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Slow Initiation in Living Polymerizations with Reversible End Capping: Kinetic Analysis of the Initiation in Carbocationic Styrene Polymerization with 2-Chloro-2,4,4-trimethylpentane/$TiCl_4$†

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Introduction

Living polymerizations with reversible end capping (i.e., living carbocationic and living radical polymerization) have been at the frontiers of research in recent years.[1−3] The primary interest of our research group is the carbocationic living polymerization of isobutylene (IB).[4−6] Scheme 1 shows a simplified representation of initiation and propagation in living IB polymerization, where $K_1 = k_1/k_{-1}$ and $K_2 = k_2/k_{-2}$ are equilibrium constants, k_i and k_p are the initiation and propagation rate constants, and I* and P_n* represent contact ion pairs. TMPCl (see Chart 1) in conjunction with $TiCl_4$ is known to be a very effective initiator of living IB polymerization. It was proposed that for this system $K_1 = K_2$ and $k_i = k_p$ (see Scheme 1), which greatly simplified the kinetic derivations.[7] In contrast, *tert*-butyl chloride is a poor initiator, even though both the *tert*-butyl and TMP cations resemble the structure of the growing PIB chain. This difference was explained by the "back strain" exerted by the methyl side groups in TMPCl.[1−3,6−9] Later it was shown that TMPCl is somewhat less reactive than PIB-Cl, with $k_{i,PIB-Cl} \approx 3k_{i,TMPCl}$. However, k_p in IB polymerization was measured to be close to the diffusion controlled value ($k_p \approx 10^8$ L/(mol s));[8−10] thus, $k_p \approx k_i$ can be assumed for kinetic simulation of TMPCl/$TiCl_4$-initiated living IB polymerization. Indeed, good agreement was found between simulation and experimental data.[6] The importance of initiator structure, especially the nature of a γ-substituent, on the rate of initiation (a two-step process—ionization and monomer cationation; see Scheme 1) in carbocationic IB polymerizations was first investigated by Mayr et al. with the 2-chloro-2-phenylpropane (CumCl)/BCl_3 initiating system.[11] They showed that the "bottleneck" of the initiation reaction sequence is the Cum-IB-Cl adduct (see Chart 1), having lower reactivity than both CumCl and Cum-IB-IB-Cl. Recently, Kim and Faust reported the investigation of penultimate effects in $TiCl_4$-coinitiated IB polymerizations.[12] For instance, the overall reactivity of Cum-IB_1-Cl (see Chart 1) was found to be nearly an order of magnitude lower than that of TMPCl. They attributed this to the negative inductive effect of the phenyl ring in Cum-IB_1-Cl, leading to much lower ionization rate and equilibrium constants, while the reactivities of Cum-IB^+ and TMP^+ were found to be similar. These factors, together with lower back strain, that is, the release of steric strain upon ionization in -St-IB-Cl, were also cited to explain the penultimate effect found in the copolymerization of IB with St.

Scheme 1. Simple Model of Living Polymerization with Reversible End Capping

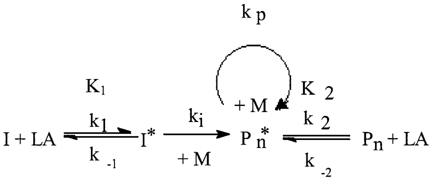
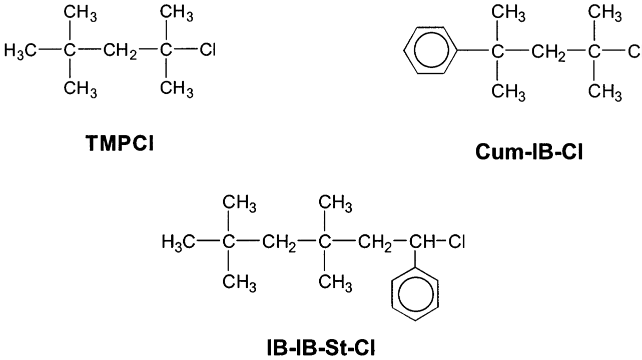


