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# "Living" Cationic Polymerization of Indene. 2. Polymerization Initiated with Cumyl Chloride/Titanium Tetrachloride and Cumyl Chloride/*n*-Butoxytrichlorotitanium Initiating Systems

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ABSTRACT: The polymerization of indene in methylene chloride solution initiated with cumyl chloride and titanium tetrachloride has been investigated as a possibly "living" system. At −40 °C, initiation is quantitative only in the presence of dimethyl sulfoxide (DMSO) as an electron-donating compound. Linear growth of the $\bar{M}_n$ with the amount of monomer converted can be observed for monomer to initiator ratios lower than 200, although transfer does take place ($k_{trM}/k_{p,-40°C} = 6 \times 10^{-4}$). At +5 °C, linear growth is observed only up to $\bar{M}_n \approx 15\,000$, initiation is quantitative without DMSO, and this compound does not reduce transfer ($k_{trM}/k_{p,+5°C} = 1.4 \times 10^{-3}$ in both cases). At −75 °C, initiation is not quantitative, even in the presence of DMSO. Common ion salts have the same effect as DMSO on the molecular weight distribution and on the "living" character, and this is attributed to a shift of equilibria between dormant covalent species, ion pairs, and free ions, favoring the exchanges between active and dormant species. This implies the existence of a reversible termination, which is confirmed by initiation with a model of the chain end (1-chloroindan). Slow exchange between active and dormant species may explain the relatively broad molecular weight distributions observed ($\bar{M}_w/\bar{M}_n \approx 2$–3). Better results ($\bar{M}_w/\bar{M}_n \approx 1.6$–2) are obtained with *n*-butoxytrichlorotitanium as coinitiator at −40 °C, without DMSO. The two parameters allowing the observation of a "living" polymerization are the propagation to initiation rate ratio, which must be low enough to allow quantitative initiation, and the monomer to initiator ratio, which must be low enough to yield low molecular weight polymers, for which transfer is undetectable. Besides, as could be expected, transfer is reduced at low temperatures. These results may be accounted for by classical carbocationic polymerization mechanisms.

## I. Introduction

Several papers reporting the obtention of living polymers by cationic polymerization have been published recently,[1–3] and various mechanisms have been proposed to account for these reactions. These results raise two questions: Are these polymerizations really living, i.e., without transfer and termination, and are they basically different from the "conventional" carbocationic polymerizations? The difficulty of providing evidence for the absence of transfer and termination has already been emphasized.[4] This is particularly the case for polymers of low molecular weights for which there may be a linear increase of the $\bar{M}_n$ with the amount of polymer formed even if transfer is significant (but cannot be detected). When such a linearity is observed, we have suggested that the polymerizations should be called "apparently living"[4] or simply "living",[5] and this terminology shall be used in the present article.

In the first paper of this series, it has been found that transfer does occur during the polymerization of indene initiated with the cumyl methyl ether/titanium tetrachloride ($TiCl_4$) initiating system at −40 °C and that it becomes undetectable only at −75 °C.[5] It has been considered that the experimental data could be accounted for by a "conventional" mechanism, the "living" character depending on two ratios: the monomer to initiator ratio ($[M]_0/[I]_0$), which determines to what extent transfer can remain undetected, and the propagation to initiation rate ratio ($R_p/R_i$). If this last ratio is low enough, initiation is quantitative and an increase of the $\bar{M}_n$ proportional to conversion can be observed. For low enough values of these two ratios, the reaction has the main features of a living polymerization.

As chlorine derivatives have been widely used as initiators (formerly called cocatalysts) in the conventional carbocationic polymerizations, it seemed interesting to check whether polymerizations initiated with a chlorine derivative, such as cumyl chloride, would support these conclusions.

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**Table I. Polymerization of Indene Initiated with the CumCl/$TiCl_4$ Initiating System[a]**

| expt no. | [indene] ($mol{\cdot}L^{-1}$) | [CumCl] ($mol{\cdot}L^{-1}$ $\times 10^3$) | $\bar{M}_n$(expt) | $\bar{M}_n$(calc) | $\bar{M}_w/\bar{M}_n$ | [N] ($mol{\cdot}L^{-1}$ $\times 10^3$) |
|---|---|---|---|---|---|---|
| 1 | 0.43 | 0 | 87 000 | | 2.3 | 0.6 |
| 2 | 0.107 | 3.0 | 6 100 | 4 150 | 4.5 | 2.0 |
| 3 | 0.215 | 3.0 | 13 200 | 8 300 | 4.8 | 1.9 |
| 4 | 0.430 | 3.0 | 25 900 | 16 600 | 4.9 | 1.9 |
| 5 | 0.650 | 3.0 | 27 150 | 25 000 | 4.2 | 2.8 |
| 6 | 0.860 | 3.0 | 38 050 | 33 200 | 3.7 | 2.6 |
| 7 | 0.43 | 1.0 | 40 000 | 50 000 | 3.6 | 1.2 |
| 8[b] | 0.43 | 3.0 | 26 000 | 16 600 | 4.2 | 1.9 |
| 9[c] | 0.43 | 3.0 | 27 300 | 16 600 | 3.2 | 1.8 |

[a] $[TiCl_4] = 2 \times 10^{-2}$ $mol{\cdot}L^{-1}$; solvent, $CH_2Cl_2$; temperature = −40 °C; yield 100%. [b] $[TiCl_4] = 10^{-1}$ $mol{\cdot}L^{-1}$. [c] $CH_2Cl_2/C_6H_{14}$ (60/40 v/v).

## II. Experimental Section

The experimental procedures and the preparations and purifications of indene, $TiCl_4$, $TiCl_3OBu$, and methylene chloride have already been described.[5] Cumyl chloride was prepared by bubbling dry hydrogen chloride through a solution of α-methylstyrene in methylene dichloride. The reaction was monitored by NMR. The solvent was evaporated and the cumyl chloride was distilled under reduced pressure. Methylene chloride solutions of this compound were prepared under vacuum; they were titrated using the Volhard method and were stored under vacuum in the dark at −30 °C to avoid decomposition. Tetra-*n*-butylammonium pentachlorotitanate was prepared by mixing methylene chloride solutions of $TiCl_4$ and tetra-*n*-butylammonium chloride in equimolar amounts. The yellow solution obtained was stored under vacuum.

