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# Notes

## Measurement of Run Number in Quasiliving Cationic Polymerization Using the Rapid Monomer Consumption Phenomenon

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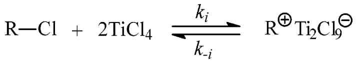
### Introduction

Quasiliving carbocationic polymerizations are so-named to denote the existence of an ionization equilibrium between reversibly terminated (dormant) chain ends and actively propagating carbocations, as illustrated in Scheme 1 for ionization by $TiCl_4$.[1,2]

**Scheme 1. Ionization Equilibrium in Quasiliving Carbocationic Polymerization**



$$R{-}Cl + 2TiCl_4 \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}} R^{\oplus}Ti_2Cl_9^{\ominus}$$

Run number (RN) is defined as the average number of monomer molecules added during one ionization−termination cycle.[3] In a recent paper, we demonstrated how RN can be measured by quantifying the number of monomer units consumed per initiating cation of the polymerization.[4] The measurement of RN by this method is made possible by the existence of a phenomenon termed rapid monomer consumption (RMC),[5] which occurs in quasiliving polymerizations whenever the ionization rate of the initiator is greater than that of the growing chain ends and the RN is significantly above unity. These conditions are met for styrene[4] (S) or isobutylene[4,5] (IB) polymerizations initiated by 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (bDCC)/$TiCl_4$. We further showed that RN may be used, in conjunction with the apparent rate constant for propagation, $k_{app}$, to calculate the apparent rate constant for ionization, $k_i$. These methods have recently been utilized by others for investigation of cationic polymerization kinetics of styrene[6] and *p*-chlorostyrene.[7]

In the absence of transfer reactions, the instantaneous RN is determined by the ratio of the rate of propagation, $R_p$, to the rate of reversible termination, $R_{-i}$, as shown in eq 1

$$\mathrm{RN} = \frac{R_p}{R_{-i}} = \frac{k_p[\mathrm{R}^+\mathrm{Ti_2Cl_9}^-][\mathrm{M}]}{k_{-i}[\mathrm{R}^+\mathrm{Ti_2Cl_9}^-]} = \frac{k_p[\mathrm{M}]}{k_{-i}} \qquad (1)$$

where $k_p$ is the absolute rate constant for propagation of paired ions and [M] is the monomer concentration. If RN can be measured under conditions of constant [M], then the quantity $k_p/k_{-i}$ can be calculated directly from eq 1. For our previous paper, we conducted such a measurement for S and IB polymerizations at −70 °C.[4] The concentration of monomer consumed during RMC, $[M]_{RMC}$, was divided by the concentration of initiating sites, $[I]_0 = 2[bDCC]$, to yield the run number of the first-formed bDCC cations:

$$\mathrm{RN}_{\lim_{\Delta[\mathrm{M}]\to 0}} = \frac{[\mathrm{M}]_{\mathrm{RMC}}}{[\mathrm{I}]_0} \qquad (2)$$

Since $k_{-i}$ is the same regardless of whether the cation originated from bDCC or from R−Cl, $[M]_{RMC}/[I]_0$ is essentially the RN for the general polymerization process.

An error arises, however, if $[M]_{RMC}$ is a significant fraction of $[M]_0$. In this case [M] in eq 1 is not constant, and the quantity $[M]_{RMC}/[I]_0$ represents an average run number, $\overline{\mathrm{RN}}$. In our previous paper, $[M]_{RMC}$ was a significant fraction of $[M]_0$ for S but not for IB polymerizations. As a result, we observed that $\overline{\mathrm{RN}}$ for S was dependent upon $[I]_0$. We interpreted this to indicate the operation of chain transfer to the bDCC initiator in S polymerizations. We now feel that that interpretation was incorrect, and in this paper we have used an integrated form of eq 2 that allows rigorous extraction of $k_p/k_{-i}$ at moderate to high monomer conversions.

### Experimental Section

The source and purification of reagents and materials and the polymerization procedure were identical to those described in our previous report,[4] except that the styrene concentration was 0.15 or 0.30 M. Reactions were conducted at a total volume of 0.2 L; molar concentrations of all reagents are given in Table 1.

