The Cationic Polymerization of 2, 4, 6-Trimethylstyrene: From "truly living" to "controlled" polymers?

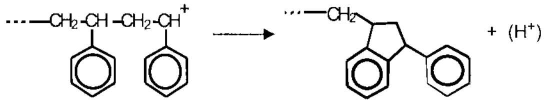
J.-P. Vairon[a], M. Moreau[a], B. Charleux[a], A. Cretol[a], R. Faust[b]*

[a]Unité de Chimie des Polymères, UMR 7610, Université P. et M. Curie, 4, Place Jussieu, 75252 Paris cedex 05, France
[b]University of Massachusetts Lowell, Chemistry Department,
1 University Avenue, Lowell, MA 01854, USA

Summary: The cationic polymerization of 2,4,6-trimethylstyrene in dichloromethane was initiated by the corresponding chloride with $GaCl_3$ and BCl_3 as Lewis acids. With $GaCl_3$, the initiator, as well as the propagating ends, are fully ionized. The resulting cation appears stable from -70 to -30 °C, leading to "truly living" polymers. With BCl_3, the ionization is very low and the ionization constant Ki was determined (2.9 10^{-3} L. mol^{-1} at -70°C). In this case the polymerization appears perfectly "controlled", with a good agreement between Mn_{th} and Mn_{exp} (up to 80000 $mol.g^{-1}$) and a very narrow polydispersity. A propagation rate constant kp_{app} = 8500 mol. L. $mol^{-1}.s^{-1}$ was estimated at -70 °C.

Introduction

Indanic cyclization, through Friedel-Craft alkylation of the penultimate aromatic ring, has long been recognized as one of the major chain transfer processes in the cationic polymerization of styrene.[1-4]



Even if at low temperature this reaction appears slower than propagation and the styryl cation is relatively stable[5], it obviously prevents any livingness for these polymers, and led Kennedy and co-workers, in their search for "quasi-living" systems[6-7] to consider the polymerization of the 2,4,6-trimethylstyrene (TMeSt)

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for which the *o*-alkylation is not possible.

In a first work[6] these authors studied the polymerization of TMeSt initiated by cumyl chloride in conjunction with either $TiCl_4$ or BCl_3 as coinitiators, in a solvent mixture (n-C_6H_{14}/CH_2Cl_2) of medium polarity. At –50°C with a low rate of monomer addition (starved feeding) a semi-controlled behavior was observed. The number of macromolecules remained constant during the polymerization and a good agreement between theoretical and experimental molar masses in the range of Mn = 5–20 10^3 $g.mol^{-1}$ was observed. The polydispersity, however, remained rather high (1.5 – 3.5).

They reexamined the polymerization[7] with the cumyl acetate/BCl_3 initiating system in CH_3Cl at –30°C using both the incremental monomer addition technique (IMA) and the one shot process (AMI), still working in semi-purity conditions (dehydration of reagents by distillation over CaH_2)[8]. It was shown that chain transfer to monomer was limited or absent and that residual water was contributing substantially to the initiation. The kinetics were not reported but the plot of Mn vs. conversion was almost perfectly linear up to Mn = 30000 $g.mol^{-1}$, and the polydispersity index was rather low (1.12 to 1.2), indicating that the polymerization was either "truly living" (no transfer, no termination) or "controlled" (reversible termination). This obviously raises the question of the extent of ionization by BCl_3 of the AcO-, Cl- or MeO- terminated dormant chains.

We decided to reexamine the polymerization of TMeSt initiated by the 2,4,6-trimethylstyryl cation, a model of the propagating end, focusing on the ionization of the hydrochlorinated TMeSt (TMeStCl) in presence of $GaCl_3$ or BCl_3 as Lewis acids leading to counteranions of very different nucleophilicities.

Experimental

The 2,4,6-trimethylstyrene (Aldrich) was thoroughly purified (> 99,5%) by vacuum distillation (spinning band) in order to eliminate most of the 2,4,6-trimethylacetophenone precursor. The initiator 1-chloro, 1-[2,4,6-trimethyl-phenyl] ethane (TMeStCl) was synthesized by hydrochloration of the monomer and then distilled under vacuum.

