Articles

Quasi-Living Cationic Polymerization of Styrene and Isobutylene: Measurement of Run Number and Calculation of Apparent Rate Constant of Ionization by $TiCl_4$

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ABSTRACT: The run number (RN), the average number of monomer units added per ionization−termination cycle, was measured at −70 °C from first-order kinetic data for cationic quasi-living polymerization of styrene and isobutylene initiated with 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (bDCC)/$TiCl_4$ in 60/40 MCHex/MeCl, via analysis of an initiation event termed rapid monomer consumption (RMC). RMC is characterized by an initial period of high polymerization rate followed by slower first-order decay in monomer concentration and is due to a larger ionization rate for the initiator compared to that for the polymer chain end. Styrene RN was found to decrease with increasing initiator concentration while that for isobutylene remained relatively unchanged; the dependence of styrene RN on initiator concentration was attributed to chain transfer to initiator during RMC. RN in the limit of zero initiator concentration was determined to be 39 and 4.7 for 0.5 M styrene and isobutylene, respectively. Apparent rate constants of chain-end ionization, k_i, of 1.3 and 15 M^{-2} s^{-1} and rate constants of ion-pair collapse of 1.9×10^7 and 7.5×10^7 s^{-1} for styrene and isobutylene, respectively, were calculated. The latter were calculated using a value for k_p of 1.5×10^9 M^{-1} s^{-1} for styrene and 7×10^8 M^{-1} s^{-1} for IB; apparent rate constants of chain-end ionization were determined independently of k_p, from k_{-i}/k_p and k_{app}.

Introduction

The recent development[1−6] of real-time in situ FTIR monitoring has revealed new details of the initiation and propagation mechanisms of carbocationic polymerizations. Using this method, we recently described a phenomenon associated with the initiation step of certain carbocationic polymerizations, termed rapid monomer consumption (RMC).[5,6] RMC is characterized by a transient period of high polymerization rate observed immediately upon initiation, followed by a slower first-order decay in the monomer concentration. Examples of systems that display RMC are styrene[6] or isobutylene[5] (IB) initiated by 5-*tert*-butyl-1,3-bis(2-chloro-2-propyl)benzene (blocked dicumyl chloride, bDCC)/$TiCl_4$ in methylcyclohexane/methyl chloride (MCHex/MeCl) cosolvents. Figure 1 shows examples of RMC for styrene and IB polymerizations initiated by bDCC under identical conditions.

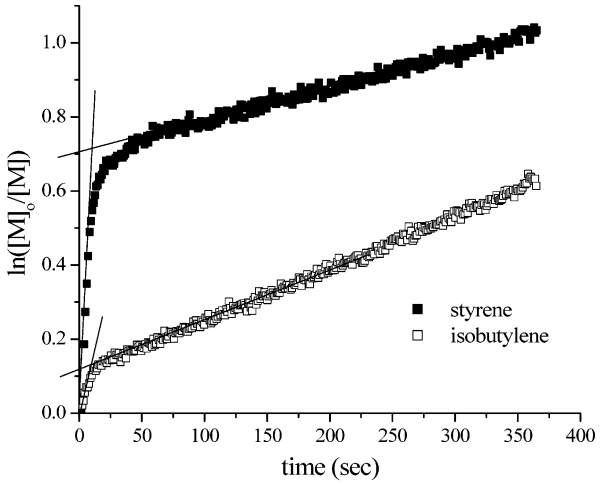

Figure 1. First-order plots for styrene and isobutylene polymerization initiated by bDCC. $[TiCl_4] = 2.78 \times 10^{-2}$ M; $[styrene]_0 = [IB]_0 = 0.5$ M; $[bDCC]_0 = 6.6 \times 10^{-3}$ M; [D*t*BP] = 4.0×10^{-3} M; [*n*-Bu_4NCl] = 5.0×10^{-4} M; 60/40 MCHex/MeCl cosolvents (v/v), −70 °C.

The presence of RMC is a direct consequence of the nature of the propagation reaction in living carbocationic polymerization. These polymerizations are termed quasi-living, to denote that the growing chains are characterized by an ionization equilibrium between reversibly terminated (dormant) chain ends and actively propagating carbocations,[7,8] as shown in Scheme 1 for a system using $TiCl_4$ as the Lewis acid co-initiator. Here, R−Cl represents a dormant polymer chain carrying a *tert*-chloride end group, and ionization is shown to involve two $TiCl_4$ in accordance with recent literature reports.[1,2,9,10] The ionized chain end, $R^+Ti_2Cl_9^-$, is shown as a paired ion only, since typical quasi-living polym-

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erization conditions involve Lewis base additives that generate common counterions and thereby suppress ion pair dissociation.

