Revisiting living and apparently living carbocationic polymerizations

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Dedicated to Professor Stanislaw Penczek in recognition of his outstanding contribution to polymer science

Abstract: This short review aims at reconsidering the behaviours of a few vinyl monomers (isobutylvinylether, *p*-methylstyrene, *p*-methoxystyrene, indene and 2,4,6-trimethylstyrene) well identified as leading to different levels of living character during their cationic polymerization. These polymerizations agree well with the general scheme of dormant-active equilibrium of propagating species. The available data, and particularly that from of our Paris group, are summed up and discussed in terms of cation stability and of absence (or non-detection) of transfer depending on the conditions of polymerization (nature of the monomer, initiating system, temperature, medium, range of considered $\overline{M}_n$, *etc*.). This living situation allows the estimation of the absolute $k_p^\pm$ (propagation rate constant) for the considered monomers, either *via* the determination of the concentration of active ionic species (ISC — ionic species concentration method) or *via* the capping method (diffusion clock or DC method). A discrepancy still persists between the two approaches as the DC method leads to $k_p^\pm$ which are 10^5 times larger. Furthermore the capping rate constants $k_c^\pm$ and the corresponding $k_p^\pm$ obtained through the DC method have led to the conclusion that the effect of a monomer substituent on the reactivity of carbocation is much larger than the effect on the reactivity of the corresponding monomer. But, from the $k_p^\pm$ values obtained by the ISC method and from the reactivity ratios in copolymerization of the styrenic monomers, we concluded that there could be an approximate compensation between carbocation and monomer reactivities.

Keywords: living polymerization, carbocationic polymerization, propagation rate constant, carbocation reactivity.

Nowe spojrzenie na karbokationową polimeryzację żyjącą i pseudożyjącą

Streszczenie: Artykuł stanowi krótki przegląd literaturowy, którego celem jest aktualizacja poglądów na temat właściwości kilku monomerów winylowych (eter izobutylowinylowy, *p*-metylostyren, *p*-metoksystyren, inden i 2,4,6-trimetylostyren), umożliwiających osiągnięcie różnych poziomów żyjącego charakteru procesów polimeryzacji kationowej. Procesy te przebiegają zgodnie z ogólnym schematem równowagi form aktywnych i nieaktywnych w reakcjach propagacji. Zebrano dostępne dane, w tym uzyskane przez paryski zespół badawczy autorów, i przedyskutowano je z punktu widzenia stabilności kationu oraz braku (bądź niewykrywalności) przeniesienia łańcucha zależnie od warunków polimeryzacji (rodzaj monomeru, układ inicjujący, temperatura, środowisko procesu, rozważany zakres $\overline{M}_n$ itp.). Żyjący charakter polimeryzacji umożliwia oszacowanie $k_p^\pm$ (stałej szybkości reakcji propagacji) dla badanych monomerów poprzez określenie stężenia aktywnych centrów jonowych (metoda ISC) lub poprzez zakończenie (*capping*) — metodą zegara dyfuzyjnego DC. Istnieje pewna rozbieżność między wynikami otrzymanymi za pomocą tych dwóch metod, metoda DC daje w rezultacie wartości $k_p^\pm$ 10^5 razy większe. Co więcej, uzyskane metodą DC stałe szybkości reakcji zakończenia $k_c^\pm$ i odpowiadająca jej wartość $k_p^\pm$ prowadzą do wniosku, że wpływ podstawników w monomerze na reaktywność karbokationu jest znacznie większy niż na reaktywność monomeru. Z drugiej strony, z wartości $k_p^\pm$ otrzymanych metodą ISC oraz stosunków reaktywności w kopolimeryzacji monomerów styrenowych wynikają zbliżone reaktywności monomerów i karbokationów.

Słowa kluczowe: polimeryzacja żyjąca, polimeryzacja karbokationowa, stała szybkości propagacji, reaktywność karbokationu.

In the absence of termination and transfer reactions (*i.e.* when the active sites are stable) a living carbocationic polymerization should occur. If initiation is complete, a consequence is a control of molecular weights with

$$DP_n = [M]_0/[I]_0 \qquad (1)$$

But it was wrongly assumed that, when this relationship is observed, this proved the stability of the active

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centres, *i.e.* in the absence of termination and irreversible transfer. This «stability» was explained in the cases of isobutylvinylether (IBVE) [1], isobutylene [2] and styrene [3] by the presence of new types of active centres such as carbocations stabilized by donors or stretched covalent bonds. We have shown that for *e.g.* IBVE [4] and indene [5, 6] that the above equation observed for $DP_n \leq 200$ was not valid for higher DP_n and that the discrepancy increased when increasing temperature. Our conclusion was that the transfer reactions occurred but were only undetected when DP_n was low and that the active sites were classic ones, ion pairs and unpaired ions in equilibrium, which are susceptible to transfer (Scheme A).

$$\sim\sim\sim CX + MtX_n \rightleftharpoons \sim\sim\sim C^+, MtX_{n+1}^- \rightleftharpoons \sim\sim\sim C^+ + MtX_{n+1}^-$$

Scheme A

Covalent species are in equilibrium with ion pairs («reversible termination», better called now «reversible deactivation») and only this equilibrium remains in the presence of a salt with a common counter ion. It was concluded that «…the narrowing of the molecular weight distribution may result from a lower propagation rate which increases the number of interconversions between covalent and ionic species… In the presence of free ions the molecular weight distribution should be broader because their lifetime is longer than that of ion pairs» [5].

MEASUREMENT OF TRANSFER CONSTANTS IN THE POLYMERIZATION OF ISOBUTYLVINYLETHER (IBVE) IN TOLUENE

Polymerization of IBVE initiated at 0 °C by $AlEtCl_2$ «alone» in toluene was in fact cocatalyzed by protonic impurities (H_2O or HCl). In the presence of ethylacetate (10 % by volume), linearity of the $\overline{M}_n$ from the origin with polymer yield has been observed by Higashimura *et al.* [7] up to $\overline{M}_n$ = 20 000. But working under vacuum with purified reagents, we found that with reagents at the same concentrations $\overline{M}_n$ was also linear up to $\overline{M}_n = 2 \cdot 10^4$ (for 20 % yield) but that a strong curvature of the plot was then observed, with a final molecular weight of $4 \cdot 10^4$, showing the occurrence of transfer [4].

For isobutylvinylether with isobutyl,1-chloroethylether (IBCE) as initiator and $AlCl_3$ as activator, polymerizations in toluene at 0 °C with ethylacetate (EA) as additive (10 % v/v) were slow enough to take samples and measure osmotic $\overline{M}_n$ at various times. A linear increase of $\overline{M}_n$ from the origin with yield was observed up to $\overline{M}_n = 2 \cdot 10^4$ with a slower increase to a plateau for larger yields, showing that transfer occurred (Fig. 1) [4].

The variation of the concentration $[N]_t$ of macromolecules against time (calculated from the $\overline{M}_n$ and the yield) was found to be linear as well in the absence as in the presence of added initiator. In the first case, the intercept gave the concentration of adventitious protonic initiator ($3 \cdot 10^{-4}$ mol/dm^3).