The polymerizations were carried out under vacuum and were terminated by addition of methanol 6 min after the start of the reaction, unless otherwise stated. The conversion was complete in all cases, even in the absence of added initiator. The incremental monomer additions (IMA) were carried out by adding new monomer, 6 min after the start of the first polymerization, to a polymerized system. The $\bar{M}_n$ reported is that of the polymer recovered after the two polymerizations and is to be compared with the $\bar{M}_n$ of a test experiment involving the first polymerization. The polyindenes were recovered by evaporating the solvent, and the molecular weights of the polymers were measured by gel permeation chromatography as already reported.[5]

## III. Results

**(A) Polymerizations Carried out at −40 °C. Initiation with the Cumyl Chloride/$TiCl_4$ Initiating System.** The results of polymerizations initiated with cumyl chloride and $TiCl_4$ at −40 °C are reported in Table I. First of all, initiation by $TiCl_4$ alone, without cumyl chloride, produces a polyindene with a high $\bar{M}_n$ ($\bar{M}_n$ = 87 000, Table I, expt 1), and in this case initiation probably results from the presence of an adventitious cocatalyst present in the solution. In the presence of cumyl chloride, the $\bar{M}_n$s of the polymers are much lower, but still higher than the values calculated assuming quantitative initiation by the cumyl chloride, and they increase with the weight of polymer formed (i.e., with the monomer concentration since conversion is always complete). This increase is practically linear for monomer to initiator ratios up to 150 ($[M] = 0.43$ $mol{\cdot}L^{-1}$; $[I] = 3 \times 10^{-3}$ $mol{\cdot}L^{-1}$; cf. Figure 1), and there is a curvature for higher values of this ratio ($[M] = 0.86$ $mol{\cdot}L^{-1}$; $[M]/[I] = 290$, expt 6). Besides, for a value of [M]/[I] equal to 430 (expt 7) the experimental $\bar{M}_n$ is lower than the calculated one.

Values of $\bar{M}_n$ higher than the calculated ones obtained at low indene concentrations can be explained by incomplete initiation, either because initiation is too slow for the cumyl chloride to be entirely reacted before all the monomer is consumed or because a fraction of the cumyl chloride is converted into byproducts which cannot initiate the polymerization (e.g., α-methylstyrene and hydrogen chloride). The curvature of the $\bar{M}_n$ vs [M] plot (expt 6) and the lower than expected $\bar{M}_n$ (expt 7) may be attributed to transfer reactions, which have been shown to take place in the case of initiation with cumyl methyl ether, also occurring in this system. An experiment carried out with a higher $TiCl_4$ concentration (0.1 $mol{\cdot}L^{-1}$ instead of $2 \times 10^{-2}$ $mol{\cdot}L^{-1}$) in an attempt to increase the initiation rate did not significantly change the $\bar{M}_n$ of the polyindene (compare expts 8 and 4). Similarly, the use of a mixture of solvents to shift a possible inonization equilibrium toward the ion pairs, supposedly less reactive, and to decrease the propagation rate failed to achieve complete initiation (compare expts 9 and 4). In all these experiments, the molecular weight distributions of the polymers are rather broad ($\bar{M}_w/\bar{M}_n$ from 3.6 to 4.9), broader than those observed without cumyl chloride. The CumCl/$TiCl_4$ initiating system alone does not yield a "living" polymer.

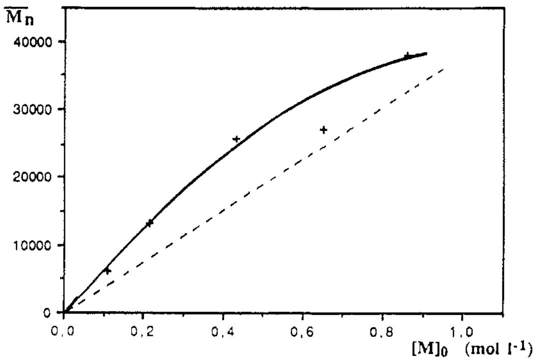


**Figure 1.** Polymerization of indene initiated with the CumCl/$TiCl_4$ initiating system at −40 °C. Variation of the $\bar{M}_n$ with the amount of monomer polymerized. Conditions: $[TiCl_4] = 2 \times 10^{-2}$ $mol{\cdot}L^{-1}$; $[CumCl] = 3 \times 10^{-3}$ $mol{\cdot}L^{-1}$; solvent, $CH_2Cl_2$; reaction time = 6 min; yield 100%; (- - -) calculated line.

In conclusion, in this system the $\bar{M}_n$s of the polyindenes result from two opposite effects: incomplete initiation, which increases the $\bar{M}_n$ by comparison with the theoretical values, and transfer, which decreases it.

**Initiation with the Cumyl Chloride/$TiCl_4$/DMSO Initiating System.** It has been reported by Kennedy[6] and by other authors[7] that addition of electron-donating compounds in isobutylene polymerization initiated with alkyl chloride compounds and $TiCl_4$ or $BCl_3$, which would otherwise yield a "nonliving" polymer, may turn it into a "living" system. Several interpretations of this phenomenon have been proposed.[8,9] In the present case, the influence of various electron-donating compounds has been investigated (Table II) by comparing the $\bar{M}_n$ of the polymer with the expected value. The molecular weight distributions are also reported in this table. Among the various compounds used, dimethyl sulfoxide (DMSO) alone yielded the expected $\bar{M}_n$ and narrower molecular weight distributions than those obtained without DMSO. 2,5-Di-*tert*-butyl-4-methylpyridine, which was used at various concentrations, had no apparent influence on the $\bar{M}_n$ of the resulting polymer (cf. expts 8 and 9 of Table II).

Consequently, DMSO was used in the following experiments (Table III). In the presence of this compound ($2.5 \times 10^{-3}$ $mol{\cdot}L^{-1}$), for [M]/[I] ratios lower than about 200, the $\bar{M}_n$ increases linearly with the weight of polymer formed and is only slightly lower than the calculated values of $\bar{M}_n$ up to 30 000, which may result from moderate transfer reactions (Figure 2, curve A). For higher values of this ratio, transfer becomes clearly detectable (curve B). The polyindene of expt 4, which has a $\bar{M}_n$ higher than the

**Table II. Influence of Additives on the Polymerization of Indene Initiated with the CumCl/$TiCl_4$ Initiating System**[a]

| electron-donating compd | concn (mol·$L^{-1}$ × $10^3$) | $\bar{M}_n$(expt) | $\bar{M}_n$(calc) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|
| none | 0 | 13 200 | 8 300 | 4.8 |
| dimethyl sulfoxide | 2.5 | 8 600 | 8 300 | 3.1 |
| dimethylformamide | 2.5 | 15 700 | 8 300 | 3.1 |
| dimethylformamide | 7.0 | 5 300 | 8 300 | 3.3 |
| dimethylacetamide | 2.5 | 10 800 | 8 300 | 3.3 |
| ethyl acetate | 2.5 | 13 200 | 8 300 | 5.0 |
| 2,4-pentanedione | 2.5 | 9 000 | 8 300 | 4.3 |
| 2,5-di-*tert*-butyl-4-methylpyridine | 0.1 | 13 500 | 8 300 | 3.9 |
| 2,5-di-*tert*-butyl-4-methylpyridine | 0.5 | 13 800 | 8 300 | 3.2 |
| tetrahydrothiophene | 2.5 | 5 400 | 8 300 | 4.0 |

[a] [Indene] = 0.215 mol·$L^{-1}$; [CumCl] = 3 × $10^{-3}$ mol·$L^{-1}$; [$TiCl_4$] = 2 × $10^{-2}$ mol·$L^{-1}$; temperature = −40 °C; solvent, $CH_2Cl_2$.