Acquisition of infrared spectra of the polymerization components in real time was carried out exactly as described previously,[4] with the following exceptions: a ReactIR 1000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD) was used at 8 $cm^{-1}$ resolution; spectra of the 0.15 M styrene reactions were acquired continuously for 428 s at 1.36 spectra/s (2 scans/spectrum), and $TiCl_4$ was added at approximately 50 s; spectra of the 0.30 M styrene reactions were acquired continuously for 642 s at 0.90 spectra/s (3 scans/spectrum), and $TiCl_4$ was added at approximately 51 s; the solvent reference absorbance value, $A_r$, was reduced by either 1.7% or 3.5% to account for the volume dilution, and thus the solvent absorbance reduction, caused by subsequent addition of either 3.5 mL (0.15 M) or 6.9 mL (0.30 M) styrene, respectively.

A simulated polymerization reaction was formulated to provide an independent check of the reaction conversion measured by FTIR. A four-neck 250 mL reactor was equipped with stir rod and paddle, temperature probe, and the DiComp probe of the ReactIR 1000 and was allowed to cool to bath temperature (−70 °C). An air background (128 scans) was taken. To the flask were added $8.0 \times 10^{-4}$ mol di-*tert*-butylpyridine (D*t*BP), $1.0 \times 10^{-4}$ mol of tetra-*n*-butylammonium chloride (*n*-$Bu_4NCl$), 116 mL of methylcyclohexane (MCHex), and 77 mL of methyl chloride (MeCl). The mixture

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**Table 1. bDCC-Initiated Styrene Run Number, Rate Constant, and Molecular Weight Data**[a]

| $[\mathrm{I}]_0 \times 10^3$, M | $[\mathrm{M}]_{\mathrm{RMC}}$, M | $\overline{\mathrm{RN}}$ | $k_p/k_{-i}$, $\mathrm{M}^{-1}$ | $k_{\mathrm{app}} \times 10^4$, $\mathrm{s}^{-1}$ | $k_pk_i/k_{-i}$, $\mathrm{M}^{-3}\,\mathrm{s}^{-1}$ | $k_i$, $\mathrm{M}^{-2}\,\mathrm{s}^{-1}$ | $\Delta T_{\max}$, °C | $\bar{M}_{\mathrm{n,th}}$,[b] g/mol | $\bar{M}_{\mathrm{n}}$, g/mol |
|---|---|---|---|---|---|---|---|---|---|
| $[\mathrm{S}]_0 = 0.15$ M | | | | | | | | | |
| 8.0 | 0.0636 | 8.0 | 69.7 | 6.43 | 104 | 1.51 | 2.3 | 2411 | 2760 |
| 6.0 | 0.0524 | 8.7 | 71.7 | 4.88 | 105 | 1.47 | 1.8 | 2670 | 2600 |
| 4.0 | 0.0359 | 9.0 | 68.3 | 3.10 | 100 | 1.47 | 1.3 | 2803 | 3480 |
| 2.0 | 0.0240 | 12 | 87.0 | 1.75 | 113 | 1.30 | 0.8 | 3610 | 3600 |
| average | | | 70 | | 103 | 1.5 | | | |
| $[\mathrm{S}]_0 = 0.30$ M | | | | | | | | | |
| 4.0 | 0.0683 | 17 | 64.5 | 2.28 | 73.8 | 1.14 | 2.1 | 5355 | 7100 |
| 4.5 | 0.0804 | 18 | 69.3 | 2.63 | 75.7 | 1.09 | 3.4 | 5458 | 6800 |
| 5.0 | 0.0867 | 17 | 68.2 | 3.08 | 79.6 | 1.17 | 3.4 | 5360 | 6400 |
| 5.5 | 0.0894 | 16 | 64.3 | 3.23 | 75.9 | 1.18 | 3.4 | 5045 | 6900 |
| 6.0 | 0.0940 | 16 | 62.7 | 3.97 | 85.7 | 1.37 | 3.3 | 5036 | 5900 |
| 6.5 | 0.0979 | 15 | 60.8 | 3.39 | 67.4 | 1.11 | 3.9 | 4590 | 7600 |
| 7.0 | 0.0991 | 14 | 57.2 | 4.29 | 79.2 | 1.38 | 3.8 | 4488 | 5300 |
| 7.5 | 0.110 | 15 | 60.8 | 4.00 | 69.0 | 1.14 | 3.8 | 4430 | 4900 |
| 8.0 | 0.114 | 14 | 60.0 | 5.38 | 87.1 | 1.45 | 3.7 | 4574 | 5700 |
| average | | | 63 | | 77 | 1.2 | | | |
| std dev | | | 3.7 | | 6.3 | 0.13 | | | |

