·L<sup>-1</sup>; temperature, -40 °C; solvent, CH<sub>2</sub>Cl<sub>2</sub>.

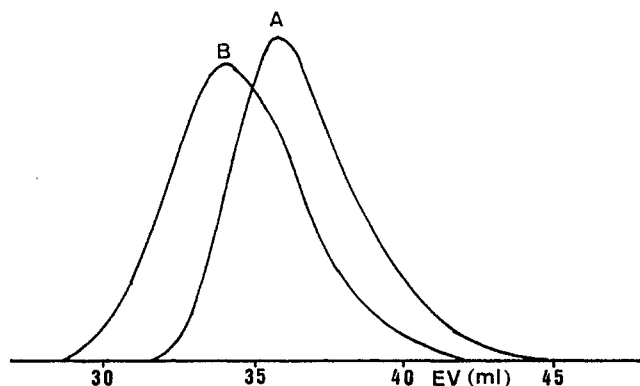


Figure 5. Polymerization of indene initiated with a functionalized polyindene [GPC analysis (refractive index detector)]. (A) Chromatogram of the polyindene used as an initiator (0.87 g,  $\bar{M}_n$  = 14 800). (B) Chromatogram of the polyindene recovered after chain extension (polymerization of 1 g of indene; yield, 100%;  $\bar{M}_n$  = 32 700).

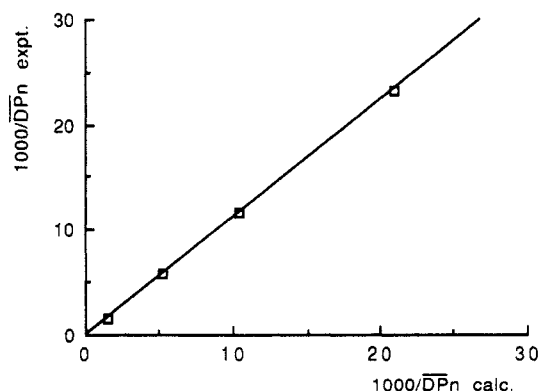


Figure 6. Measurement of the transfer rate constant to the monomer in the polymerization of indene at -40 °C. Conditions: initiation system, CumOMe/TiCl<sub>3</sub>OBu; solvent, CH<sub>2</sub>Cl<sub>2</sub>. Concentrations as in Table VIII.

the  $\bar{M}_n$  increases with initial monomer concentration but is consistently double the calculated values. In this case, a nearly linear dependence of the  $\bar{M}_n$  on the amount of polymer is observed; in other words, the concentration of chains formed is the same in all experiments, but lower than that of the added water. This might be accounted for by assuming rapid but partial initiation (50% yield) and "living" polymerization.

Table IX  
Influence of the Concentration of Water on the  
Polymerization of Indene in the Presence of TiCl<sub>4</sub> and  
TiCl<sub>3</sub>OBu<sup>a</sup>

[indene] (mol·L <sup>-1</sup> )	10 <sup>3</sup> [H <sub>2</sub> O] (mol·L <sup>-1</sup> )	Lewis acid ( $2 \times 10^{-2}$ mol·L <sup>-1</sup> )	$\bar{M}_n$ (expt)	$\bar{M}_n$ (calc)	10 <sup>3</sup> [N] (mol·L <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
0.215	0	TiCl <sub>4</sub>	106 000		0.2	2.5
0.215	1	TiCl <sub>4</sub>	130 000	25 000	0.2	2.7
0.108	1	TiCl <sub>3</sub> OBu	27 000	12 500	0.5	1.9
0.215	1	TiCl <sub>3</sub> OBu	57 000	25 000	0.4	2.0
0.430	1	TiCl <sub>3</sub> OBu	91 800	50 000	0.5	2.2

<sup>a</sup> Solvent, CH<sub>2</sub>Cl<sub>2</sub>; temperature, -40 °C.

The results of polymerizations with hydrogen chloride and TiCl<sub>4</sub> are in Table X. HCl was introduced by breaking a bulb of gaseous HCl at room temperature before cooling the solution, and quantitative dissolution in the solution was assumed. These experiments have been carried out in the presence of DMSO. The first experiment, without added water or HCl, yields a polymer having the same  $\bar{M}_n$  as that of the first experiment of Table I, obtained without DMSO. The polymer obtained in the presence of HCl ( $1.4 \times 10^{-3}$  M) has a lower  $\bar{M}_n$  (79 000), but which is still higher than the calculated value. This suggests that HCl has created extra chains but that initiation has not been quantitative. An increase of the monomer concentration yields a polymer having a higher  $\bar{M}_n$ , which is not proportional to the increment of monomer. Another experiment, carried out with TiCl<sub>3</sub>OBu and hydrogen chloride also gave a polymer with a high molecular weight.