**Table III. Polymerization of Indene Initiated with the CumCl/$TiCl_4$ Initiating System in the Presence of DMSO**[a]

| expt no. | [indene] (mol·$L^{-1}$) | [CumCl] (mol·$L^{-1}$ × $10^3$) | $\bar{M}_n$(expt) | $\bar{M}_n$(calc) | $\bar{M}_w/\bar{M}_n$ | [N] (mol·$L^{-1}$ × $10^3$) |
|---|---|---|---|---|---|---|
| 1 | 0.43 | 0 | 65 000 |  | 2.4 | 0.8 |
| 2 | 0.215 | 3.0 | 8 600 | 8 300 | 3.1 | 2.9 |
| 3 | 0.43 | 3.0 | 15 500 | 16 600 | 3.1 | 3.2 |
| 4[b] | 0.63 | 3.0 | 27 100 | 24 500 | 3.7 | 2.7 |
| 5 | 0.86 | 3.0 | 30 300 | 33 200 | 3.2 | 3.3 |
| 6 | 0.43 | 1.5 | 29 300 | 33 200 | 2.8 | 1.7 |
| 7 | 0.215 | 1.0 | 25 000 | 25 000 | 2.8 | 1.0 |
| 8 | 0.43 | 1.0 | 43 000 | 50 000 | 2.5 | 1.1 |
| 9 | 0.86 | 1.0 | 71 200 | 100 000 | 2.1 | 1.4 |

[a] [$TiCl_4$] = 2 × $10^{-2}$ mol·$L^{-1}$; [DMSO] = 2.5 × $10^{-3}$ mol·$L^{-1}$; solvent, $CH_2Cl_2$; temperature = −40 °C; yield 100%. [b] Incremental monomer addition. First polymerization: cf. expt no. 3; $[M]_0$ = 0.43 mol·$L^{-1}$.

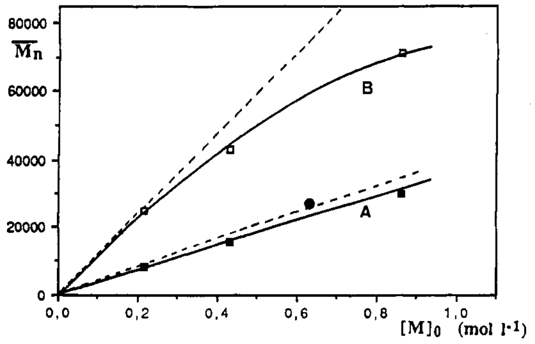


**Figure 2.** Polymerization of indene initiated with the CumCl/$TiCl_4$/DMSO initiating system at −40 °C. Variation of the $\bar{M}_n$ with the amount of monomer polymerized. Conditions: [$TiCl_4$] = 2 × $10^{-2}$ mol·$L^{-1}$; solvent, $CH_2Cl_2$; reaction time = 6 min; yield 100%; (- - -) calculated line. [CumCl]: (■) 3 × $10^{-3}$ mol·$L^{-1}$; (●) 3 × $10^{-3}$ mol·$L^{-1}$ (IMA, second addition after 6 min); (□) 1 × $10^{-3}$ mol·$L^{-1}$.

calculated value, was obtained by incremental monomer addition. In this experiment, 0.2 mol·$L^{-1}$ of indene was added 6 min after the start of the first polymerization (initial monomer concentration: 0.43 mol·$L^{-1}$).

The corresponding Mayo plot, which includes all the points of Figure 2, has a positive intercept which yields the value of the transfer constant ($k_{trM}/k_p$ = 6 × $10^{-4}$, Figure 3). The linearity of the plot, even for low values of $1/DP_{n0}$, (i.e., $[C]_0/[M]_0$), shows that transfer reactions of zero order with respect to the monomer[4] (transfer to the solvent or "spontaneous" transfer to the counterion), if they take place at all, are negligible. The $\bar{M}_w/\bar{M}_n$ values are smaller than in the previous experiments (2.1–3.3 instead of 3.6–4.9). With the CumCl/$TiCl_4$ initiating system, DMSO is necessary to obtain the characteristics of a "living" system.

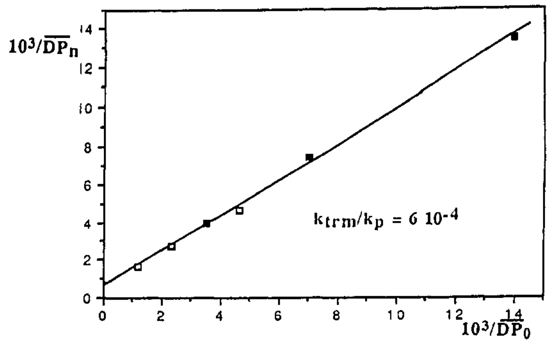


**Figure 3.** Measurement of the transfer rate constant to the monomer in the polymerization of indene at −40 °C. Conditions: initiating system, CumCl/$TiCl_4$/DMSO; solvent, $CH_2Cl_2$; [$TiCl_4$] = 2 × $10^{-2}$ mol·$L^{-1}$; [DMSO] = 2.5 × $10^{-3}$ mol·$L^{-1}$. [CumCl]: (■) 3 × $10^{-3}$ mol·$L^{-1}$; (□) $10^{-3}$ mol·$L^{-1}$.

**Initiation with the 1-Chloroindan/$TiCl_4$/DMSO Initiating System.** The possibility of a reversible termination has been considered in our previous paper.[5] In the present case, reversible termination by collapse of the carbocationic pentachlorotitanate ion pair should yield a polyindene with a chlorinated end group. If this is the case, the model of the chlorinated end group, 1-chloroindan, should be the initiator for this polymerization. The results of polymerizations initiated with 1-chloroindan instead of cumyl chloride are reported in Table IV. As with cumyl chloride, the presence of DMSO is necessary to obtain the expected $\bar{M}_n$ (compare expts 1 and 3 of Table IV). This shows the possibility of a reversible termination in the case of initiation by $TiCl_4$:

$$\sim\sim\sim C\text{–}Cl + TiCl_4 \overset{K_i}{\rightleftarrows} \sim\sim\sim C^+,TiCl_5^- \qquad (1)$$

The data are similar to those obtained with cumyl chloride, but there is some scatter and the Mayo plot has an intercept of 1.4 × $10^{-3}$ instead of 6 × $10^{-4}$.

**Polymerizations Initiated with the CumCl/$TiCl_4$ Initiating System in the Presence of a Common Ion Salt.** Addition of a common ion salt to an initiating system yielding a bimodal molecular weight distribution often suppresses one of the peaks.[10] This has been attributed to a shift of a dissociation equilibrium suppressing the free ions, the remaining ion pairs being the only propagating species.