"Semi purity" conditions: Dichloromethane (Aldrich) was dried over molecular sieves, refluxed and distilled from CaH_2. $GaCl_3$ (Aldrich) and BCl_3 (Aldrich) were used as received. Polymerizations were performed in a glove box under nitrogen.

"High purity" conditions: The solvent was washed with aqueous potassium hydroxide, and then dehydrated under vacuum either on sublimated P_2O_5 and/or sodium films. The crystalline $GaCl_3$ was sublimated and the liquid BCl_3 dehydrated over 3Å molecular sieves, both under vacuum, before distribution of their CH_2Cl_2 solutions in sealed ampoules. Polymerizations were performed in a sealed reactor. After quenching by a methanol/pyridine mixture, polymers were precipitated in methanol, filtered and dried overnight.

Number average molar masses were determined by SEC using polystyrene calibration modified by a correction factor obtained from a MALDI-TOF MS (for the lowest mass) and a triple detection SEC (RI, LS, viscosity). This factor appears constant over the whole considered MM range ($1 - 8\ .10^4$ g.mol^{-1}),

$$Mn_{PTMeS} = 1.1\ (\pm\ 0.04).\ Mn_{eq\text{-}PS}$$

Ionization of TMeStCl by $GaCl_3$ or BCl_3

When mixing a CH_2Cl_2 solution of $GaCl_3$ ($4.3\ 10^{-3}$ mol. L^{-1}) in four-fold excess with TMeStCl under vacuum at –70 °C a strong UV absorption (333 nm, ε = 19800 L. mol^{-1}.cm^{-1}) immediately develops and levels off. A similar observation with the same system was previously found by Schimmel and Mayr[9] (335 or 342 nm, ε = 25700 L. mol^{-1}.cm^{-1}) using either TMeStCl or the dimeric halide.

We also followed this ionization by ^1H NMR spectroscopy in CD_2Cl_2 at –78 °C. The spectrum (Fig. 1) shows exclusively the resonances of the cation, with no residual TMeStCl, indicating complete ionization of the chloride. Furthermore the trimethylstyryl cation appears perfectly stable from –78 to –30 °C. Importantly, ionization is complete only in the presence of at least two equivalents of $GaCl_3$, which suggests the presence of dimeric $Ga_2Cl_7^-$ counter anions.

When using BCl_3 a very low absorption develops immediately, which must be

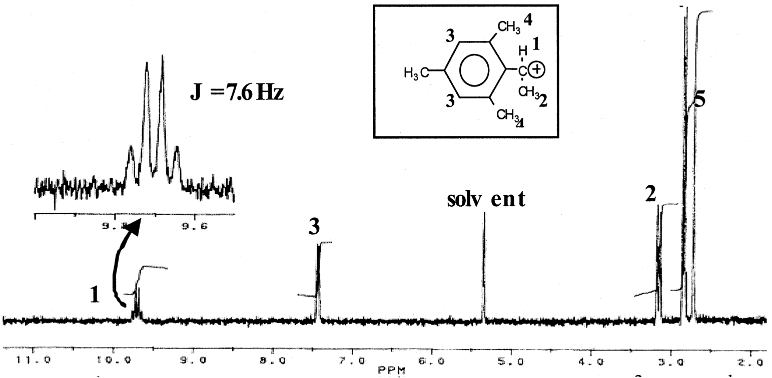
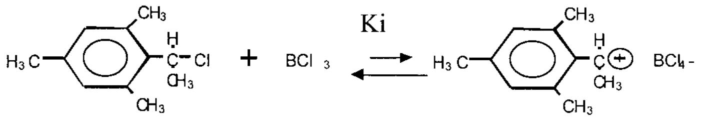


Figure 1: ^{1}H NMR spectrum of a mixture of TMeStCl (7.2 10^{-2} mol. L^{-1}) and $GaCl_3$ (14.5 10^{-2} mol. L^{-1}) in CD_2Cl_2 at –78 °C, showing the complete ionization of the chloride.

separated from a slowly increasing absorption at a similar wavelength (325 nm), which corresponds to a complex of BCl_3 with residual traces of 2,4,6-trimethylacetophenone in the TMeStCl. Column chromatography of TMeSt on silica gel, using hexane as eluent, completely eliminated the ketone derivative as confirmed by GC-MS and gave identical results concerning the ionization of the halide.