In conclusion, water and hydrogen chloride are not efficient initiators for the polymerization of indene in the presence of TiCl<sub>4</sub>. With TiCl<sub>3</sub>OBu and water, the features of the polymerization are however near those of a "living" process.

#### IV. Discussion

The first point is that "living" polymers can be obtained with initiating systems which are not very different from those used for years in conventional cationic polymerizations. The use of initiators (then called cocatalysts) associated with a variety of Lewis acids has been widely spread and did not lead to "living" polymers.

However, in an early article about what they called quasiling polymerization of indene, Kennedy and colleagues<sup>16</sup> already observed at -50 °C in CH<sub>2</sub>Cl<sub>2</sub>, in the presence of TiCl<sub>4</sub>/H<sub>2</sub>O and TiCl<sub>4</sub>/2-chloroindane as initiating systems, an approximately linear increase in the molecular weight of polyindene with the amount of monomer polymerized and, this for  $\bar{M}_n$  = 40 000–60 000. However, the plot did not pass through the origin and the number of macromolecules increased with polymer yield. The authors attributed this increase to transfer reactions. How can this be understood if transfer to monomer is not easily detected at -40 °C up to 40 000 in the present work? While it is possible that these data were in part resulting from a problem of monomer purity (not indicated), the main reason was probably slow initiation resulting from

Table X  
Influence of the Concentration of Hydrogen Chloride on the Polymerization of Indene in the Presence of  $\text{TiCl}_4$  and  $\text{TiCl}_3\text{OBU}^a$

[indene] (mol·L <sup>-1</sup> )	10 <sup>3</sup> [HCl] (mol·L <sup>-1</sup> )	Lewis acid (2 × 10 <sup>-2</sup> mol·L <sup>-1</sup> )	10 <sup>2</sup> [DMSO] (mol·L <sup>-1</sup> )	$\bar{M}_n$ (expt)	$\bar{M}_n$ (calc)	10 <sup>3</sup> [N] (mol·L <sup>-1</sup> )	$\bar{M}_w/\bar{M}_n$
0.215	0	$\text{TiCl}_4$	2.5	106 000		0.2	2.5
0.215	1.4	$\text{TiCl}_4$	2.5	79 000	17 800	0.3	2.5
0.646	1.4	$\text{TiCl}_4$	2.5	117 000	53 600	0.6	2.7
0.215	1.4	$\text{TiCl}_3\text{OBU}$	0	104 000	17 800	0.2	2.1

<sup>a</sup> Solvent,  $\text{CH}_2\text{Cl}_2$ ; temperature,  $-40^\circ\text{C}$ .

very slow monomer addition giving continuously new polymer chains.

The polymerizations described in the present paper are very similar to those reported by Kennedy for *p*-methylstyrene (for  $\bar{M}_n$  up to 25 000 and  $\bar{M}_w/\bar{M}_n = 2.6$ – $5.4^3$  at  $-30^\circ\text{C}$ ) and more recently for *p*-chlorostyrene (for  $\bar{M}_n$  up to 10 000 and  $\bar{M}_w/\bar{M}_n = 1.37$ – $1.8^5$  at  $-80^\circ\text{C}$ ), and similar conclusions may be drawn for all these systems. The main features of these polymerizations are as follows: (1) a linear increase of the  $\bar{M}_n$  with conversion is observed, (2) the concentration of macromolecules is equal to or very near the initiator concentration, (3) this is sometimes still true after a new monomer addition, and (4) the molecular weight distribution is relatively broad ( $\bar{M}_w/\bar{M}_n > 2$ ).

To observe a living polymerization, the first condition should be quantitative initiation, leading to features 1 and 2. This is not a necessary condition for the formation of a living polymer, but it is a primary requirement to observe its presence. The initiating system should have a high efficiency to ensure complete transformation of the initiator into macromolecules before complete conversion is obtained and, consequently,  $R_i/R_p$  should be sufficiently high, and this is the case with CumOMe/ $\text{TiCl}_4$ .

The results obtained here with water or HCl may be due to incomplete initiation. These compounds have been generally assumed to be the adventitious initiators instrumental in polymerizations carried out in the presence of Lewis acids "alone", but the results were sometimes ambiguous.