In the present case, addition of tetra-*n*-butylammonium chloride or of tetra-*n*-butylammonium pentachlorotitanate to the CumCl/$TiCl_4$ initiating system (without DMSO) causes a lowering of the $\bar{M}_n$ from 26 000 to 14 000, which is near the calculated value for a living polymer (Table V). Besides, the molecular weight distribution is significantly narrower (2.4 instead of 4.9). The common ion salt has an effect similar to that of DMSO. It may be assumed that the salt shifts a dissociation equilibrium toward the formation of the ion pairs and covalent species. The broadening of the molecular weight distribution in the absence of salt could result either from a higher reactivity of the free ions or only from their slower interconversion into ion pairs and covalent species, or from both:

$$\sim\sim\sim C\text{–}Cl + TiCl_4 \rightleftarrows \sim\sim\sim C^+,TiCl_5^- \rightleftarrows \sim\sim\sim C^+ + TiCl_5^- \qquad (2)$$

The results of comparative experiments carried out with cumyl methyl ether (4.5 × $10^{-3}$ mol·$L^{-1}$) are reported in

Table IV. Polymerization of Indene Initiated with the 1-Chloroindan/$TiCl_4$ Initiating System in the Presence of DMSO[a]

| expt no. | [indene] (mol·L$^{-1}$) | [1-chloroindan] (mol·L$^{-1}$ × $10^3$) | $\bar{M}_n$(expt) | $\bar{M}_n$(calc) | $\bar{M}_w/\bar{M}_n$ | [N] (mol·L$^{-1}$ × $10^3$) |
|---|---|---|---|---|---|---|
| 1 | 0.215 | 3.0 | 15 500 | 8 300 | 3.7 | 1.6 |
| 2 | 0.215 | 1.5 | 14 300 | 16 600 | 3.0 | 1.8 |
| 3 | 0.215 | 3.0 | 7 800 | 8 300 | 3.0 | 3.2 |
| 4 | 0.43 | 3.0 | 13 200 | 16 600 | 3.6 | 3.8 |
| 5 | 0.86 | 3.0 | 24 500 | 33 200 | 3.0 | 4.0 |

[a] [$TiCl_4$] = 2 × $10^{-2}$ mol·L$^{-1}$; [DMSO] = 2.5 × $10^{-3}$ mol·L$^{-1}$ (except expt 1, where [DMSO] = 0); solvent, $CH_2Cl_2$; temperature = −40 °C.

Table V. Influence of Common Ion Salts on the Polymerization of Indene (0.43 mol·L$^{-1}$) Initiated with $TiCl_4$ (2 × $10^{-2}$ mol·L$^{-1}$) in the Presence of CumOMe (4.5 × $10^{-3}$ mol·L$^{-1}$) and CumCl (3 × $10^{-3}$ mol·L$^{-1}$)[a]

| initiating system | common ion salt (mol·L$^{-1}$ × $10^3$) | yield (%) | $\bar{M}_n$(calc) | $\bar{M}_n$(expt) | [N] (mol·L$^{-1}$ × $10^3$) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|---|
| CumOMe (4.5 × $10^{-3}$ mol·L$^{-1}$) | 0 | 100 | 11 100 | 10 600 | 4.7 | 2.3 |
|  | n-$Bu_4NCl$ (8 × $10^{-3}$) | 100 | 10 100 | 9 450 | 5.2 | 2.0 |
| CumCl (3 × $10^{-3}$ mol·L$^{-1}$) | 0 | 100 | 16 600 | 25 900 | 1.9 | 4.9 |
|  | n-$Bu_4NCl$ (8 × $10^{-3}$) | 100 | 16 600 | 13 500 | 3.7 | 2.4 |
|  | n-$Bu_4NTiCl_5$ (8 × $10^{-3}$) | 100 | 16 600 | 14 450 | 3.4 | 2.4 |

[a] Solvent, $CH_2Cl_2$; temperature = −40 °C; reaction time for all experiments, 6 min.

Table VI. Polymerization of Indene Initiated with a Mixture of Cumyl Methyl Ether and Cumyl Chloride at −40 °C[a]

| CumCl (mol·L$^{-1}$ × $10^3$) | CumOMe (mol·L$^{-1}$ × $10^3$) | $\bar{M}_n$(expt) | $\bar{M}_n$(calc) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|
| 1.5 | 1.5 | 16 000 | 16 600 | 3.2 |

[a] [$TiCl_4$] = 2 × $10^{-2}$ mol·L$^{-1}$; reaction time = 6 min; yield 100%.

Table VII. Polymerization of Indene Initiated with the CumCl/$TiCl_3OBu$ Initiating System (without DMSO)[a]

| expt no. | [indene] (mol·L$^{-1}$) | [CumCl] (mol·L$^{-1}$ × $10^3$) | $\bar{M}_n$(expt) | $\bar{M}_n$(calc) | $\bar{M}_w/\bar{M}_n$ | [N] (mol·L$^{-1}$ × $10^3$) |
|---|---|---|---|---|---|---|
| 1 | 0.215 | 3.0 | 6 450 | 8 300 | 2.4 | 3.6 |
| 2 | 0.43 | 3.0 | 13 500 | 16 600 | 2.0 | 3.7 |
| 3[b] | 0.63 | 3.0 | 22 100 | 24 500 | 2.1 | 3.8 |
| 4 | 0.86 | 3.0 | 27 200 | 33 200 | 1.9 | 3.7 |
| 5 | 0.215 | 1.0 | 20 000 | 25 000 | 1.8 | 1.2 |
| 6 | 0.43 | 1.0 | 43 700 | 50 000 | 1.6 | 1.1 |
| 7 | 0.86 | 1.0 | 79 000 | 100 000 | 2.0 | 1.2 |

[a] [$TiCl_3OBu$] = 2 × $10^{-2}$ mol·L$^{-1}$; solvent, $CH_2Cl_2$; temperature, −40 °C. [b] Incremental monomer addition. First polymerizaton: cf. expt no. 2; $[M]_0$ = 0.43 mol·L$^{-1}$.

the same table. Tetra-n-butylammonium chloride has little effect on the molecular weight distribution.

In the case of initiation with cumyl methyl ether, one might have thought that, although the counterion initially formed is the methoxytetrachlorotitanate ($TiCl_4OMe^-$), pentachlorotitanate ions ($TiCl_5^-$) would be rapidly formed through reactivation by the excess $TiCl_4$ of the dormant chlorinated end groups (if it is assumed that reversible termination involves the addition of a chlorine atom from the $TiCl_4OMe^-$ anion). If this was the case, the propagation would involve mainly pentachlorotitanate counterions at the end of the polymerization, and a common ion effect would have been observed with n-$Bu_4NCl$ in the polymerizations initiated with cumyl methyl ether as has been found with cumyl chloride.