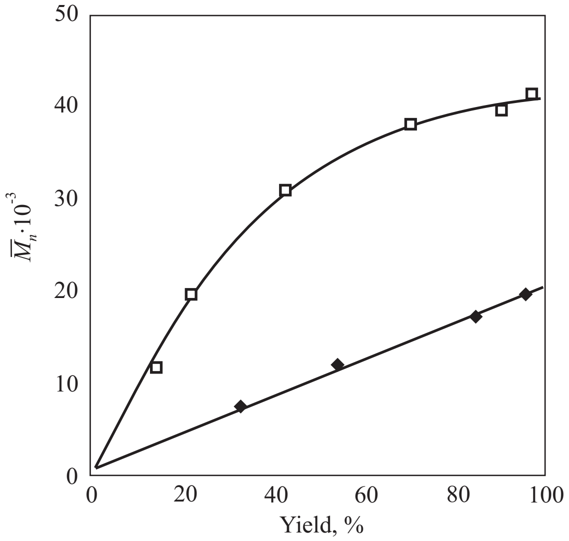


Fig. 1. Variation of $\overline{M}_n$ with conversion in the polymerization of IBVE in toluene at 0 °C in presence 10 % (v/v) of ethylacetate. Initiation with $AlEtCl_2$ (0.01 mol/dm^3) and adventitious cocatalyst: ◆ data of [9], ☐ data of [4, 10]

Such a relationship has been shown to occur for a transfer of apparently first order (zero order in monomer) with a number of macromolecules formed by transfer

$$[N]_{tr} = k_{tr} / k_p \ln ([M]_0/[M]_t) \cdot t \qquad (2)$$

increasing linearly with time (Fig. 2) [4], and the total concentration of macromolecules is given by

$$[N]_t = [N]_0 + k_{tr} / k_p \ln ([M]_0/[M]_t) \cdot t \qquad (3)$$

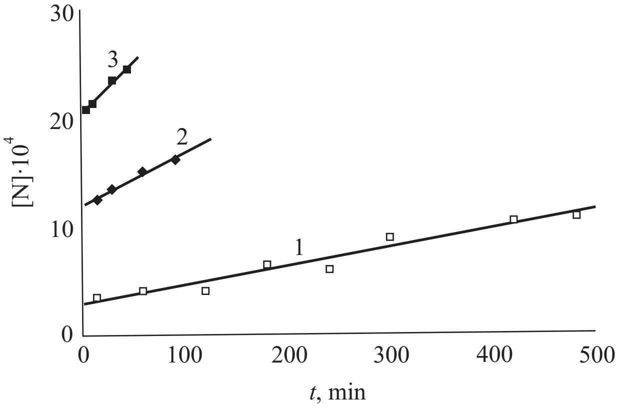


Fig. 2. Polymerization of IBVE (0.76 M), initiated with $AlCl_3$ (10^{-2} M) and isobutyl 1-chloroethyl ether (IBCE) in the presence of ethylacetate (0.5 M). Variation of the concentration of macromolecules with polymer yield at variable IBCE concentrations: 1— no added initiator (initiation by adventitious cocatalyst ~$3 \cdot 10^{-4}$ M); 2 — [IBCE] = 10^{-3} M; 3 — [IBCE] = $2 \cdot 10^{-3}$ M

For a bimolecular transfer to monomer (first order in [M]), the total concentration of macromolecules is given by

$$[N]_t = [N]_0 + k_{trm} / k_p ([M]_0 - [M]_t) \quad (4)$$

and increases linearly with monomer conversion [4]. This has been found to be the case for polymerizations in the absence of donor additive and initiated by Ph_3C^+, $AlCl_4^-$ at 0 °C. The $\overline{M}_n$ of the polymers increased linearly with $[M]_0$ varying from 0.19 to 0.76 mol/dm^3 and a plot of $1/DP_n$

$$1 / DP_o = [N]_0/[M]_0 \quad (5)$$

gave $k_{trm}/k_p = 8 \cdot 10^{-4}$ [11].

Similar polymerizations with the addition of $5 \cdot 10^{-2}$ mol/dm^3 of ethylacetate led to a strong decrease of the propagation rate (*e.g.* 20 % yield in 60 min) and to a narrower molecular weight distribution, $\overline{M}_w/\overline{M}_n \sim 1.5$ instead of 3 [11]. But the concentration of macromolecules still increased linearly with conversion, showing the preponderance of transfer to monomer with $k_{trm}/k_p = 5.8 \cdot 10^{-4}$ at 0 °C, and $(DP_n)_0$ at intercept equal to $[M]_0/[I]_0$. With the IBCE/$AlCl_3$ initiator (with $[AlCl_3]/[IBCE] = 10$), an increase of ethylacetate (EA) concentration from 0.5 to 1.9 mol/dm^3 still gave a decrease of k_p attributed to a complexation equilibrium by EA giving dormant species. Polymerization still occurs very slowly in pure EA solution. The reduction of direct transfer to monomer in the presence of high concentrations of ethylacetate was explained by a propagation mechanism involving monomer solvated cationic species in equilibrium with inactive species solvated by EA.

TRANSFER CONSTANTS IN POLYMERIZATIONS OF STYRENE, α-METHYLSTYRENE, *p*-METHYLSTYRENE AND INDENE

In the case of styrene, α-methylstyrene and indene, we found that the two types of transfer (first and second order) could be distinguished in experiments for which the polymer formed by transfer can be isolated from that resulting from initiation when using grafting reactions. The last one was grafted on a polyisobutylene backbone bearing $PhCH_2Cl$ initiating groups [12, 13].

In the solvent mixture CH_2Cl_2/methylcyclohexane (50/50, v/v) in order to preserve solubility of both the polyisobutylene and the grafts, and using $AlEt_2Cl$ as coinitiator, transfer constants were measured for several monomers. The product was fractionated by selective solvent extraction into three fractions: ungrafted backbone, graft copolymer and the styrene type homopolymer. The fractions were characterized and analyzed (^{1}H NMR, SEC) and the $\overline{M}_n$ measured by membrane or vapour phase osmometry. With styrene at -55 °C, $k_{trm}/k_p = 2.4 \cdot 10^{-3}$ and the occurrence of zero order transfer to monomer could not be excluded [12]. With α-methylstyrene at -50 °C, the transfer constants were found to be $k_{trm}/k_p = 10^{-4}$ and $k_{tr}/k_p = 4 \cdot 10^{-4}$ [13]. With indene at -55 °C only transfer to monomer was detected ($k_{trm}/k_p = 7.5 \cdot 10^{-4}$) [12].

Direct determination of the transfer constant for indene [14] at -75 °C [CumOMe/$TiCl_4$ (cumyl methyl ether/titanium tetrachloride) initiation] led to a Mayo plot of $1/DP_n$ *vs.* $1/DP_0$ passing through the origin and to a linear variation of $\overline{M}_n$ *vs.* $[M]_0$ up to $\overline{M}_n \sim 10^5$ showing that transfer to monomer was absent.

For polymerizations of *p*-methylstyrene [14] at -40 °C with the same initiating system, the Mayo plot gave a transfer constant to monomer $k_{trm}/k_p = 10^{-3}$. But at -75 °C, linearity of $\overline{M}_n$ *vs.* $[M]_0$ was observed up to $\overline{M}_n = 80\,000$ and the Mayo plot of $1/DP_n$ passed through the origin with no sign of transfer as was the case for indene. Nevertheless results different from indene were observed when a second monomer batch was added at the end of a first polymerization. Even if the second addition was made after less than one minute, the final polymer was bimodal and the main peak had only shifted to a larger value. If the second addition was made after 6 minutes, there was no change in the $\overline{M}_n$ of the main peak. In both cases, the appearing second peaks corresponded to larger $\overline{M}_n$ showing that these polymer fractions were probably initiated by HCl issued from indanic cyclization by alkylation of the penultimate phenyl ring. This cyclization is sterically hindered in the case of indene which explains the much better livingness.