The initiating role of water in the polymerization of indene in the presence of  $\text{TiCl}_4$ , in methylene chloride solution, has already been investigated.<sup>17,18</sup> It could not be concluded whether at  $-70^\circ\text{C}$  in the absence of added initiator the complete conversion obtained, even in super dry conditions (all-glass sealed apparatus), resulted from cocatalysis or from direct initiation by the metal halide. However, in the presence of a large excess of cumyl methyl ether, as is the case in the present paper, the contribution of these reactions may be small and perhaps negligible.

In the case of  $\text{TiCl}_3\text{OBU}$ , the influence of water and hydrogen chloride on the polymerization of cyclopentadiene<sup>19</sup> and of  $\alpha$ -methylstyrene<sup>20</sup> has been investigated. The results clearly show the existence of initiation (cocatalysis) by water. In dry conditions, the polymerization of  $\alpha$ -methylstyrene stopped at low yields (4–10%), but started again and went to completion upon addition of water. Water is an initiator, but although the  $\bar{M}_n$  of the polymers were in the range of the theoretical values, there was no simple relationship between the experimental figures and the concentration of added water.

These results are in agreement with the experiments carried out in the present work. With  $\text{TiCl}_4$ , the high  $\bar{M}_n$  obtained (with respect to the calculated values) shows that water in relatively large amounts ( $10^{-3}$  mol·L<sup>-1</sup>) is not an efficient initiator. With the  $\text{H}_2\text{O}/\text{TiCl}_3\text{OBU}$  initiating system,  $\bar{M}_n$  increases linearly with the weight of monomer polymerized and is only double the calculated values (Table IX). The initiating efficiency of water in this case is 50%.

Conversely, CumOMe/ $\text{TiCl}_4$  and CumOMe/ $\text{TiCl}_3\text{OBU}$  are conventional initiating systems which ensure quantitative initiation without addition of an electron-donating compound (high  $R_i/R_p$ ).

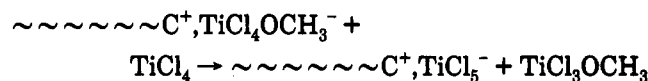
One of the requirements for a living polymerization is that all the macromolecules retain their propagating ability (absence of termination). In the present case, the observation of conditions 1–3 does not give information on the possible occurrence of termination reactions,<sup>13,14</sup> and the expected  $\bar{M}_n$  can always be obtained as long as there are enough active centers left to carry out the polymerization to completion.

Polymerizations with the CumOMe initiator went to completion in less than 5 s. However, in experiments involving monomer addition after the first polymerization, the addition was made 6 min after the start of the reaction, and the polymer still had the expected  $\bar{M}_n$  and a similar molecular weight distribution. This shows that termination was absent during this time.

It has been proposed that the presence of free ions favors transfer reactions, and that their concentration could be reduced either by using solvents of lower dielectric constant or by the addition of a common ion salt.<sup>21,22</sup> Another suggestion has been that electron donors could solvate the ionic species, stabilizing them and suppressing transfer and termination.<sup>11</sup> With the use of the CumOMe/ $\text{TiCl}_4$  initiating system at  $-40^\circ\text{C}$ , there is no visible change in the importance of transfer reactions and in the molecular weight distribution of the polymer obtained either by adding DMSO or by decreasing the polarity of the solvent ( $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_{14}$  60/40 mixture instead of  $\text{CH}_2\text{Cl}_2$ ). Preliminary experiments with tetra-*n*-butylammonium chloride as a common ion salt led only to a limited narrowing of the molecular weight distribution (from 2.3 to 2.0).

The relatively low transfer constant at  $-40^\circ\text{C}$  and the absence of transfer at  $-75^\circ\text{C}$  may result from the nature of the counterion, assumed to be methoxytetrachlorotitanium. But we shall see in the next paper that very similar results have been obtained by using as initiator cumyl chloride or chloroindane, with the addition of dimethyl sulfoxide, which is not necessary in the present case.

In the case of CumOMe/ $\text{TiCl}_4$ , the structure of the counterion is not well defined, since chlorine exchange might occur between  $\text{TiCl}_4$  and  $\text{TiCl}_4\text{OMe}$ :



An exchange of this type, yielding  $\text{TiCl}_5^-$ , is improbable when  $\text{TiCl}_3\text{OBU}$ , which should yield a methoxybutoxytrichlorotitanium anion, is used instead of  $\text{TiCl}_4$ . In this case, a very low transfer constant and narrower molecular weight distributions were obtained at  $-40^\circ\text{C}$ .