Chart 1. Initiator Structures



Carbocationic styrene (St) polymerization initiated with TMPCl is of great interest because this reaction mimics blocking polystyrene (PS) from living PIB in polyisobutylene−polystyrene (PIB−PS) block copolymer synthesis. In this case, after the addition of the first St unit an IB-IB-St-Cl structure arises (Chart 1). In line with Faust's work, this could be expected to have much lower overall reactivity than -IB-IB-Cl, leading to slow initiation. In addition, back strain of the IB−IB diad is released, which is expected to further reduce reactivity. Indeed, slow initiation was consistently found experimentally in carbocationic St polymerization initiated by TMPCl/$TiCl_4$.[13−16] This Note will discuss important findings of the study aimed at detailed investigations of the kinetics of initiation in this system, which may be generally applicable to living systems with reversible end capping.

Experimental Section

Materials. TMPCl was synthesized as reported.[4,5] $TiCl_4$, dimethyl acetamide (DMA), di-*tert*-butylpyridine (D*t*BP), and methanol were used as received (Aldrich). Methyl chloride (MeCl) was dried by passing it through a column filled with BaO and $CaCl_2$. Methylcyclohexane (MeCHx) was refluxed with CaH_2 for at least 24 h and distilled freshly before use. Styrene (St) was purified by chromatography over aluminum oxide (Aldrich).

Instrumentation. Polymer molecular weights (MWs) and molecular weight distributions (MWDs) were determined by SEC with a Waters system as described.[16] The ASTRA (Wyatt Technology) software was used to obtain absolute MW data with $dn/dc = 0.183$ for polystyrene in THF. Initiator consumption data were obtained from MW data: $[I] = [I]_0 - [P_n]$, where P_n = g of PIB formed/M_n, where M_n is the measured molecular weight, and I_{eff} (%) $= [I]_0 - [I]/[I]_0 \times 100$.

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† Dedicated to Prof. J. P. Kennedy on the occasion of his 75th birthday.

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Table 1. Initial Rates and Apparent Rate Constants of Initiation ($k_{i,app}$) in the Carbocationic Polymerization of St Initiated by the TMPCl/TiCl$_4$ System[a]

$[I]_0$ (mol/L)	$[TiCl_4]_0$ (mol/L)	react. time (min)	St conv (%)	SEC M_n ($\times 10^3$)	SEC MWD	$(d[I]/dt)_0$ (mol/(L s))	$k_{i,app}$ (L^2/(mol^2 s))
0.05	0.05	15	90	8.8	2.6	0.125	1.25
0.05	0.03	30	100	6.4	3.1	0.092	1.53
0.05	0.025	30	90	5.3	3.4	0.077	1.55
0.05	0.0125	40	82	11.7	2.8	0.035	1.39
0.004	0.016	40	80	45.2	1.6	0.040	1.23

[a] $[St]_0 = 2$ mol/L, [DMA] = 0.002 mol/L, [D*t*BP] = 0.007 mol/L, MeCHx/MeCl = 60/40, $T = -75$ °C.

Procedures. The polymerizations were carried out in a Mbraun LabMaster 130 glovebox equipped with an integral cold bath under dry nitrogen at −75 °C, as reported earlier for IB polymerizations.[4,5,17] A recipe for reaction 1 in Table 1 is given as follows: a 500 mL round-bottomed three-neck flask was charged with 138 mL of MeCHx and cooled to the reaction temperature (−75 °C). MeCl (99 mL), condensed at the reaction temperature, was added, followed by 2.29 g (2.29 mL or 0.015 mol) of TMPCl, 0.4 g (0.49 mL or 0.0021 mol) of D*t*BP, 0.054 g (0.057 mL or 0.00061 mol) of DMA, and 64.32 g (71 mL or 0.6 mol) of St. The mixture was stirred until all ingredients were at the reaction temperature. Polymerization was started with the addition of 2.93 g (1.7 mL or 0.015 mol) of TiCl$_4$ dissolved in 10 mL of MeCHx and prechilled to the reaction temperature. The total volume was 300 mL. Polymerizations were monitored in real time using a low-temperature fiber-optic probe equipped with a transmission (TR) head.[18] Four or five aliquots of 2 mL samples were taken in 5−10 min intervals for gravimetric conversion and MW measurements.