TRANSFER IN «LIVING» POLYMERIZATION OF INDENE

Polymerizations of indene in methylene chloride have been investigated at different temperatures with various initiating systems. With $TiCl_4$ as coinitiator, polymerizations are always rapid and stopped-flow studies of the lifetime of the (indanyl)$^+$ carbocations have shown their constant concentration [5, 6].

The kinetics were followed by vacuum calorimetry, the yield being quantitative in a few seconds at -60 °C and -40 °C but in 20 s at 0 °C. The apparent rate constants measured from first order plots for [M] with time increase as temperature decreases, leading to an apparent negative activation energy $E_g^{\pm}$ (ANAE) for propagation of -3.27 kcal/mol. These ANAE have been observed previously in many non-living polymerizations (styrene, *p*-methoxystyrene, isobutylene, cyclopentadiene, α-methylstyrene) [15].

$$E_g^{\pm} = \Delta H_i + E_p^{\pm} \quad (6)$$

The explanation given is that with both living and non living systems, ANAE are governed by the predominance, over the activation energy for propagation, of the ΔH_i of ionization of the dormant covalent species as K_i increases strongly when temperature is lowered.

With cumyl chloride (CumCl) as initiator and $TiCl_4$ as coinitiator [5], at various temperatures, the $\overline{M}_n$ was always larger than the theoretical value even if a linear increase was observed up to $\overline{M}_n \sim 15\,000$. This was the result of incomplete initiation. Complete initiation was attempted by adding dimethylsulfoxide ($2.5 \cdot 10^{-3}$ mol/dm^3

for [TiCl$_4$] = 2 · 10^{-2} mol/dm^3 and [CumCl] = 1 to 3 · 10^{-3} mol/dm^3) which may increase the initiation rate and decrease the propagation rate [16]. But at -75 °C the molecular weights were much larger (~double) than the theoretical ones due to incomplete initiation. At -40 °C, theoretical $\overline{M}_n$ were obtained up to 30 000 with a deviation for larger values, with $\overline{M}_w/\overline{M}_n$ = 2.1 to 2.8, and a Mayo plot gave $k_{trm}/k_p = 6 \cdot 10^{-4}$.

With CumCl and TiCl$_3$OBu as coinitiator [5], the results at *e.g.* -40 °C were similar. The $\overline{M}_n$ increase was linear up to ~2 · 10^4 but the observed $\overline{M}_n$ was 7.9 · 10^4 for a theoretical value of 10^5, showing the occurrence of transfer, and $\overline{M}_w/\overline{M}_n$ was a little lower (1.6 to 2).

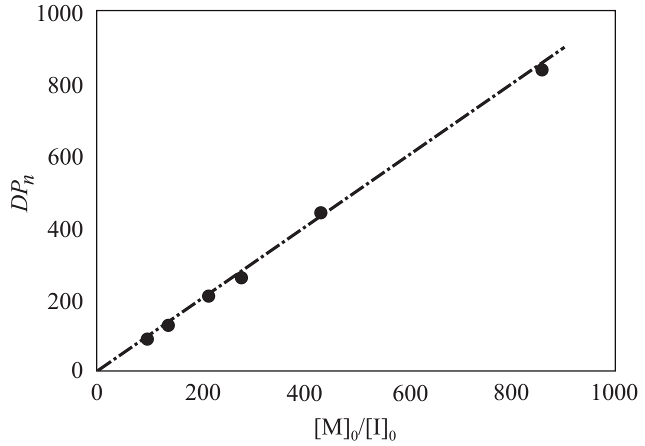


Fig. 3. Polymerization of indene with the CumOCH$_3$/TiCl$_4$ initiating system at –75 °C in CH$_2$Cl$_2$. Dependence of DP_n (full conversion) on [M]$_0$/[I]$_0$, –•–•– calc. DP_n in absence of transfer

With CumOMe/TiCl$_4$ initiation [6a] at -75 °C, the molecular weight increased linearly with the amount of monomer polymerized up to $\overline{M}_n = 10^5$ (DP_n ~ 800) (Fig. 3).

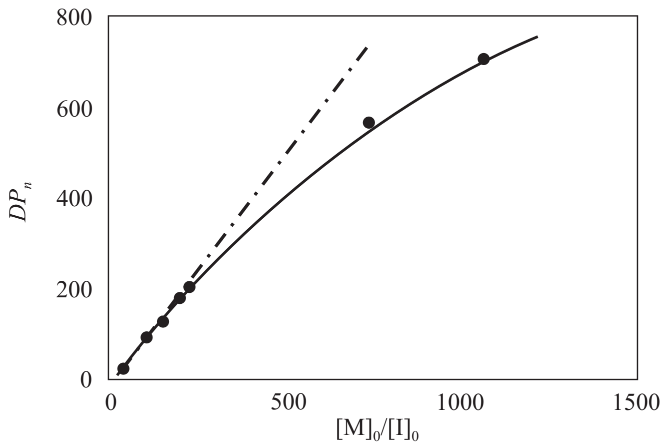


Fig. 4. Polymerization of indene with the CumOCH$_3$/TiCl$_4$ initiating system at -40 °C in CH$_2$Cl$_2$. Dependence of DP_n (full conversion) on [M]$_0$/[I]$_0$, –•–•– calc. DP_n in absence of transfer, —— calc. curve for $k_{trm}/k_p = 5 \cdot 10^{-4}$

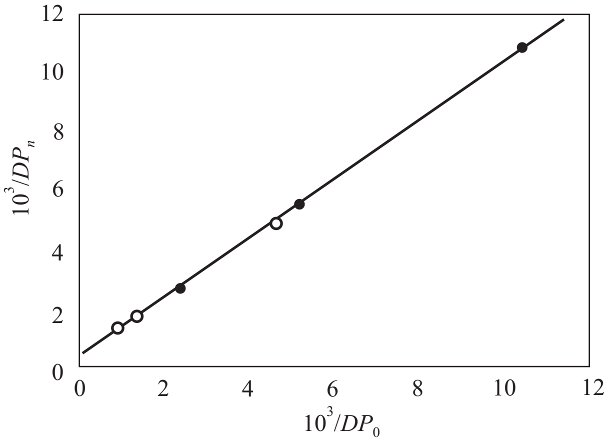


Fig. 5. Polymerization of indene with the CumOCH$_3$/TiCl$_4$ initiating system at -40 °C in CH$_2$Cl$_2$. Measurement of transfer constant to monomer $k_{trm}/k_p = 5 \cdot 10^{-4}$

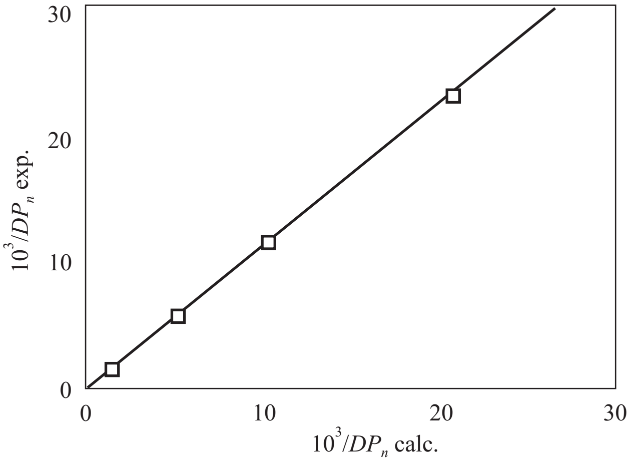


Fig. 6. Measurement of transfer constant to monomer in the polymerization of indene -40 °C in CH$_2$Cl$_2$. Initiating system: CumOMe (1 to 4.5 · 10^{-3} M), TiCl$_3$OBu (2 · 10^{-2} M)

But at -40 °C the variation was no more linear for $DP_n \geq 300$ (Fig. 4), and a Mayo plot of 1/DP_n *vs.* [I]$_o$/[M]$_o$ gave a transfer constant of $k_{trm}/k_p = 5 \cdot 10^{-4}$ (Fig. 5). This shows that at -40 °C and above, the polymers are not really living, but cannot be distinguished from a living system at -75 °C.