[a] $[\mathrm{TiCl_4}] = 2.78 \times 10^{-2}$ M, $[\mathrm{D}t\mathrm{BP}] = 4.0 \times 10^{-3}$ M, $[n\text{-}\mathrm{Bu_4NCl}] = 5.0 \times 10^{-4}$ M, 60/40 MCHex/MeCl, −70 °C. [b] $\bar{M}_{\mathrm{n,th}} = [2M_{\mathrm{S}}([\mathrm{M}]_0 - [\mathrm{M}])]/[\mathrm{I}]_0 + M_{\mathrm{bDCC}}$ (g/mol). $M_{\mathrm{S}} = 104.15$ g/mol (molecular weight of styrene monomer), and $M_{\mathrm{bDCC}} = 287$ g/mol (molecular weight of bDCC initiator).

was allowed to equilibrate, and FTIR spectra were collected for 300 s (0.90 spectra/s, 3 scans/spectrum) to obtain an average solvent reference absorption, $A_r$. Then 2.8 mL of styrene monomer (room temperature) was added and allowed to equilibrate to −70 °C, and spectra were similarly collected for 300 s. Finally, 4.02 g of PS (initiated from bDCC, $M_n$ = 3000 g/mol) was added to yield a mixture that is identical, except for the absence of $\mathrm{TiCl_4}$, to a polymerization with $[\mathrm{I}]_0 = 2[\mathrm{bDCC}] = 0.0134$ M and $[\mathrm{M}]_0 = 0.30$ M, carried to 59% conversion,. Spectra were collected of this mixture for 300 s.

The gel permeation chromatography (GPC) system equipped with a Wyatt Technology mini-DAWN has been described.[8]

## Results and Discussion

For the RMC period, eq 1 can be expressed as shown in eq 3, where [P] is the concentration of polymer chains formed by termination of initiating cations.

$$\mathrm{RN} = \frac{R_p}{R_{-i}} = \frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}[\mathrm{P}]} = \frac{k_p[\mathrm{M}]}{k_{-i}} \tag{3}$$

Separating variables and integrating yields

$$\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]} = \frac{k_p}{k_{-i}}[\mathrm{P}] \tag{4}$$

At the end of the RMC period, the monomer concentration remaining, $[\mathrm{M}]_r$, is equal to $([\mathrm{M}]_0 - [\mathrm{M}]_{\mathrm{RMC}})$ and $[\mathrm{P}] = [\mathrm{I}]_0$. Insertion of these boundary conditions yields the following equation:

$$\frac{k_p}{k_{-i}} = \frac{1}{[\mathrm{I}]_0}\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]_0 - [\mathrm{M}]_{\mathrm{RMC}}} = \frac{1}{[\mathrm{I}]_0}\ln\frac{[\mathrm{M}]_0}{[\mathrm{M}]_r} \tag{5}$$

Equation 5 allows calculation of the quantity $k_p/k_{-i}$ from $[\mathrm{M}]_{\mathrm{RMC}}$ data when $[\mathrm{M}]_{\mathrm{RMC}}/[\mathrm{M}]_0 > 0.10$, i.e., when a significant fraction of the monomer is consumed during RMC.