The absence of a significant common ion effect leads us to infer that the active centers present in the polymerizations initiated with the CumOMe/$TiCl_4$ initiating system are different from those formed with the CumCl/$TiCl_4$ system and that they are presumably methoxytetrachlorotitanate anions. This may result either from reversible termination by preferential addition of a methoxy end group (instead of a chlorine atom) or from a relatively slow reactivation of the dormant chains, the main part of the polymerization involving the initially formed methoxytetrachlorotitanate anions. Preliminary NMR analysis of the end groups of low molecular weight polyindenes did not yield conclusive results.

To check the behavior of a system in which both counterions are present, polymerization of indene (0.43 mol·L$^{-1}$) was initiated with a mixture of CumOMe and CumCl (1.5 × $10^{-3}$ mol·L$^{-1}$ each; [$TiCl_4$] = 2 × $10^{-2}$ mol·L$^{-1}$) without DMSO (cf. Table VI). The $\bar{M}_n$ of the resulting polyindene has the value calculated assuming quantitative initiation by both compounds (16 000), while initiation by the equivalent amount of cumyl chloride is not quantitative (see Table I, expt 4). The molecular weight distribution is narrower than with CumCl alone (3.2 instead of 4.9) but wider than in the case of initiation by CumOMe alone (2.3). It may be assumed that the presence of propagating species resulting from initiation by cumyl methyl ether slows down the global propagation rate, thus allowing complete initiation by the cumyl chloride, even in the absence of DMSO, but that the presence of two different types of growing centers broadens the molecular weight distribution (compared with that observed with initiation by CumOMe alone).

**Initiation with the Cumyl Chloride/n-Butoxytrichlorotitanium Initiating System.** It has previously been shown that the n-butoxytrichlorotitanium/cumyl methyl ether initiating system yields polyindenes with $\bar{M}_n$s in good agreement with the calculated values, and it has been postulated that initiating systems producing alkoxytitanate counterions give better results than those involving pentachlorotitanate counterions. This is confirmed by the data of Table VII, obtained with the cumyl chloride/$TiCl_3OBu$ system (without DMSO), which show a fairly good agreement between the experimental and calculated $\bar{M}_n$, although transfer is apparent at high [M]/[I] ratios, as in the other systems (Figure 4). The polyindenes obtained have the narrowest molecular weight distributions observed with cumyl chloride (from 1.6 to 2.4), which should be expected if the global polymerization rate is smaller with this weaker Lewis acid.

**(B) Polymerizations Carried Out at −75 °C (CumCl/$TiCl_4$/DMSO).** Transfer is generally less important at low temperatures. Consequently, some experiments were carried out at −75 °C, at which temperature a "living" polymer could be obtained with cumyl methyl ether. However, when cumyl chloride is used as the initiator, the $\bar{M}_n$s of the polymers are consistently higher than the

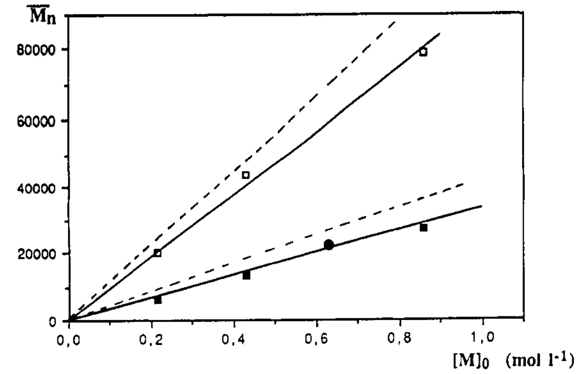


**Figure 4.** Polymerization of indene initiated with the CumCl/$TiCl_3OBu$ initiating system at −40 °C (without DMSO). Variation of the $\bar{M}_n$ with the amount of monomer polymerized. Conditions: [$TiCl_3OBu$] = $2 \times 10^{-2}$ mol·L$^{-1}$; solvent, $CH_2Cl_2$; reaction time = 6 min; yield 100%; (- - -) calculated line. [CumCl]: (■) $3 \times 10^{-3}$ mol·L$^{-1}$ (without DMSO); (●) (IMA, after 6 min); (□) $1 \times 10^{-3}$ mol·L$^{-1}$ (without DMSO).

**Table VIII. Polymerization of Indene Initiated with the Cumyl Chloride/$TiCl_4$ Initiating System in the Presence of DMSO at −75 °C**[a]

| expt no. | [indene] (mol·L$^{-1}$) | [DMSO] (mol·L$^{-1}$ × 10$^3$) | $\bar{M}_n$(expt) | $\bar{M}_n$(calc) | $\bar{M}_w/\bar{M}_n$ | [N] (mol·L$^{-1}$ × 10$^3$) |
|---|---|---|---|---|---|---|
| 1 | 0.215 | 0 | 124 000 | 8 300 | 3.1 | 0.2 |
| 2 | 0.107 | 2.5 | 15 100 | 4 150 | 3.1 | 0.82 |
| 3 | 0.215 | 2.5 | 28 800 | 8 300 | 3.3 | 0.86 |
| 4 | 0.43 | 2.5 | 48 000 | 16 600 | 3.7 | 1.04 |
| 5 | 0.86 | 2.5 | 62 400 | 33 200 | 4.4 | 1.6 |

[a] [$TiCl_4$] = $2 \times 10^{-2}$ mol·L$^{-1}$; [DMSO] = $2.5 \times 10^{-3}$ mol·L$^{-1}$ (except expt 1, where [DMSO] = 0); solvent, $CH_2Cl_2$.

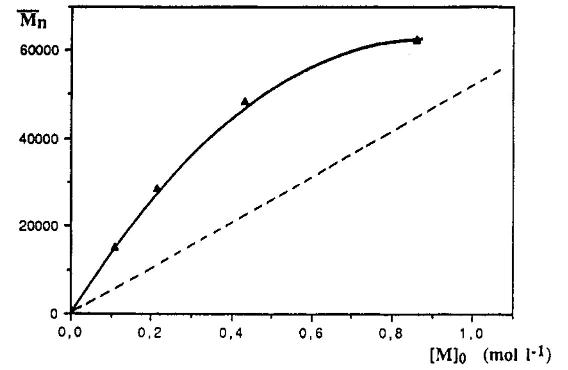


**Figure 5.** Polymerization of indene initiated with the CumCl/$TiCl_4$/DMSO initiating system at −75 °C. Variation of the $\bar{M}_n$ with the amount of monomer polymerized. Conditions: [$TiCl_4$] = $2 \times 10^{-2}$ mol·L$^{-1}$; solvent, $CH_2Cl_2$; reaction time = 6 min; yield 100%; [CumCl] = $3 \times 10^{-3}$ mol·L$^{-1}$; [DMSO] = $2.5 \times 10^{-3}$ mol·L$^{-1}$; (- - -) calculated line.

calculated values (Table VIII, Figure 5). They increase with the concentration of indene, but the plot has a curvature at high indene concentration. The high values of $\bar{M}_n$ are the consequence of incomplete initiation, and the curvature might be attributed to more efficient initiation at high monomomer concentration, to the incidence of transfer reactions, or to both. But since transfer has been found to be very low in these conditions with cumyl methyl ether, it should not be much more important in the present case (cf. results obtained at −40 °C). These results show that the initiation to propagation rate ratio is less favorable with cumyl chloride than with cumyl methyl ether.