With CumOMe/TiCl$_3$OBu initiation [6a] at -40 °C, the $\overline{M}_n$ variation was linear up to 8 · 10^4, transfer being undetectable up to $\overline{M}_n$ = 7.5 · 10^4 from a Mayo plot (Fig. 6).

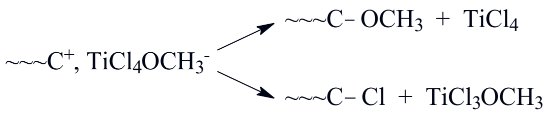
For both initiating systems, the observed $\overline{M}_w/\overline{M}_n$ still varies between 1.7 and 2.2, showing that initiation is not rapid enough to reach a narrow distribution.

REACTIVATION OF POLYINDENE END GROUPS

With CumOMe/TiCl$_4$ initiation in CH$_2$Cl$_2$ solution, complete conversion is achieved in a few seconds and an addition of monomer 6 min later caused a further growth of the chains showing that the active centres retain their propagating ability long after polymerization.

We have shown that a terminated polymer (by introduction of methanol) is still an initiator. A first polymerization at -40 °C with CumOMe/$TiCl_4$ gave a polyindene of $\overline{M}_n = 14\,800$ ($\overline{M}_{n,th} = 14\,800$), and $\overline{M}_w/\overline{M}_n = 2.2$ which after 6 min was precipitated in methanol and characterized. It was then used as initiator, coupled with $TiCl_4$, for the same concentration of monomer (0.43 mol/dm^3) and gave a polymer of $\overline{M}_n = 32\,700$ ($\overline{M}_{n,th} = 31\,800$) and $\overline{M}_w/\overline{M}_n = 2.7$.

Termination by methanol may give two different end groups (Scheme B).



Scheme B

In order to obtain a complete initiation even with the chloride end group, dimethylsulfoxide ($2.5 \cdot 10^{-3}$ mol) was added in the second polymerization.

These results are in favor of active or potentially active centres stable for long times (> 6 min) resulting from the reversible deactivation of the active centres (Scheme C).

$$\sim\sim\sim C-OCH_3 + TiCl_4 \rightleftharpoons \sim\sim\sim C^+, TiCl_4OCH_3^-$$

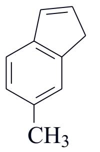
$$\sim\sim\sim C-Cl + TiCl_4 \rightleftharpoons \sim\sim\sim C^+, TiCl_5^-$$

Scheme C

A review of these results [14], and their comparison with those obtained with isobutylene and *p*-methylstyrene for which a linearity of $\overline{M}_n$ up to ~10^5 with the amount of monomer polymerized has been observed at -70 °C, is compatible with values of transfer constants to monomer measured in «conventional» systems [4]. In these «apparently living» systems, irreversible termination at low temperature had never been detected. The main «termination» process by capture of a Cl^- from the counterion is in fact a reversible deactivation followed by a reactivation. We concluded that the control of the polymerizations already achieved could be accounted for by the mechanisms of conventional polymerization, transfer reactions included [14].

POLYMERIZATION OF METHYL-6-INDENE

The para substitution of styrene has led to a decrease of $I_p = \overline{M}_w/\overline{M}_n$ as observed with *p*-methylstyrene, and thus to a better control of $\overline{M}_n$.



(I)

Polymerization of methyl-6-indene [Formula (I)] was studied in order to have a similar decrease by comparison with indene [17].

With CumOMe/$TiCl_4$ as initiating system at -40 °C in CH_2Cl_2, in absence of additive, $k_{trm}/k_p = 2 \cdot 10^{-4}$ while $k_{trm}/k_p = 7 \cdot 10^{-4}$ with indene. I_p was about 2 in both cases.

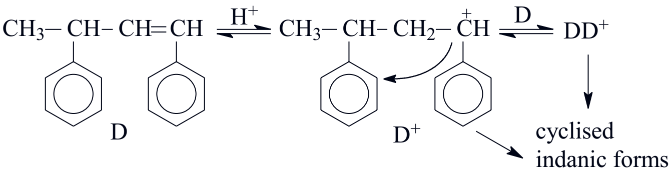
With CumOMe/BCl_3 at -40°C, both initiation and propagation are slower, $\overline{M}_n$ was larger than $\overline{M}_{th}$ due to incomplete initiation and I_p was still ~1.70. But in the presence of common ion salt (benzyltributylammonium chloride), initiation became complete and an excellent agreement between experimental and theoretical molecular weights was observed ($\overline{M}_n = \overline{M}_{th} = 1.28 \cdot 10^5$) together with a narrower distribution ($I_p = 1.36$) as expected from the suppression of unpaired ions.

With trimethylstyrylchloride (TMStCl) as initiator coupled with BCl_3 at -40 °C, $k_{trm}/k_p = 3 \cdot 10^{-4}$ and $I_p = 1.53$ but when the salt is added, $\overline{M}_n = \overline{M}_{th} = 6.3 \cdot 10^4$ and $I_p = 1.29$. This shows that the transfer is still operative at -40 °C.

LIFETIMES OF CARBOCATIONS AND MEASUREMENTS OF k_p

Lifetimes of propagating cations in non-living polymerizations of styrene, in chlorinated hydrocarbon solution and initiated by protonic acids, have been reached using the stopped-flow technique [18]. They range between hundreds of milliseconds to several seconds depending on temperature.

Using CF_3SO_3H as polymerization initiator in CH_2Cl_2, we calculated the propagation rate constants for styrene from the absorbance of carbocations at 340 nm assuming a molar extinction coefficient ε_{340} similar to that observed for the carbanion at the same wavelength [$\varepsilon = 10^4$ dm^3/(mol·cm)]. This gave a k_p of *e.g.* 10^3 dm^3/(mol·s) at -62 °C and $9 \cdot 10^4$ dm^3 /(mol·s) at -10 °C [18c, 18d, 19]. The assignment of the transient absorption to the polystyryl cation has been disputed. However this absorption at 340 nm was also observed when reacting the styrene dimer D with F_3CSO_3H, and assigned to the dimeric cation D^+ which should be similar to the propagating polystyryl cation (Scheme D).



Scheme D

SEC has shown that only oligomers are formed (mainly DD) together with a mixture of cyclic components resulting from the indanic cyclization of D^+ and DD^+ [19, 20].

The lifetimes of the dimeric cation were close to those observed for styrene polymerization at same temperatures, and the decay of the 340 nm absorbance was accompanied with the slow evolution of new peaks which were assigned to cations resulting from protonation of indanic products. This confirms first that the 340 nm absorbance could reasonably be assigned to the styryl cation, and second that the indanic cyclization is by far the dominating termination process in the cationic polymerization of styrene.