Careful experiments performed in Lowell and in Paris (Fig.2) allowed to reach similar values of the ionization constant (scheme 1) at –70 °C ($K_i = 2.9 \pm 0.4\ 10^{-3}$ L. mol^{-1}). If we consider the initiator as a representative model of the propagating ends, it is clear that the low nucleophilicity of the $Ga_2Cl_7^-$ counteranion leads to full ionization and the formation of a stable carbocation whereas the strongly nucleophilic BCl_4^- counteranion collapses reversibly with the cation. As transfer processes appear limited or absent[7], a "truly living" behavior may be expected when using $GaCl_3$ as coinitiator, and a "controlled" situation with reversible termination should be expected when using BCl_3.

Scheme 1



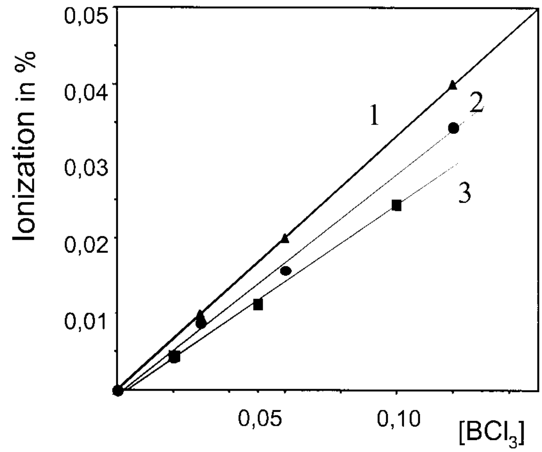


Figure 2: Ionization of TMeStCl with BCl_3 in CH_2Cl_2 at –70 °C.
$[TMeStCl]_o = 0.1$ mol. L^{-1}.
In presence of ketone traces (1) Paris (2) Lowell. In absence of ketone (3) Lowell.

Polymerization of TMeSt Initiated by TMeStCl/$GaCl_3$

These polymerizations were performed in CH_2Cl_2 solution at – 70 and – 40 °C, all under high purity conditions (see Experimental) except Expt 1. They are very rapid and complete within a few seconds. Since the polymerizations were too fast, the kinetics could not be followed by conventional techniques but may be relevant of stopped-flow and continuous-flow experiments.

It can be seen in Table 1 that the agreement between theoretical and experimental M_n is excellent, for polymerization carried out in semi-purity as well as in high purity conditions.

This indicates that every initiator molecule leads to a growing chain and confirms the absence of chain transfer to monomer, as expected from the previous

Table 1. Polymerizations of 2, 4, 6-trimethylstyrene initiated with TMeStCl – $GaCl_3$ in CH_2Cl_2 solution. $[GaCl_3]_o$ = 5 to 6 .10^{-3} mol. L^{-1}

Expt	T (°C)	$[M]_o$ (mol. L^{-1})	$[I]_o$ x 10^4 (mol. L^{-1})	[DTBP] x 10^3 (mol. L^{-1})	Mn_{th} (g.mol^{-1})	Mn_{exp} (g.mol^{-1})	M_w/M_n
1[a)]	- 70	0.136	20.0	3.0	9930	10350	1.89
2	"	0.08	5.7	3.0	20440	20500	1.89
3	"	0.08	5.7	-	20440	21500	2.31
4	"	0.16	5.7	-	40980	39800	1.93
5	- 40	0.08	2.8	3.0	41710	46300	1.57

[a)] *Expt in glove-box*

observations of Faust and Kennedy[7]. No significant difference was observed for a polymerization performed in the presence or absence of 2,6-di-tert-butylpyridine (DTBP), which indicates that the residual water concentration is much lower than the concentration of the initiator.