**(C) Polymerizations Carried out at +5 °C (CumCl/$TiCl_4$ and CumCl/$TiCl_4$/DMSO).** At higher temperatures, initiation may be faster, but transfer must also be more important. It was found that, for polymerizations carried out at 5 °C, without DMSO, and for [M]/[I] ratios up to 150, the $\bar{M}_n$s of the resulting polyindenes have the values expected for a living polymer (Table IX, Figure 6, curve A). The molecular weight distributions are narrower than those obtained at −40 °C in the presence of DMSO (1.7–1.9 instead of 2.2–3.3). As in the previous systems, at higher [M]/[I] ratios, the curvature of the plot of $\bar{M}_n$ vs the amount of polymer formed shows the incidence of transfer (Figure 6, curve B). As transfer takes place at −40 °C, it should be still more important at +5 °C, but the $R_p/R_i$ ratio may be more favorable at this temperature and allows complete initiation and the formation of a "living" polymer when the molecular weights are low enough.

**Table IX. Polymerization of Indene Initiated with the CumCl/$TiCl_4$ Initiating System at +5 °C with and without DMSO**[a]

| expt no. | [indene] (mol·L$^{-1}$) | [CumCl] (mol·L$^{-1}$ × 10$^3$) | [DMSO] (mol·L$^{-1}$ × 10$^3$) | $\bar{M}_n$ (expt) | $\bar{M}_n$ (calc) | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|---|
| 1 | 0.107 | 3.0 | 0 | 4 000 | 4 150 | 1.8 |
| 2 | 0.215 | 3.0 | 0 | 8 500 | 8 300 | 1.8 |
| 3 | 0.43 | 3.0 | 0 | 17 000 | 16 600 | 1.9 |
| 4[b] | 0.86 | 3.0 | 0 | 16 100 | 33 250 | 2.4 |
| 5[c] | 0.86 | 3.0 | 0 | 17 000 | 33 250 | 2.4 |
| 6 | 0.215 | 1.0 | 0 | 19 000 | 25 000 | 1.7 |
| 7 | 0.43 | 1.0 | 0 | 30 900 | 50 000 | 1.8 |
| 8 | 0.86 | 1.0 | 0 | 44 300 | 100 000 | 2.0 |
| 9 | 0.215 | 1.0 | 2.5 | 16 800 | 25 000 | 1.7 |
| 10 | 0.43 | 1.0 | 2.5 | 28 000 | 50 000 | 1.8 |
| 11 | 0.86 | 1.0 | 2.5 | 41 000 | 100 000 | 2.2 |

[a] [$TiCl_4$] = $2 \times 10^{-2}$ mol·L$^{-1}$; solvent, $CH_2Cl_2$. [b] Incremental monomer addition (0.43 mol·L$^{-1}$) after 6 min. [c] Second incremental monomer addition (0.43 mol·L$^{-1}$) after 45 s.

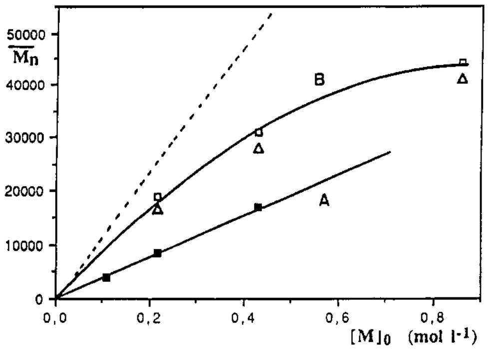


**Figure 6.** Polymerization of indene initiated with the CumCl/$TiCl_4$ initiating system at +5 °C. Variation of the $\bar{M}_n$ with the amount of monomer polymerized. Conditions: [$TiCl_4$] = $2 \times 10^{-2}$ mol·L$^{-1}$; solvent, $CH_2Cl_2$; reaction time = 6 min; yield 100%; (- - -) calculated line. [CumCl]: (■) $3 \times 10^{-3}$ mol·L$^{-1}$ (without DMSO); (□) $1 \times 10^{-3}$ mol·L$^{-1}$ (without DMSO); (△) $1 \times 10^{-3}$ mol·L$^{-1}$ ([DMSO] = $2.5 \times 10^{-3}$ mol·L$^{-1}$).

However, the possibility of a compensation between partial initiation and transfer cannot be entirely ruled out. To investigate this point, a few experiments were carried out in the presence of DMSO for high values of the [M]/[C] ratio (expts 9–11 of Table IX). In this case initiation should be quantitative, since it is already so at −40 °C, and the difference between the calculated and measured values of the $\bar{M}_n$ should result exclusively from transfer. The $\bar{M}_n$s of the polymers are not significantly lower than those obtained without DMSO (Figure 6, curve B). This suggests that initiation is practically quantitative at this temperature, even without DMSO, and that the deviations from the calculated values are due to transfer. This also shows that the addition of DMSO does not suppress or decrease transfer. The Mayo plot yields a

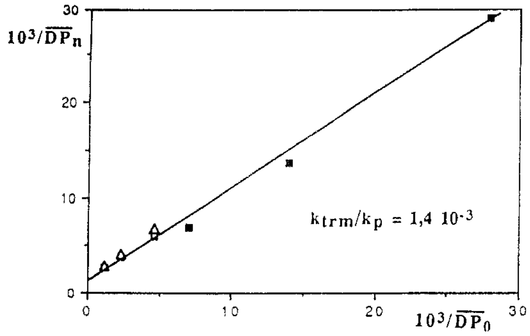


**Figure 7.** Measurement of the transfer constant to the monomer in the polymerization of indene at +5 °C. Conditions: initiating system, CumCl/$TiCl_4$/DMSO; solvent, $CH_2Cl_2$; [$TiCl_4$] = 2 × $10^{-2}$ mol·$L^{-1}$. [CumCl]: (■) 3 × $10^{-3}$ mol·$L^{-1}$ (without DMSO); (□) $10^{-3}$ mol·$L^{-1}$ (without DMSO); (△) $10^{-3}$ mol·$L^{-1}$ ([DMSO] = 2.5 × $10^{-3}$ mol·$L^{-1}$.

value of the transfer constant equal to 1.4 × $10^{-3}$ (Figure 7). This plot includes all the experimental points (with and without DMSO), except expts 4 and 5, which involve incremental monomer additions.