But it was objected that the 340 nm absorbance may correspond to both uncomplexed and monomer complexed cations and that the really active species might be the naked ion in much lower concentration, which could explain the propagation rate constants of about 10^9 dm^3/(mol · s) obtained for styrene and several *p*-substituted styrenes by the «diffusion-clock» method [21—23].

Many other propagation rate constants in CH_2Cl_2 in a wide range of temperatures gave global k_p for styrene and styrene derivatives of the order of 10^4 to 10^5 dm^3/(mol·s) derived from measurements of ionic species concentrations (ISC method) (see Table 9 in ref. [24]).

But several studies by R. Faust *et al.* of living polymerizations at low temperatures have given $k_p^\pm$ of 10^9 to $6 \cdot 10^9$ dm^3/(mol·s) for *p*-methylstyrene [21], styrene [22] and *p*-chlorostyrene [23] at -80 °C. They were deduced from the competition between propagation and deactivation reaction with strong nucleophiles with the assumption that deactivation is diffusion controlled with a rate constant $k_c = k_{diff} = 3 \cdot 10^9$ dm^3/(mol·s) DC method.

These values of $k_p^\pm$ are about 10^5 times larger than those measured by the ISC method, and it was shown that this large difference cannot be explained (as well as the differences in K_i, k_i, k_{-i} of the terminal halides) by the high electrophilicity of the growing carbocations [24, 25]. The discrepancies between 2,4,6-trimethylstyrene and *p*-methylstyrene were particularly discussed, as well as the assumption that rate constants of capping ($k_{12,capp}$) are identical with cross-propagation rate constants in copolymerization ($k_{12,copol}$) [25].

STABILITY OF THE INDANYL CATION AND MEASUREMENT OF THE IONIZATION EQUILIBRIUM CONSTANT K_i AND OF THE PROPAGATION RATE CONSTANT $k_p^\pm$

Protonation of indene in CH_2Cl_2 by triflic acid gave an absorption maximum at 330 nm remaining stable for 2 min at 0 °C and more than 10 min at -65 °C. With the indene dimer (2-α-indanyl indene), which does not polymerize at low temperature, and an excess of CF_3SO_3H ([TfOH]/[dimer] = 15) the absorbance of the indanyl cation at 325 nm remained unchanged after 10 min at -66 °C, giving a molar extinction coefficient $\varepsilon_{325} = 15.5 \cdot 10^3$ dm^3/(mol·cm) [24, 49].

Ionization of 1-chloroindane with $SnCl_4$ at -65 °C in CH_2Cl_2 is only partial and first order both in chloride and Lewis acid. A value of the ionization equilibrium constant $K_i = 2 \cdot 10^{-2}$ dm^3/mol was calculated from the absorbance at 325 nm, assuming the same ε as for the indene dimer [26]. Ionization of 1-chloroindane by $TiCl_4$ is also partial, *e.g.* 6 %, at -67 °C and led to $K_i = 13$ dm^3/mol whith $TiCl_5^-$ as counter ion.

In the case of polymerization of indene in CH_2Cl_2 initiated by cumylchloride with $SnCl_4$ (or $TiCl_4$) as activator, the apparent propagation rate constants were measured at -15 and -40 °C, in the presence of 2,6-di-*tert*-butyl-4-methylpyridine. The proton trap neutralizes HCl possibly formed by reaction of adventitious water with the Lewis acid and generates a common ion salt $DTBP^+$, $SnCl_5^-$ which suppresses the free cations. Thus the obtained apparent propagation rate constants are related to ion pairs,

$$k_1^\pm = k_p^\pm [P_n^\pm] = k_p^\pm K_i[\text{CumCl}][\text{SnCl}_4] \quad (7)$$

A global energy for propagation $E_g^\pm = -1.4$ kcal/mol was measured, which assuming an enthalpy of ionization ΔH_i of ~2.5 kcal/mol (for comparison $\Delta H_i \sim 3.5$ for the 2,4,6-trimethylstyrylchloride), led to an ionization equilibrium constant $K_\text{i} = 10^{-2}$ dm^3/mol and then to $k_p^\pm = 7 \cdot 10^4$ dm^3/(mol·s) at -40 °C [24, 26].

COPOLYMERIZATION OF INDENE AND *p*-METHYLSTYRENE

In «living» copolymerization of indene and *p*-MeSt in CH_2Cl_2 at -80 °C initiated by cumyl chloride/BCl_3, the copolymer had the theoretical $\overline{M}_n$ and the rates of copolymerization were independent of the molar ratios of comonomers [27]. We have shown that this was possible only if their rate constants of cross-propagation and propagation are similar, *i.e.* of the order of 10^4 to 10^5 dm^3/(mol·s) as found for various styrenes [24].

LIVINGNESS AND PROPAGATION RATE CONSTANTS FOR *p*-METHOXYSTYRENE

Most cationic polymerizations of *p*-MeOSt were studied in non-living conditions with initiation by various conventional initiators. Our group has used Ph_3C^+, $SbCl_6^-$ as initiator (I) in CH_2Cl_2 solution [28]. The rapid monomer consumption (complete in 10—30 s) was followed by adiabatic calorimetry and that of the initiation by spectrophotometry. First orders were observed both in M and I for the initiation reaction. The overall second order in M found for its consumption corresponds to a first order for propagation. A kinetic scheme including termination and transfer was proposed leading to $k_p = 2.8 \cdot 10^4$ dm^3/(mol·s) at +10 °C.

Experiments in the presence of a common anion salt, triisoamyl, *n*-butylammonium hexachloroantimonate ($TABN^+$, $SbCl_6^-$), have shown that for the initiation step the k_{in} value at 10 °C is independent of the salt concentration and that $k_{in}^{+} = k_{in}^{\pm}$ [29]. Assuming $K_D = 3 \cdot 10^{-5}$ at 10 °C for the dissociation of ion pairs (justified by comparison with several similar electrolytes) the propagation rate constants on ion pairs and unpaired ions were determined [$k_p^{+} = 4.6 \cdot 10^4$ dm^3/(mol·s); $k_p^{\pm} = 1.1 \cdot 10^4$ dm^3/(mol·s)] confirming that the reactivities of both species in the propagation step are rather close.

Stopped-flow spectroscopic study of polymerization initiated by various protonic or Lewis acids in $(CH_2Cl)_2$ at 30 °C were made following a broad absorbance at 380 nm assumed to be that of the growing carbocation and reaching a maximum after 20—40 ms [30—33]. The rapid monomer consumption (*e.g.* 40 % in 0.3 s) was simultaneously followed at 295 nm. The active sites concentration, measured at 380 nm, was based on an extinction coefficient $\varepsilon = 2.8 \cdot 10^4$ dm^3/(mol·cm) obtained from the ionization of CH_3OPh-$CHOHCH_3$ in H_2SO_4 assuming complete conversion into the monomeric cation with a maximum at 348 nm. The derived composite k_p at 30 °C ranged between $4 \cdot 10^3$ with I_2 as initiator and $1.3 \cdot 10^5$ dm^3/(mol·s) with CF_3SO_3H. However it was shown later [34] that the cation derived from *p*-MeOSt absorbs at 340 nm and that the absorbance maximum at 380 nm cannot be that of the active carbocation, but might result from species in equilibrium with it.