The reaction exotherm is an inherent experimental difficulty associated with the use of RMC to measure $k_p/k_{-i}$. Although $k_p$ has been reported to be insensitive to temperature for reactive olefins such as S[6] and IB,[9] $k_{-i}$ is not; thus, it is important that the data used to calculate $k_p/k_{-i}$ from eq 5 are collected under isothermal or nearly isothermal conditions. This is a particular problem for the S/$\mathrm{TiCl_4}$/60:40 MCHex:MeCl system because $k_p/k_{-i}$ and $[\mathrm{M}]_{\mathrm{RMC}}$ are large.[4] Attempting to reduce the exotherm by reducing $[\mathrm{TiCl_4}]$ is futile. We have observed that reduction of the Lewis acid concentration has little effect upon $[\mathrm{M}]_{\mathrm{RMC}}$, and this is consistent with expectation, since it would reduce $k_p$ and $k_{-i}$ in exactly the same proportion. Lower $[\mathrm{TiCl_4}]$ does increase the duration of the RMC; however, with regard to the total temperature rise observed in the reactor, it makes little difference whether the RMC occurs, for example, within 25 or 250 s. In either case, a glass batch reactor is essentially adiabatic for these short time periods. Short of a change in solvent composition and/or Lewis acid identity, the only way to reduce the exotherm is through reduction in $[\mathrm{M}]_0$, $[\mathrm{I}]_0$, or both. Reduction of $[\mathrm{M}]_0$ is effective but results in loss of detection sensitivity by FTIR-ATR. For the experiments in this paper, we chose $[\mathrm{M}]_0 = 0.15$ or 0.30 M, which effectively limited the total temperature rise to <4 °C.

Table 1 lists two series of styrene polymerizations conducted using the bDCC/$\mathrm{TiCl_4}$/D*t*BP/*n*-$\mathrm{Bu_4NCl}$ system in 60/40 MCHex/MeCl cosolvents, one for 0.15 M and the other for 0.30 M initial monomer concentration. $[\mathrm{I}]_0$ ($= 2[\mathrm{bDCC}]_0$) was varied over as broad a range as possible. For $[\mathrm{M}]_0 = 0.30$ M, we found that $[\mathrm{I}]_0 > 8 \times 10^{-3}$ M resulted in exotherms higher than our arbitrarily imposed limit of 4 °C, and $[\mathrm{I}]_0 < 4 \times 10^{-3}$ M led to loss of control over initiation due to competition by direct initiation.[4] A representative first-order plot, for $[\mathrm{M}]_0 = 0.15$ M and $[\mathrm{I}]_0 = 6 \times 10^{-3}$ M, is shown in Figure 1. The end of the RMC period was taken as the point of intersection of the lines obtained by linear regression of the RMC and post-RMC segments of the curve. The apparent rate constant of the post-RMC polymerization was obtained as the slope of the latter. The polymerizations were terminated at the end of data collection, at a reaction time of approximately 378 s ($[\mathrm{M}]_0 = 0.15$ M) or 591 s ($[\mathrm{M}]_0 = 0.30$ M), and the final conversions and corresponding theoretical number-average molecular weights, $\bar{M}_{\mathrm{n,th}}$, were calculated using FTIR-ATR data. Experimental number-average molecular weights, $\bar{M}_{\mathrm{n}}$, were obtained using GPC analysis of the isolated polymers.

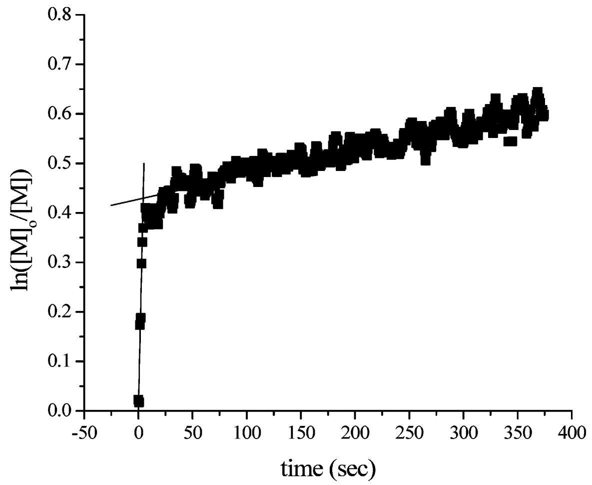

**Figure 1.** Representative first-order plot showing RMC for styrene polymerization initiated by bDCC. $[TiCl_4] = 2.78 \times 10^{-2}$ M; $[S]_0 = 0.15$ M; $[bDCC]_0 = 3.0 \times 10^{-3}$ M; $[DtBP] = 4.0 \times 10^{-3}$ M; $[n\text{-}Bu_4NCl] = 5.0 \times 10^{-4}$ M; 60/40 MCHex/MeCl cosolvents (v/v), −70 °C.