These two last runs show that the incremental monomer addition experiments do not lead to polymer growth. In these experiments, 0.43 mol·$L^{-1}$ of indene was first polymerized, and the same amount of monomer was added in the second reaction. The global yield was 100% in both cases, and the $\bar{M}_n$ of the final polyindene has half the calculated value and corresponds to that observed for the first polymerization of 0.43 mol·$L^{-1}$ of monomer. The polymerization started again upon addition of monomer, and the number of chains formed during the second reaction was the same as in the first polymerization. In expts 4 and 5, the second addition of monomer took place respectively 6 min and 45 s after the start of the first reaction, that is to say long after the end of polymerization in both cases. The $\bar{M}_n$s are similar for both experiments. The second initiation is not due to adventitious cocatalyst (estimated concentration: 3 × $10^{-4}$ mol·$L^{-1}$) present in the 2 mL of solution (indene and $CH_2Cl_2$) added to the initial reaction medium (20 mL), since in that case the final $\bar{M}_n$ should have been about 30 000 (taking into account the value of the transfer constant) instead of 17 000. The simplest explanation for this result is that all the chains have undergone transfer at the end of the polymerization and that consequently, the second reaction is initiated by chlorinated oligomers, which makes the increase of $\bar{M}_n$ practically nonmeasurable.

## IV. Discussion and Conclusion

Control of the $\bar{M}_n$s can be achieved to a variable extent depending on the experimental conditions, but the polyindenes obtained with cumyl chloride as the initiator do not have not all the features of a living polymer. These systems should be called "apparently living" or "living".

In conventional carbocationic polymerizations, the initiating systems generally involve a metal halide and adventitious cocatalysts or added initiators (generally alkyl chlorides). These systems have been widely investigated and generally did not yield "living" polymers for two reasons. First, the adventitious cocatalysts (water or hydrogen chloride) are not efficient enough to achieve complete initiation, and this may be also the case for most of the added initiators. Besides, with adventitious cocatalyst present in low concentration the monomer to initiator ratio is high, and this makes transfer apparent.

In a previous paper,[4] it was proposed that "apparently living" polymerizations generally do not involve particular active centers but are special cases of conventional polymerizations with quantitative initiation resulting from a low $R_p/R_i$ ratio. When this requirement is fulfilled, control of the $\bar{M}_n$ can be achieved as long as the [M]/[I] ratio is low enough to mask transfer or if temperature is low enough. The results obtained in this work, which will be discussed here, are in agreement with this view.

**(1) Initiation with $TiCl_4$. (a) Reversible Termination.** The possibility of a reversible termination has already been postulated in the previous article.[5] Its occurrence is confirmed by the results of the initiation with the $TiCl_4$/1-chloroindan system. Since initiation with 1-chloroindan is quantitative in the polymerizations carried out at −40 °C in the presence of DMSO, it can be concluded that each chloroindan molecule reacts with $TiCl_4$ and ionizes at least once during the timespan of a polymerization. This should also happen in the case of the reactivation of chlorinated end groups resulting from the reversible termination. Consequently, the growth of a macromolecule may be visualized as a succession of propagation periods interrupted by the reversible formation of a covalent species according to eq 1.

**(b) Influence of a Common Ion Salt.** The polyindenes prepared with $TiCl_4$ and CumCl in the presence of a common ion salt ($n$-$Bu_4NCl$ and $n$-$Bu_4N^+$,$TiCl_5^-$) without DMSO have the $\bar{M}_n$ expected for a "living" polymer, which implies that initiation is complete in this case. Besides, the molecular weight distribution is narrower than with the $TiCl_4$/CumCl initiating system (2.4 instead of 4.9) and similar to those observed in the presence of DMSO. The effect of a common ion salt is probably to shift an ionization equilibrium toward the formation of ion pairs and covalent species (see eq 2).

In a recent paper, Matyjaszewski concluded that, in cationic polymerization, the reactivities of free ions and ion pairs are not as different as in anionic polymerizations,[11] and may even be the same, and considered the problem of exchanges between the various species. But the broad molecular weight distributions (or the bimodality) often observed has been generally accounted for assuming propagation on free ions and ion pairs having different rate constants.[10] For instance, Kennedy and co-workers[12] found that tetra-$n$-butylammonium chloride decreases the polymerization rate of isobutylene initiated with alkyl chlorides and $TiCl_4$. They concluded that the salt suppresses the free ions and proposed an evaluation of $k_p^{+/-}$ and of the ionization constant between the covalent species and the ion pairs. They even considered the possibility of the existence of several types of nondissociated species (ion pairs and "polarized" species), the latter implying a pseudocationic mechanism.

Anyway, in the present case, complete initiation results from a decrease of the $R_p/R_i$ ratio in the presence of salt. The salt should not increase the initiation rate but can decrease the propagation rate by shifting the ionization and dissociation equilibria toward the left, suppressing the free ions and thus increasing the proportion of dormant covalent species, if dissociation is large enough. The decrease of the amount of ionic species may slow down the polymerization enough to allow complete initiation, whatever the values of $k_p^+$ and $k_p^{+/-}$.

The narrowing of the molecular weight distribution may result from the lower propagation rate, which increases the number of interconversions between covalent and ionic species during the formation of the macromolecules, thus averaging the molecular weights. Besides, the reduction of the proportion of the free ions (or their suppression) may have a similar effect, independently of their prop-

**Table X. Influence of the Reaction Temperature on the Polyindenes Formed by Initiation with Cumyl Chloride/$TiCl_4$ Systems**

| initiating system | temp (°C)<br>+5 | <br>−40 | <br>−75 |
|---|---|---|---|
| CumCl/$TiCl_4$ | complete initiation, transfer | incomplete initiation, transfer | incomplete initiation, transfer nonmeasurable |
| CumCl/$TiCl_4$/DMSO | complete initiation, transfer | complete initiation, transfer | incomplete initiation, transfer nonmeasurable |

**Table XI. Approach to a "Living" Polymerization: Influence of the Structure of the Assumed Counterion on the Linearity of the Molecular Weights of the Polyindenes with the Amount of Polymer Formed and on the $M_w/M_n$[a]**

| Lewis acid | initiator | assumed counterion | $\bar{M}_w/\bar{M}_n$ | "living" polymer |
|---|---|---|---|---|
| $TiCl_3OBu$ | CumOMe | $TiCl_3OBuOMe^-$ | 1.6–1.7 | yes |
| $TiCl_3OBu$ | CumCl | $TiCl_4OBu^-$ | 1.6–2.4 | yes |
| $TiCl_4$ | CumOMe | $TiCl_4OMe^-$ + (?) $TiCl_5^-$ | 1.9–2.3 | yes |
| $TiCl_4$ | CumCl | $TiCl_5^-$ | 3.6–4.9 | no |
| $TiCl_4$ | CumCl + DMSO | $TiCl_5^-$ | 2.1–3.2 | yes |
| $TiCl_4$ | 1-chloroindan + DMSO | $TiCl_5^-$ | 3.0–3.7 | yes |

[a] Temperature = −40 °C; solvent, $CH_2Cl_2$.

agation rates, because the bimolecular recombination of free ions is less favored than the unimolecular conversion of an ion pair into covalent species. In the presence of free ions the molecular weight distribution should be broader, because their lifetime is longer than that of the ion pairs.