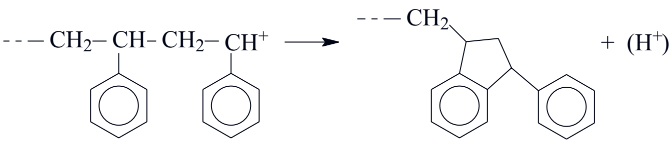
Living polymerizations of *p*-MeOSt were reported by R. Faust *et al*. [35]. Best results (moderate rates, theoretical $\overline{M}_n$ s, polydispersities <1.1) were obtained for initiation by *p*-MeOStCl and $SnBr_4$ in CH_2Cl_2 in presence of di-*tert*-butylpyridine at temperatures ranging from -60 to -20 °C. Linear plots of $\overline{M}_n$ *vs*. conversion were observed, even up to $\overline{M}_n = 1.2 \cdot 10^5$ at -30 °C. The living character was confirmed by chain extension experiments and a lifetime of the living ends of ~30 min under monomer starved conditions was estimated at -30 °C. Polymerizations were first order both in [M] and in [$SnBr_4$], and the apparent propagation rate constant k_1 was reached from the linear plots of ln([M]$_o$/[M]) *vs*. time. The quantitative ionization of *p*-MeOStCl with both $SnBr_4$ and $TiCl_4$, used as a model for the propagating cation, led to similar absorption maxima at 344—348 nm with ε_{348} ~28 000 dm^3/(mol·cm) at -30 °C, in accordance with previous literature results. Ionization constants $K_i = 9.16 \cdot 10^{-3}$ dm^3/mol at -30 °C and $K_i = 3.11 \cdot 10^{-2}$ dm^3/mol at -60 °C were obtained allowing the determination of the absolute propagation rate constants on ion pairs $k_{p(-30)}^{\pm} = 1.07 \cdot 10^5$ dm^3/(mol·s) and $k_{p(-60)}^{\pm} = 3.83 \cdot 10^4$ dm^3/(mol·s).

Competition experiments with phenylsilane as capping agent gave rather close values [$k_{p(-30)}^{\pm} = 18 \cdot 10^4$ dm^3/(mol·s) and $k_{p(-60)}^{\pm} = 3 \cdot 10^4$ dm^3/(mol·s)]. When using $TiCl_4$ as coinitiator, competition experiments led to similar results.

All these values are of the same order of magnitude as those measured for the living polymers of indene and 2,4,6-trimethylstyrene using the ionic species concentration method (ISC).

LIVING CHARACTER OF THE CATIONIC POLYMERIZATION OF 2,4,6-TRIMETHYLSTYRENE

In the case 2,4,6-trimethylstyrene (TMeSt), the *o*, *p*-substitution of the aromatic ring prevents intra- and intermolecular alkylation observed with styrene (Scheme E), and should simultaneously enhance the stability of the propagating cation, leading thus to a living behaviour of the polymerization.



Scheme E

This was reported in an early study on the polymerization of TMeSt initiated by the cumyl acetate/BCl_3 initiating system in CH_3Cl at -30 °C [36]. It was concluded that chain transfer to monomer was limited or absent but residual water was still contributing to the initiation. The plot of $\overline{M}_n$ *vs*. conversion was almost perfectly linear up to ~$2 \cdot 10^4$, but the polydispersity index remained high (5.6 to 2.6) during the course of the polymerization.

In collaboration with R. Faust, we reexamined the polymerization of TMeSt initiated by its chloride TMeStCl with BCl_3 as coinitiator in CH_2Cl_2 in the range -20 to -70 °C using highly purified reagents and in presence of proton trap (DTBP) [37, 38]. The ionization equilibrium constant of TMeStCl in presence of BCl_3 in CH_2Cl_2, and thus of the chlorinated chain end, was determined by spectrophotometry at different temperatures,

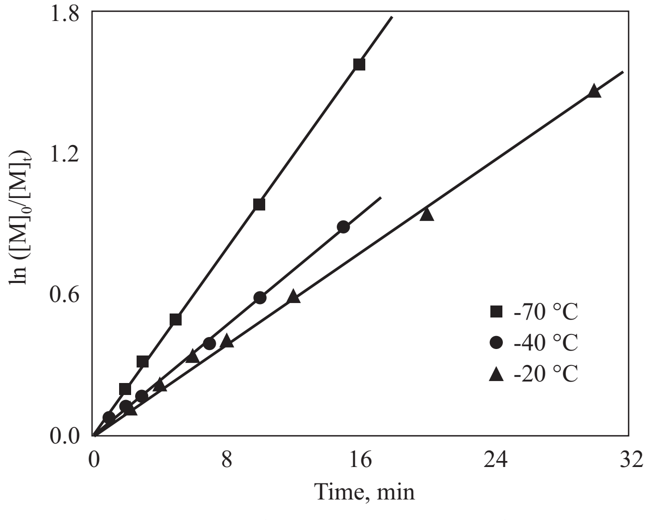


Fig. 7. First-order plots of ln([M]$_0$[M]) *vs*. time for the cationic polymerization of 2,4,6-trimethylstyrene initiated by TMeStCl/BCl_3 in CH_2Cl_2 in presence of proton trap for different temperatures. [TMeStCl] = 10^{-3} M, [TMeSt] = 0.136 M, [BCl_3] = $5 \cdot 10^{-2}$ M, [DTBP] = $3 \cdot 10^{-3}$ M

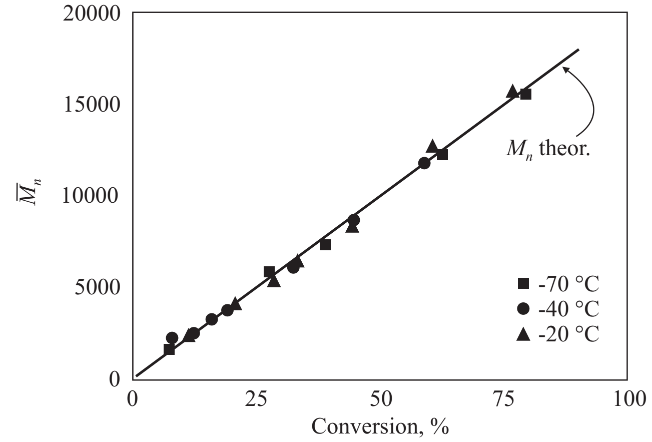


Fig. 8. Linear variation of $\overline{M}_n$ with conversion at different temperatures in the cationic polymerization of 2,4,6-trimethylstyrene initiated by TMeStCl/BCl_3 in CH_2Cl_2 in presence of proton trap (DTBP). Same conditions as in Fig. 7

using the molar extinction coefficient of $TMeSt^+$ [λ_{max} = 334 nm, ε = 25 700 $dm^3/(mol \cdot cm)$ at -70 °C] already reported for complete ionization by reacting the chloride with $GaCl_3$ [39].With the much more nucleophilic BCl_4^-, the ionization is very low but perfectly reversible when varying the temperature which indicates the stability of the cation in equilibrium with the dormant chloride. The ionization constant K_i varies from $2.30 \cdot 10^{-3}$ dm^3/mol at -70 °C to $4.05 \cdot 10^{-4}$ dm^3/mol at -20 °C and ΔH_i = -14.8 kJ/mol.

The TMeSt polymerization behaves as a perfectly living system with linear variation of ln ($[M]_0/[M]$) *vs.* time and linear variation of $\overline{M}_n$ *vs.* conversion (Fig. 7, 8). A narrow polydispersity was observed at all temperatures (-70 °C to -20°C), decreasing during the course of the reaction down to 1.03—1.05 for complete conversion (Fig. 9) in agreement with the absence of separate initiation step (use of an initiating carbocation identical to the propagating one). An ideal «no transfer» situation should lead to a linear Mayo plot of $1/DP_n$ *vs.* $1/DP_{n,th}$ going through the originin ($k_{trm}/k_p = 0$) at any temperature. This was verified, but the plot gathering all available data over the -70 ° to -20 °C range with $\overline{M}_n$ varying from 2 to $8 \cdot 10^4$ was not accurate enough to discard a possible very low transfer to monomer (average $k_{trm}/k_p < 4 \cdot 10^{-4}$).