The results are summarized in Table 1. As would be expected, increasing $[I]_0$ resulted in increasing $[M]_{RMC}$ and decreasing $\overline{RN}$; however, $k_p/k_{-i}$ calculated using eq 5 was essentially independent of $[I]_0$. The kinetic parameters measured at $[M]_0 = 0.15$ M were slightly higher than those measured at $[M]_0 = 0.30$ M. This could be due to a combination of slightly higher reaction medium polarity and lower average reaction temperature (lower exotherms) obtained in the former series. The anomalously high kinetic parameters obtained for $[I]_0 = 2.0 \times 10^{-3}$ M are due to a contribution to the initiation process by direct initiation by the Lewis acid. In our previous paper,[4] we showed that under similar conditions additional sources of initiation become significant when the concentration of purposefully added initiator, $[I]_0$, decreases below about $2.5 \times 10^{-3}$ M. Therefore, the data for $[I]_0 = 2.0 \times 10^{-3}$ M were excluded from the average values listed in Table 1 for $k_p/k_{-i}$, $k_pk_i/k_{-i}$, and $k_i$. The $[M]_0 = 0.30$ M series provided sufficient data to yield meaningful statistical analysis. According to our mechanistic/kinetic model, these nine experiments should yield the same value for $k_p/k_{-i}$. This is indeed what was observed. The average value for $k_p/k_{-i}$ was 63 $M^{-1}$, with a standard deviation of 3.7 $M^{-1}$. Therefore, the uncertainty in the measurement appears to be about ±6%. Larger uncertainties were observed for $k_pk_i/k_{-i}$ and $k_i$. The initial RN for these polymerizations at $[M]_0 = 0.30$ M was 19.

Experimentally determined molecular weights were consistently higher than theoretical molecular weights, which were calculated from the monomer conversion determined by FTIR at the end of the post-RMC polymerization (Table 1). We do not feel that this is due to low initiator efficiency. The shape of the curve in Figure 1 suggests that bDCC is quantitatively and rapidly exhausted in the presence of excess monomer. Also, for bDCC to fail to produce a polymer chain, it must fail to initiate styrene from both initiating sites, an unlikely occurrence. We checked the absolute accuracy of the FTIR data using a solution of styrene monomer and polystyrene, which simulated a polymerization with 0.12 M styrene monomer remaining; FTIR analysis was in good agreement with the known styrene concentration, yielding a measurement of 0.13 M. This suggests that the discrepancy is most likely due to high experimental $M_n$. These are polydisperse samples of low molecular weight, and some fractionation of the polymers could be occurring during workup, leading to preferential loss of lower molecular weight species.

## Conclusions

When the RMC method is used to determine $\overline{RN}$ of a quasiliving polymerization under isothermal conditions, $k_p/k_{-i}$ may be rigorously obtained using eq 5 regardless of the monomer conversion at the end of the RMC and independently of the initiator concentration. The value thus obtained may be used in conjunction with the apparent rate constant for propagation to determine $k_i$, the apparent rate constant for ionization.

We retract our previous conclusion that chain transfer to bDCC initiator operates during the RMC period of S cationic polymerization. Instead, the observed decrease in $[M]_{RMC}/[I]_0$ with increasing $[I]_0$ reflects the increasingly significant depletion of the monomer concentration that occurs during the RMC.

The rate constants $k_p/k_{-i}$ and $k_i$ for cationic styrene polymerization at −70 °C, measured using the bDCC/$TiCl_4$/D*t*BP/*n*-$Bu_4NCl$ system in 60/40 MCHex/MeCl cosolvents at $[M]_0 = 0.3$ M and at nine different different initiator concentrations, yielded average values of $k_p/k_{-i} = 63\ M^{-1}$ and $k_i = 1.2\ M^{-2}\ s^{-1}$. These values are in good agreement with those previously reported by us.[4]

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