**(c) Influence of DMSO and of the Reaction Temperature.** The first observation is that DMSO does not act as a scavenger for the adventitious initiator, as has been suggested by Balogh et al. in the case of the isobutene/$TiCl_4$ system.[13] Polymerizations of indene initiated with $TiCl_4$ in the absence of cumyl chloride, assumedly initiated by residual water, goes to completion in the presence of DMSO (cf. Table III, expt 1). Another possibility might be that initiation by $TiCl_4$ does not involve a proton donor at low temperature.[14]

Besides, experiments carried out with and without DMSO at +5 °C yield polymers with similar molecular weights (cf. expts 6–11 of Table IX). Consequently, the DMSO does not hinder transfer reactions, at least at +5 °C, and this is probably also true at lower temperatures.

Table X summarizes the influence of DMSO on the polymerization at various temperatures for the $TiCl_4$/CumCl and the $TiCl_4$/CumCl/DMSO initiating systems. The first conclusion which can be drawn from this table is that the obtention is a truly living polymer with these systems is probably not possible, unless there is an optimal temperature between −40 and −75 °C at which initiation might be complete in the presence of DMSO (or another donor), with negligible transfer.

The main observations may be summarized as follows: (i) at −75 °C, initiation is incomplete, even in the presence of DMSO; (ii) at −40 °C, the characteristics of the polymer obtained in the presence of DMSO are those of a "living" polymer; (iii) at +5 °C, the influence of DMSO is only marginal.

These results may be accounted for on purely kinetic grounds: The activation energy of the polymerization of indene initiated with $TiCl_4$ was found to be negative,[14] and we have recently observed that $k_p$ increases at low temperature in the case of the "living" polymerization of indene initiated with the CumCl/$TiCl_4$/DMSO initiating system. This may be explained assuming a shift of the ionization and dissociation equilibria with temperature. These equilibria may be schematically represented as in eq 2.

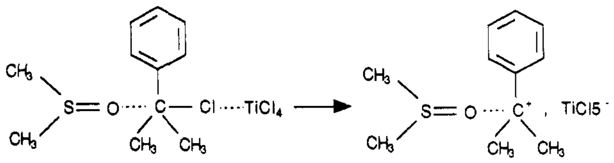
Consequently, it may be assumed that at higher temperatures the equilibria are shifted toward the left side and that the formation of dormant covalent species is favored. This would lower the propagation rate and allow complete initiation. Besides, if the activation energy for initiation is positive, initiation and reactivation are faster at higher temperatures.

The narrowing of the molecular weight distribution at +5 °C may result from two causes: (1) The decrease of the propagation rate would increase the number of exchanges which take place during the formation of a chain, and this would lead to narrower molecular weight distributions of the resulting polymers. (2) The diminution of the concentration (or the suppression) of free ions at high temperatures would have a similar effect, since the bimolecular recombination of two ions to yield an ion pair, and eventually a covalent species, is less probable than the unimolecular transformation of an ion pair into covalent species.

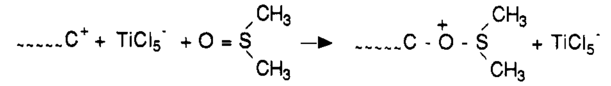
As the temperature decreases, ionization increases and also the concentration of the free ions, and the polymerization is faster, too fast to allow complete initiation at 40 °C in the absence of DMSO. It is still faster at −75 °C, and complete initiation cannot be achieved, even in the presence of DMSO.

The effect of the DMSO is to decrease the propagation to initiation rate ratio and to allow complete initiation. The DMSO may affect this ratio in two ways:

(a) The initiation rate (and also the reinitiation rate) may be increased by the intervention of DMSO in the initiation reaction through a "push–pull" effect of the electron donnor DMSO, which would enhance the ionization of a covalent species:[15]



(b) The DMSO may also decrease the propagation rate by complexing the free ions, giving inactive oxonium ions or complexes, as in the case of the polymerization of isobutyl vinyl ether initiated with trifluoromethanesulfonic acid in the presence of alkyl sulfides.[16]



$$\text{-----}C^+ + TiCl_5^- + O=S(CH_3)_2 \longrightarrow \text{-----}C-\overset{+}{O}-S(CH_3)_2 + TiCl_5^-$$

In this case, the DMSO would decrease the concentration of really active species present at a given time, "dormant" species being formed at both ends of the series of equilibria.

**(2) Influence of the Counterion.** Table XI summarizes the results of experiments carried out with cumyl methyl ether[5] and with cumyl chloride at −40 °C. The initiating systems having an alkoxy group in one of the components (either cumyl methyl ether or $TiCl_3OBu$) yield "living" polymers without the addition of DMSO. A common feature of these systems is that the assumed counterion is an alkoxychlorotitanate ($TiCl_{5-n}(OR)_n^-$)

instead of $TiCl_5^-$. It can be inferred from this observation that the counterion plays an important part in the possibly of observing a "living" polymerization.

Possible explanations are either that the propagation rate constant on the ion pairs may be lower with the alkoxytitanate counterions than with $TiCl_5^-$ or that the ionization constant may be lower in the former system. This would decrease the propagation rate and increase the number of interconversions between dormant and propagating species during a polymerization and would make the molecular weight distribution narrower. A reduction of the concentration of free ions if $K_d$ is lower would have the same effect.

In conclusion, the results obtained with cumyl methyl ether and with cumyl chloride as initiators can be accounted for by the conventional mechanisms of cationic polymerizations.

There are two basic requirements for the achievement of a "living" polymerization. The first one is the control of initiation, i.e., a value of the $R_p/R_i$ ratio low enough to allow complete initiation. Given complete initiation and a convenient choice of experimental conditions, transfer may be undetectable up to a limited value of the monomer to initiator ratio. The rather large molecular weight distributions observed result from sluggish reactivation of the chains following reversible termination. The complete conversions invariably obtained and the similar $\bar{M}_w/\bar{M}_n$ observed for IMA experiments suggest that irreversible termination, if it takes place at all, is negligible. The beneficial influence of DMSO in the case of cumyl chloride may be explained by purely kinetic reasons.

However, the hypothesis of a "stabilization" of the active centers through interaction of the electron-donating compound with the ion pairs cannot be discarded even if transfer reactions were not modified in its presence. But the progressive passage from a "nonliving" to a "living" polymerization with a lowering of the reaction temperature in the case of cumyl methyl ether and the influence of common ion salts, which cannot be explained by a complexation, are in favor of the kinetic explanation for the passage from a "conventional" cationic polymerization to an "apparently living" one. Recently, several authors have proposed criteria to assess the "livingness"[17] or the "degree of livingness"[18] of these polymerizations.

To clear the respective roles of initiation and propagation, as well as that of DMSO, in the control of the molecular weights and of their distributions for "apparently living" carbocationic systems, kinetic measurements using adiabatic calorimetry are now being carried out, and the results will be reported in a forthcoming paper.

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