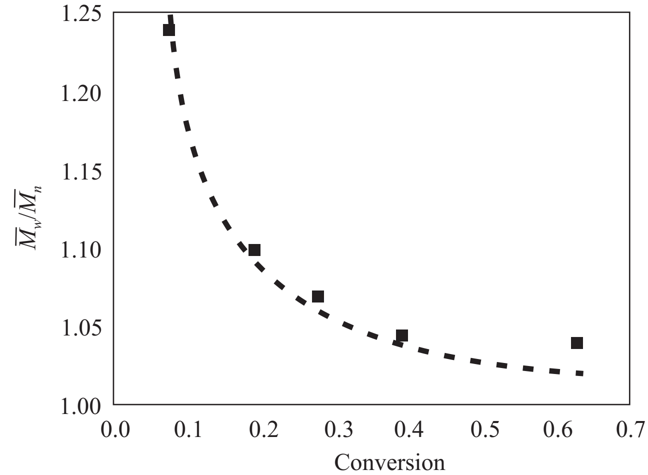


Fig. 9. Polydispersity index *vs.* conversion for the polymerization of 2,4,6-trimethylstyrene at -70 °C in CH_2Cl_2 in presence of proton trap (DTBP). Same conditions as Fig. 7

$$\mathrm{P_nCl} + \mathrm{BCl_3} \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} \mathrm{P_n^+BCl_4^-} \qquad (8)$$

The kinetics of polymerization have been treated in terms of a living system, where equilibrium exists between dormant (P_nCl) and propagating chain ends ($P_n^+BCl_4^-$) as shown in eq. (8), k_i is the rate constant of ionization (activation) and k_{-i} is the rate constant of recombination (deactivation). Only ion pairs are considered due to the common anion effect of the pyridinium salt. The rate of polymerization is expressed as (eq. 9)

$$R_p = -\mathrm{d}\,[\mathrm{TMeSt}]/\mathrm{d}t = k_p^{\pm}\,[\mathrm{P_n^+}][\mathrm{TMeSt}] = k_1\,[\mathrm{TMeSt}] \qquad (9)$$

which leads to,

$$\ln \frac{[\mathrm{TMeSt}]_0}{[\mathrm{TMeSt}]_t} = k_1 t = k_p^{\pm} K_i\,[\mathrm{BCl_3}]_o [\mathrm{P_nCl}]_0\, t \qquad (10)$$

where: k_1 is the first order apparent rate constant of propagation obtained from the plot of ln ($[M]_0/[M]$) *vs.* time, K_i is the equilibrium constant of ionization and [P_nCl] is the concentration of dormant ends, which since the extent of ionization is small, closely equals the total chain end concentration. The absolute propagation rate constant $k_p^{\pm}$, obtained from eq. 10, varies from $1.35 \cdot 10^4$ $dm^3/(mol \cdot s)$ at -70 °C to $3.78 \cdot 10^4$ $dm^3/(mol \cdot s)$ at -20 °C, with $E_p^{\pm}$ = 9.0 kJ/mol.

The rate constant of ionization k_i and of deactivation k_{-i} have been determined. The k_{-i} can be obtained from the $k_p^{\pm}$ and the polydispersity versus conversion plot by curve fitting as derived by Müller *et al.* [40] for living systems when the ratio ionic to dormant species is ≤ 10^{-2}, which is the case for the present polymerization. The ionization rate constant k_i is then determined from the K_i values. The obtained k_{-i} values increased from $1.42 \cdot 10^3$ to $6.98 \cdot 10^3$ s^{-1} when increasing the temperature from -70 °C to -20 °C, whereas k_i was slightly decreasing from 3.27 to 2.82 $dm^3/(mol \cdot s)$ in the same temperature range. The ionization equilibrium is thus essentially governed by the rate of deactivation, with a higher extent of ionization when decreasing the temperature, in accordance with the negative value of the apparent activation energy for propagation usually observed in cationic polymerization of ethylenic monomers [15].

Competition experiments have been carried out in CH_2Cl_2 at -70 °C in presence of proton trap using

2-chloroprene, a weak enough π-nucleophile, as capping agent. A value of $k_p^{\pm} = 8.3 \cdot 10^4$ $dm^3/(mol \cdot s)$ was obtained, in reasonable agreement with that given by the ISC experiments. In contrast, the linear free energy relationship approach [41] of k_p led to a value at 20 °C of $3 \cdot 10^7$ $dm^3/(mol \cdot s)$, three orders of magnitude higher than that extrapolated at the same temperature from the ISC experiments.

COMPARISON OF RECOMBINATION RATE CONSTANTS FOR INDENE AND 2,4,6-TRIMETHYLSTYRENE WITH THOSE OF STYRENE AND ISOBUTYLENE

For reactions propagating on ion pairs $P_n^+MtX_n^-$, the rate constant k_{-i} of recombination of P_n^+ and X^- has been obtained by two methods [24]:

— from the rapid monomer consumption (RMC) observed at the beginning of polymerization [42], giving the number of monomer molecules added during one cycle of ionization or «run number» [43] equal to

$$RN = k_p^{\pm}[M] / k_{-i} \tag{11}$$

— from the plot of polymer distribution *vs.* conversion [40], as mentioned in the previous section.

For 2,4,6-trimethylstyrene (TMeSt), the recombination rate constant k_{-i} was measured from $k_p^{\pm}/k_{-i}$ obtained by the second method and $k_p^{\pm}$ by the ionic species concentration method (ISC). With BCl_4^- as counterion, values of k_{-i} equal to $3.9 \cdot 10^3$ s^{-1} and $1.4 \cdot 10^3$ s^{-1} were respectively obtained at -40 °C and -70 °C.

For indene, k_{-i} was calculated from $k_p^{\pm}/k_{-i}$ obtained by RMC and $k_p^{\pm}$ by ISC, and with $SnCl_5^-$ as counterion, this led to $k_{-i} = 5.2 \cdot 10^2$ s^{-1} at -40 °C. As expected for ions recombination, k_{-i} slightly decreases when increasing the bulkiness of the counterion.

The values of $k_p^{\pm}/k_{-i}$ obtained from RMC for styrene (78 dm^3/mol at -70 °C) and isobutylene (6.3 dm^3/mol at -40 °C) are of the same order of magnitude as those for TMeSt (6.9 dm^3/mol at -40 °C) and indene (190 dm^3/mol at -40 °C).

But since the $k_p^{\pm}$ obtained by the diffusion clock method (DC) for styrene (-80 °C, $TiCl_4$) or isobutylene (-40 °C, BCl_3) are of the order of 10^9 $dm^3/(mol \cdot s)$, the resulting k_{-i} would be respectively $4.7 \cdot 10^7$ s^{-1} and $2.7 \cdot 10^8$ s^{-1}, *i.e.* 5 or 6 orders of magnitude larger than the values measured for TMeSt or indene. Such a large difference cannot be explained by a nucleophilicity of $polySt^{\pm}$ and $polyIB^{\pm}$ carbocations 10^5 times larger than $polyTMeSt^{\pm}$ and $poly(indene)^{\pm}$, and rather would indicate that the $k_p^{\pm}$ (and diffusion-limited propagation) obtained by the DC method are questionable.