As the chain ends are structurally identical to the initiator, it is reasonable to consider that they are also fully ionized when the $Ga_2Cl_7^-$ counteranion is used. If we assume that the propagating carbocation is stable similarly to the monomeric and dimeric cations, then every chain bears a stable carbocation, which propagates till complete monomer consumption and is only destroyed upon addition of the quencher. The situation is basically similar to the "living" behavior observed in anionic polymerization.

A still open question concerns the observed high polydispersity. Slow initiation relative to propagation cannot explain the results as it was shown[10] that in case of simultaneous initiation and propagation, the polydispersity index should remain below 1.375. Slow exchange between ion pairs and free ions may explain the broad molecular weight distributions, however, this explanation is questionable since it is now generally accepted that kp+ and kp± may be similar due to the large size of the counter-anion. Although we cannot completely eliminate the possibility that the stability of polymer cation is different from monomeric and dimeric cations, and therefore a slow termination may be operational, the most likely explanation of the high polydispersity may be the very rapid nature of the polymerization (inefficient mixing, local temperature jump, etc..).

Polymerization of trimethylstyrene initiated by TMeStCl / BCl_3

A series of polymerizations were performed both in semi-purity and high purity conditions.

Table 2 gives the results obtained from polymerizations under vacuum with highly dehydrated reagents. The reaction is drastically slowed down when BCl_3 is used in place of $GaCl_3$, and the time needed for complete conversion ranges between 30 to 60 min. This agrees well, as was observed for the initiator, with a much lower ionization of the chain ends, and thus a much lower concentration of propagating carbocations in equilibrium with dormant ends when BCl_3 was used.

There is a reasonable agreement between theoretical and experimental molar masses although it is not as good as in the previous case. The fluctuations are not systematic and most probably result from experimental inaccuracies, particularly for the highest molar masses. Nevertheless the distributions are remarkably narrow, which indicates that the control of the reaction is good. The addition of DTBP reduces the rate of polymerization and may be explained with a common anion effect of the pyridinium salt formed from still existing traces of moisture.

In order to confirm the "controlled" behavior of the polymerization with BCl_4^- as counteranion, the conversion and molar masses were followed versus time for a polymerization performed in semi-purity (glove-box) conditions.

Linear plots of Figures 3-4 together with the monotonous decrease of the polydispersity confirm that the reaction is well controlled up to complete conversion. The concentration of chains remains constant during the course of the polymerization but the observed difference between theoretical and experimental molar masses (Fig. 4) indicates that since the very beginning there is a constant excess (30%) of chains with respect to initiator.

Table 2. Polymerizations of TMeSt initiated by TMeStCl–BCl_3 in CH_2Cl_2 solution under high purity conditions. $[M]_o$= 0.08 mol. L^{-1} $[BCl_3]_o$= 3 .10^{-3} mol.L^{-1}

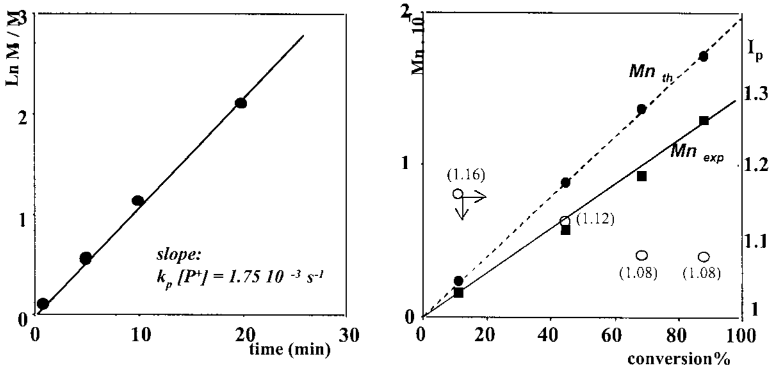
Expt	T (°C)	$[I]_o$ .10^4 (mol.L^{-1})	[DTBP] .10^3 (mol.L^{-1})	Time [a] (min)	Conv. (%)	$M_{n,th}$ (g.mol^{-1})	$M_{n,exp}$ (g.mol^{-1})	M_w/M_n
6	- 60	2.8	-	32	100	41710	44300	1.09
7	- 40	5.7	-	32	100	20490	24100	1.02
8	"	5.7	3.0	52	92	18850	19200	1.08
9	"	2.8	-	30	100	41710	48000	1.08
10	"	2.8	3.0	30	69	28780	22200	1.10
11	"	1.5	-	32	100	77870	76500	1.03
12	"	0.8	-	45	100	146000	104400	1.09
13	- 20	1.5	-	32	100	79450	85500	1.07