Results and Discussion

Reaction Order in TiCl$_4$. The rate of initiation in regards to [TiCl$_4$] is shown in eq 1, and the linearized form is shown in eq 2:

$$\frac{-d[I]}{dt} = C[TiCl_4]^n \tag{1}$$

$$\ln\left[\frac{-d[I]}{dt}\right] = n \ln[TiCl_4] + \ln C \tag{2}$$

The reaction order, n, can be measured experimentally from the initial rate of initiator consumption plots. The use of the initial rate method is recommended for reactions with unknown mechanisms, or when isothermal conditions cannot be ensured.[19] Initiator consumption rates were measured at $[TMPCl]_0 > [TiCl_4]_0$, with the exception of the last experiment with $[TMPCl]_0 > [TiCl_4]_0$. The $\ln([I]_0/[I])$ plots were not linear, so the initial rate was considered only. Interestingly, the $\ln([M]_0/[M])$ plots were linear at both $[TMPCl]_0 > [TiCl_4]_0$ and $[TMPCl]_0 < [TiCl_4]_0$, and the TiCl$_4$ order of the propagation rate was found to be 1.22 and 1.83, respectively (the details of propagation rate kinetics will be published separately). Strong electron pair donors (EDs) such as DMA are known to reduce the rate of polymerization,[13] but at high monomer concentration isothermal conditions cannot be achieved. Despite this, the TiCl$_4$ order of 1.83 at $[TMPCl]_0 < [TiCl_4]_0$ agrees with literature data. No data are available in the literature for $[TMPCl]_0 > [TiCl_4]_0$. Table 1 summarizes experimental data obtained for $[TMPCl]_0 > [TiCl_4]_0$, with the exception of the last experiment, where $[TMPCl]_0 < [TiCl_4]_0$. The $\ln[d[I]/dt]_0$ versus $\ln[TiCl_4]_0$ plot is linear, with a slope of $n = 1.06$. Thus, the order of initiation in TiCl$_4$ was found to be $n = 1$, similar to the case of carbocationic IB polymerizations initiated with $[TMPCl]_0 > [TiCl_4]_0$.[4,5]

Rate of Initiation. Using the simplified model shown in Scheme 1, the rate of initiator consumption was derived as follows:[6,7]

$$\frac{-d[I]}{dt} = \frac{k_1[I][LA](k_i/k_{-1})[M]}{1 + (k_i/k_{-1})[M]} \tag{3}$$

For living IB polymerizations initiated by TMPCl, $k_i \approx k_p \approx 10^8$ L/(mol s), $k_{-1} \approx 10^7$ s^{-1},[7,10] and $[M]_0 \approx 1-2$ mol/L; thus

$$\frac{k_i}{k_{-1}}[M] > 1$$

Since $[TiCl_4] \approx [TiCl_4]_0$, we get

$$\ln\frac{[I]_0}{[I]} = k_1[LA]_0 t \tag{4}$$

Indeed, in living IB polymerization the rate of initiator consumption was found to be directly proportional to k_1 and $[TiCl_4]_0$,[4,5,7] and no monomer concentration dependence has been reported. In TMPCl-initiated St polymerization, however, we expected P$_1$-Cl (IB-IB-St-Cl) to have much lower reactivity than TMPCl, on the basis of the arguments presented in the Introduction, rendering the addition of the second St unit the rate-determining step of the initiation rate. With this,

$$\frac{k_i}{k_{-1}}[M] < 1$$

and then

$$\frac{-d[I]}{dt} = \frac{k_1}{k_{-1}}k_i[I][LA]_0[M] \tag{5}$$

If our hypothesis is correct, in the case of St polymerization the rate of initiator consumption will depend not only on $[TiCl_4]_0$ but also on [M] as well, as shown in eq 5. It is noted that K_1 and k_i for this case are lumped equilibria and initiation rate constants for the addition of the first and second St units, with the reactivity of P$_1$ (IB-IB-St-Cl) being the rate-determining step. The effect of monomer concentration on the rate of initiation, that is, the initiation efficiency, was verified experimentally and is demonstrated in Figure 1. Initiation is still relatively slow compared to TMPCl-initiated IB polymerizations, but at $[TiCl_4]_0 = 0.04$ mol/L and $[St]_0 = 2$ mol/L, 100% initiator efficiency was achieved at about 70% monomer conversion.