A tentative explanation has been proposed [24, 26] and discussed for the large difference (a factor of 10^4—10^5) between the rate constants of propagation k_p measured from the rate and the active sites concentration (ISC) and those obtained from the competition for the active site between the monomer M and a strong nucleophile N used for capping (DC).

Propagation — and capping by N — would occur in two steps, involving first an equilibrium of complexation by M or N then followed by an unimolecular rearrangement with respective rate constants $k_{p(1)}$ and $k_{c(1)}$ [eq. (12, 13)].

$$P^{\pm} + M \underset{}{\overset{K_M}{\rightleftharpoons}} P^{\pm}, M \xrightarrow{k_{p(1)}} PM^{\pm} \tag{12}$$

$$P^{\pm} + N \underset{}{\overset{K_N}{\rightleftharpoons}} P^{\pm}, N \xrightarrow{k_{c(1)}} PN^{\pm} \tag{13}$$

This is compatible with a second order propagation with

$$k_p^{\pm} = k_{p(1)} K_M \tag{14}$$

and with $K_M < 0.1$ and $K_N \geq 100$ [24].

In DC method, the $k_p^{\pm}$ have been obtained by assuming that growing carbocations poly(*p*-ClSt)$^{\pm}$, poly(St)$^{\pm}$, and poly(*p*-MeSt)$^{\pm}$ add monomer at diffusion limited rate. But this assumption has led to disputable conclusions about carbocations relative reactivities and are in disagreement with statistical copolymerization data.

These large values of k_p have led to the conclusion that for a vinyl monomer «...the effects of substituents on carbocation reactivity is much larger than their effect on monomer reactivity». For example, at -40 °C, «the (*p*-MeOSt)$^+$ cation is about 10^6 times less reactive compared to the (*p*-MeSt)$^+$ cation» while «the *p*-MeOSt monomer is only 42 times more reactive than *p*-MeSt and 300 times more reactive than styrene» [44]. Such a difference in carbocation reactivities is in disagreement with the electrophilicity parameters *E* of (*p*-MeOSt)$^+$ (4.7) and (*p*-MeSt)$^+$ (6.7) which predict a difference by a factor of 100, the $(E + N)$ values being about 8 and the k_p^+, calculated from the Mayr's linear free energy relationship, being of the order of 10^8 for the two monomers. More recently, it was stated that «the (*p*-ClSt)$^+$ cation is 1 billion times more reactive than (*p*-MeOSt)$^+$, whereas the reactivity of *p*-MeOSt monomer is only about 800 times higher than that of *p*-ClSt» [45].

We have also shown [25, 46] that diffusion controlled propagation and cross-propagation rate constants obtained by the DC method for *p*-chlorostyrene, styrene, *p*-methylstyrene and other monomers are not compatible with the reactivity ratios (r_1, r_2) in their copolymerization. The ideal situation $r_1 = 1/r_2$ is in agreement with an inverse relationship between the reactivities of the monomer and the corresponding cation for a series of monomers as was proposed earlier [47].

CONCLUSIONS

We first showed in the case of isobutylvinyl ether that polymerizations said to be living occurred with transfer reactions and that a living process was only approached at low temperature and/or when the theoretical molecular weight was not too large.

A similar situation was found with indene, transfer to monomer being detected at -40 °C and undetected at -70 °C for theoretical $\overline{M}_n$ up to 10^5. This is much better than for styrene and *p*-methylstyrene for which transfer and termination involving the penultimate end group occur, while they are absent for steric reasons in the cases of indene and 2,4,6-trimethylstyrene. For this last monomer also, transfer to monomer could theoretically occur. It was not detected between -70 and -20 °C, but the available data and relevant Mayo plot were not precise enough to definitely discard this eventuality.

The stabilities of the carbocations of indene and 2,4,6-trimethylstyrene are much better than those of other substituted styrenes. Their UV absbsorption maxima remained unchanged for minutes (or more) and at much higher temperatures than for styrenes. The most stable carbocations are those of 2,4,6-trimethylstyrene because the trisubstitution of the aromatic ring inhibits reactions of carbocations with the polymer chains. Even if the stability of the indanyl cation was also observed, it has nevertheless been shown that branching [48] may occur in polyindenes of very high molecular weight. In the case of *p*-methoxystyrene, conditions to observe a stability of the carbocation and a living behaviour have also been clearly identified [35].

The kinetics of initiation and propagation could be explained by the classical equilibria of ionization of dormant end groups by the Friedel Craft halide giving ion pairs, and of the further dissociation of the latter into unpaired ions. The determination of the equilibrium constant of ionization of the models of active species, *i.e*. the first ionized monomer unit, together with the rates of propagation has permitted to measure the propagation constants k_p for *p*-methoxystyrene, 2,4,6-trimethylstyrene and indene at different temperatures, *e.g*. of the order of $10^4—10^5$ dm^3/(mol·s) at -40 °C.

Apart the ideal case which can be encountered in anionic polymerization (no termination, no transfer), the control of «livingness» in ionic chain polymerization consists in searching for interelated conditions (structure of monomer, temperature, solvent, initiating system, additives, *etc*.) for which ionized (paired or unpaired) propagating species of relative stability are maintained in very low concentration by a reversible deactivation equilibrium shifted towards highly dominating dormant species. These species should present, on average, periods of instantaneous activity shorter than the time between two chain-breaking or transfer processes. This may lead, under suitable conditions, to undetectable transfer processes even for high molecular weights and to an apparently living situation.

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

— *B. Parzuchowska, P. Parzuchowski* — Polimery uwalniające tlenek azotu(II)

— *I. Zarzyka* — Oligomery zawierające fragmenty strukturalne imidazolidynotrionu otrzymywane z kwasu parabanowego i mocznika (*j. ang.*)

— *I. Jacukowicz-Sobala, A. Ciechanowska, E. Kociołek-Balawejder* — Polimer hybrydowy zawierający tlenki żelaza otrzymany z wykorzystaniem polimeru redoksowego. Cz. I. Synteza i charakterystyka (*j. ang.*)

— *E. Irzmańska, K. Dyńska-Kukulska, M. Jurczyk-Kowalska* — Charakterystyka zjawisk mikrostrukturalnych zachodzących na powierzchni rękawic ochronnych w wyniku oddziaływania czynników mechanicznych i chemicznych (*j. ang.*)

— *B. Janowski, K. Pielichowski, R. Kwiatkowski* — Układy nanohybrydowe poliuretan (PUR)/funkcjonalizowany silseskwioksan (PHIPOSS). Cz. II. Rentgenowskie badania strukturalne metodami WAXD i SAXS

— *D. Ziółkowska, I. Syrotynska, A. Shyichuk* — Oznaczanie biguanidu poliheksametylenowego metodą fotometrycznego miareczkowania roztworem czerni amidowej 10B (*j. ang.*)

— *D. Paukszta, M. Szostak, M. Rogacz* — Właściwości mechaniczne kompozytów kopolimerów polipropylenu napełnionych słomą rzepakową (*j. ang.*)

— *K. Formela, M. Cysewska, J. Haponiuk* — Wpływ konfiguracji oraz prędkości obrotowej ślimaków na właściwości produktów termomechanicznej regeneracji odpadów gumowych prowadzonej przy użyciu współbieżnej wytłaczarki dwuślimakowej (*j. ang.*)