[a] *Addition of quencher*

If we consider that the proton trap (3 .10^{-3} mol. L^{-1}) consumed a stoichiometric amount of protons, the residual water in these semi-purity experiments can be estimated to be ~ 3.3 .10^{-3} mol. L^{-1}. This value is comparable to what was obtained previously by Faust and Kennedy[7] for polymerizations performed in conditions close to our "semi-purity" ones.

If we consider that the ionization constant of the chain ends is similar to that of the initiator TMeStCl at –70 °C (K_i 3. 10^{-3} L. mol^{-1}), the concentration of active cations in equilibrium with dormant ends should be $[P_n^+]$ 2 .10^{-7} mol. L^{-1}. Thus, the slope of the plot of Figure 3 leads to an approximate value of the apparent propagation rate constant of k_p 8500 L.mol^{-1}.s^{-1} at –70 °C. Owing to the noticeable amount of residual water in this semi-purity experiment, the concentration of the pyridinium salt is much higher than $[P_n^+]$. Thus the active cationic species should essentially be ion pairs and the above value corresponds to $k_p\pm$, even if the possible difference between $k_p\pm$ and k_p+ remains small. This experimental propagation rate constant is of same order of magnitude as that

Figures 3 and 4. Polymerization of 2,4,6-trimethylstyrene initiated by TMeStCl /BCl_3 in CH_2Cl_2 at –70 °C. $[M]_o = 0.136$ mol. L^{-1} ; $[TMeStCl]_o = 10^{-3}$ mol. L^{-1} ; $[BCl_3]_o = 5.3 .10^{-2}$ mol. L^{-1}; $[DTBP]_o = 3 .10^{-3}$ mol. L^{-1}



First order plot of monomer conversion.

Variation of Mn and Mw/Mn with conversion.

observed for styrene polymerization[5,11] but it is definitely much lower than the one (10^7 L. $mol^{-1}.s^{-1}$) predicted for TMeSt from Linear Free Energy Relationship[12].

Conclusion

This study deals with the different behaviors observed for the cationic polymerization of 2, 4, 6-trimethylstyrene initiated by trimethylstyryl halide of structure similar to that of the chain end, in presence of Lewis acids, $GaCl_3$ and BCl_3, generating counteranions of very different nucleophilicities. The *o,p*-substitution of the monomer ring prevents intramolecular cyclization, allowing thus a control of the polymerization. With $Ga_2Cl_7^-$, a weak nucleophile, ionization is complete, the concentration of active species is equal to that of the initiator ($P_n^+ = [I]_o$), and the polymers appear "truly living" as conventionally observed in anionic polymerization. To our knowledge such a "true living" behavior (perfectly stable cations, no reversible termination, no significant transfer) was not yet reported in the cationic polymerization of ethylenic monomers. With BCl_4^-, a strong nucleophile, ionization is very low and the chain ends are essentially dormant chlorides in equilibrium with a very low concentration of active cations ($P_n^+ \quad 10^{-4}.[I]_o$). This situation dominated by the reversible collapse of the counteranion is typical to that reported in the last two decades for the so called “living“ cationic polymerizations.

A tentative determination of the k_p of trimethylstyrene polymerization led to a value of same order of magnitude that already obtained for styrene at the same temperature and for same solvent, both of them being much smaller than the one expected from the Linear Free Energy Relationship. Nevertheless an accurate kinetic study remains to be done, using adequate techniques like stopped or/and continuous flow devices.

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