Initiation with a terminated polyindene (cf. paragraph F) shows that the end groups of "dead" macromolecules retain their propagating ability even after termination. According to Kennedy, the terminations of polymerizations of isobutylene<sup>1</sup> and styrene<sup>2</sup> with alcohols yield chlorinated



end groups. If this is also the case with indene, termination may be represented as in eq 2, giving a chloroindan end group. This implies that conventional polymerizations initiated with arylalkyl chlorides should also yield living polymers, provided the  $R_i/R_p$  ratio is high enough. This will be seen in the next article.

Does reversible termination take place also during the polymerization process? In this case termination should be written as an equilibrium. The active centers involved in the polymerization would not be active throughout the whole reaction, but each chain end would be successively active and dormant and possibly undergo several reactivations. Rapid initiation would yield the expected concentration of active chains with an equilibrium between the growing and dormant species.

However, there are still various aspects of this reaction which are not completely understood. While the relatively high values of  $\bar{M}_w/\bar{M}_n$  (1.7–3 according to the counterion and the experimental conditions) may be tentatively explained by a relatively slow exchange between active and inactive sites, this has not been proven and more detailed kinetic data are needed to check this point. This could allow the verification of whether the narrowing of  $\bar{M}_w/\bar{M}_n$  with a change of counterion results simply from a slowing down of the reaction permitting a larger number of exchanges during chain growth.

The last requirement to obtain living polymer is the absence of transfer.

This condition is not met at  $-40^\circ\text{C}$  with  $\text{TiCl}_4$ , and the results show a transfer to the monomer ( $k_{\text{trM}}/k_p = 5 \times 10^{-4}$ ). However, this transfer is masked at low monomer concentrations, and apparent linearity between  $\bar{M}_n$  and  $[\text{M}]_0$  is observed up to  $\bar{M}_n = 40\,000$ .

For complete conversion, which is the case here, the expression

$$\overline{\text{DP}}_n = \frac{1}{[\text{I}]_0/[\text{M}]_0 + k_{\text{trM}}/k_p}$$

shows that the important parameter, which determines the range of monomer concentrations in which apparently living polymerization can be observed, is the ratio  $[\text{I}]_0/[\text{M}]_0$ . At  $-40^\circ\text{C}$ , apparent linearity is still observed for  $[\text{M}]_0 = 0.86\text{ mol}\cdot\text{L}^{-1}$  and  $[\text{I}]_0 = 4.5 \times 10^{-3}\text{ mol}\cdot\text{L}^{-1}$  (experiment 11, Table III), i.e. a  $[\text{I}]_0/[\text{M}]_0$  ratio of about  $5 \times 10^{-3}$ , 10 times the value of the transfer constant. For lower values of this ratio,  $\bar{M}_n$  is no longer proportional to  $[\text{M}]_0$  (cf. experiment 15, Table III). At  $-75^\circ\text{C}$ , transfer can no longer be detected for  $\bar{M}_n$  up to 100 000, and the polymerization might be considered as truly living.

## Conclusions

Our provisional conclusion concerning these systems is that there is no basic difference in the polymerization mechanism for systems said to be living and those of conventional cationic polymerizations. We have shown that the same relative amount of transfer occurs in a region in which the  $\bar{M}_n$  are proportional to polymer yield and in a region in which this proportionality is no longer observed. The polymerizations we have been calling "living" in this paper, and which could better be called apparently living,

include reactions which are not living when they are carried out at  $-40^\circ\text{C}$ , since transfer reactions are quite significant and since the occurrence of partial definitive termination cannot be excluded. For all practical purposes, these polymerizations became indistinguishable from living ones when they were carried out at  $-75^\circ\text{C}$ , the main reason being that the transfer constant becomes either very small and not measurable, or nil. Consequently, a given system may be improved toward greater livingness by a change in experimental conditions. The two main factors governing the living character are (1) the  $R_p/R_i$  ratio, which must be low to ensure quantitative initiation (One of the possible effects of added electron-donating compounds may be to increase  $R_i$  and to decrease  $R_p$ , thus assuring quantitative initiation. In the following paper, we shall see that other types of initiating systems may lead to similar results, but only in the presence of additives which are necessary in order to decrease  $R_p/R_i$ ) and (2) the initiator to monomer ratio, which should be high enough to mask the transfer reactions (This limits the molecular weights obtainable and explains why the range of molecular weights reported in most cases was well below 30 000).

It is possible to choose the experimental conditions to improve livingness, for instance by operating at lower temperatures, which reduces and possibly suppresses transfer.

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**Registry No.**  $\text{TiCl}_4$ , 7550-45-0;  $\text{TiCl}_3\text{OBu}$ , 142895-82-7; indene, 95-13-6; indene (homopolymer), 9003-64-9; CumOMe, 27476-56-8.