Equation 5 can be integrated analytically for low conversion, when $[M] \approx [M]_0$:

$$\left(\ln\frac{I_0}{I}\right)_{t\to 0} = k_{i,app}[LA]_0[M]_0 t \tag{6}$$

where $k_{i,app} = k_i(k_1/k_{-1})$. Apparent initiaton rate constant ($k_{i,app}$) data were obtained from the initial slopes of

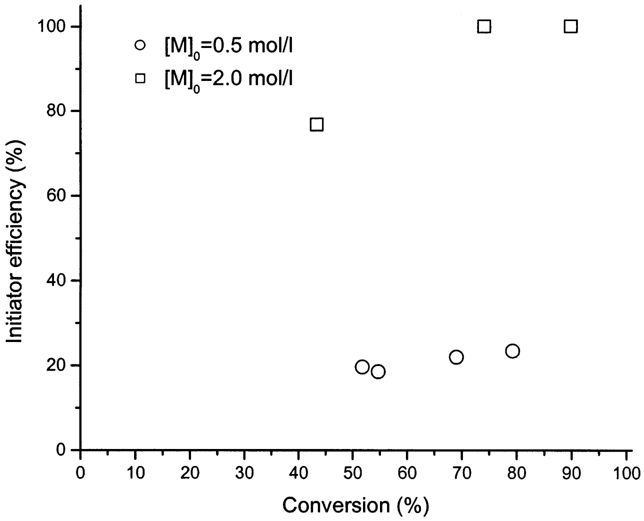

Figure 1. Effect of monomer concentration on initiation efficiency: $[TMPCl]_0 = 0.004$ mol/L, $[TiCl_4]_0 = 0.04$ mol/L, $[DMA] = 0.002$ mol/L, $[DtBP] = 0.007$ mol/L, MeCHx/MeCl = 60/40, andSM $T = -75$ °C.

experimental initiator consumption plots using eq 6 and are listed in Table 1. It can be seen that $k_{i,app}$ values are constant within experimental error and independent of $[TiCl_4]_0$, verifying that initiation is first order in $TiCl_4$, similar to the case of living IB systems.[4,5]

Slow initiation in St polymerization initiated by $TMPCl/TiCl_4$ can be rationalized as follows. In living polymerizations with reversible end capping, the average number of monomer units incorporated within a productive ionization period (run length) was defined as $l = (k_p/k_{-1})[M]$, which in turn is defined by the average lifetime of the active center.[20] In the case of IB polymerization initiated by $TMPCl/TiCl_4$, the lifetime of the active center is nearly identical during initiation and propagation. In the case of St, the lifetime of the growing polystyryl cation—once it is ionized—is expected to be longer than that of the TMP cation, due to the resonance stabilization of the phenyl ring. However, ionization of PIB-Cl is expected to be faster than that of PS-Cl, due to the negative inductive effect of the aromatic ring and the lack of back strain in the latter. In addition, the IB-IB-St-Cl structure that arises in the first step is expected to have much lower overall reactivity than -IB-IB-Cl.[12] Thus, the overall rate of initiation of St polymerization from TMPCl is expected to be slow in comparison to that of IB polymerization. This is in agreement with our recent finding (to be published) that the overall rate of carbocationic St polymerization is higher than that of IB polymerization under identical conditions. On the other hand, IB-St copolymerization is reportedly extremely slow,[12,21] which was explained with the penultimate effect in the −St-IB-Cl sequence.[12] The molecular weight distribution of PS obtained by living carbocationic polymerizations is relatively broad,[13−16] indicating large l values.

In summary, controlled/living polymerizations with reversible end capping are governed by the overall dynamics of the system. Better understanding of the kinetics can aid the synthetic chemist in achieving optimal conditions. Depending on the relative rates of initiation, propagation, and end capping, monomer concentration may play a significant role. On the basis of the results presented in this Note, and more detailed kinetic investigations, optimized conditions were found and living carbocationic polymerization of St was achieved, yielding high molecular weight PS ($M_n \approx$ 50 000 g/mol)—the details of this work will be published shortly.

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