Scheme 1. Ionization Equilibrium in Quasi-Living Carbocationic Polymerization

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

A given quasi-living chain may undergo many ionization−termination cycles during its lifetime. The average number of monomer molecules added during one cycle is termed the run number, RN,[11] and this quantity is determined by the ratio of the rate of propagation to the rate of reversible termination as shown in eq 1

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

where k_p is the rate constant of propagation, k_{-i} is the rate constant of ion-pair collapse, and [M] is the monomer concentration. The first-order (apparent) rate constant of propagation, k_{app}, may be expressed in terms of the ionization equilibrium in Scheme 1 as follows:

$$k_{app} = \frac{-d\ \ln[M]}{dt} = k_p[R^+Ti_2Cl_9^-] \cong k_p\frac{k_i}{k_{-i}}[R{-}Cl][TiCl_4]^2 \quad (2)$$

where k_i is the apparent rate constant for ionization. It should be noted that the right side of eq 2 is a valid approximation only for small k_i/k_{-i}.

During initiation, k_i and [R−Cl] are replaced by k_I, the rate constant of ionization for the initiator, and $[I]_0$, the initial concentration of initiating sites, respectively. Because $[I]_0 \cong$ [R−Cl] after the period of RMC, any difference between k_{app} during initiation vs during propagation is due to a difference in the rate constant of ionization for the initiator and the dormant chain end, resulting in a different concentration of active species. RMC is observed whenever $k_I > k_i$, and RN is significantly greater than unity. Thus, the initial, relatively high rate of monomer consumption observed in Figure 1 is due to the large rate constant of ionization of the cumyl chloride groups of bDCC compared to the *sec*-benzylic or *tert*-aliphatic chloride groups of growing polystyrene (PS) or polyisobutylene (PIB) chains, respectively. The RMC phenomenon is absent in IB polymerization systems involving an aliphatic initiator such as 2-chloro-2,4,4-trimethylpentane (TMPCl) because the ionization rate for this initiator is similar to that of the dormant PIB chain end.

During investigation of the quasi-living carbocationic polymerization of styrene, using the bDCC/$TiCl_4$/D*t*BP/*n*-Bu_4NCl initiation system, we noted that RN, measured from conversion data during RMC (described later), varied inversely with initiating site concentration (2[bDCC]). This finding is contrary to theory, assuming that deactivation of an ionized chain end occurs exclusively through reversible termination, and it suggests the operation of chain transfer to the initiator during RMC. The possible operation of such a process during RMC was mentioned by us in our first paper on this subject.[5] In the present paper, we examine this issue in detail for both styrene and IB polymerizations co-initiated by $TiCl_4$ and report values for k_{-i}/k_p obtained by extrapolation of RN data to zero initiator concentration. These were combined with temperature-corrected apparent rate constants of propagation to calculate k_i, the apparent rate constant of ionization by $TiCl_4$ of quasi-living PS and PIB carbocationic chains.

Experimental Section

Materials. Isobutylene and methyl chloride (Matheson Gases) were dried by passing the gas through a column packed with $CaSO_4$ or $CaSO_4$/4 Å molecular sieves, respectively. Styrene (99%, Aldrich) and 2,6-di-*tert*-butylpyridine (97%, Aldrich) were freshly distilled over CaH_2. Titanium tetrachloride (99%, Aldrich) was freshly distilled. Synthesis of bDCC has been previously reported.[9] Tetraheptylammonium chloride (He_4NCl, 95%, Acros) was dried over molecular sieves in a CH_2Cl_2 solution. Anhydrous methylcyclohexane (99+%, Aldrich) and tetra-*n*-butylammonium chloride (99+%, Fluka) were used as received.

Instrumentation. A ReactIR 4000 reaction analysis system (light conduit type) (ASI Applied Systems, Millersville, MD) equipped with a DiComp (diamond composite) insertion probe, a general purpose type PR-11 platinum resistance thermometer (RTD), and a CN76000 series temperature controller (Omega Engineering, Stamford, CT) was used to collect infrared spectra of the polymerization components in real time. Number- (M_n) and weight-average (M_w) molecular weights and polydispersity index (PDI, M_w/M_n) were determined using a gel permeation chromatography (GPC) system equipped with a Wyatt Technology mini-DAWN on-line MALLS detector, as previously described.[12]

Procedures. Polymerizations were carried out within a glovebox, equipped with an integral, cryostated heptane bath. Initial concentrations of monomer (0.5 M), Lewis base ([D*t*BP] = 4.0×10^{-3} M), co-initiator ([$TiCl_4$] = 2.78×10^{-2} M), and common ion salt precursor ([*n*-Bu_4NCl] = 5.0×10^{-4} M or [He_4NCl] = 5.8×10^{-4} M) and cosolvent composition (MCHex/MeCl 60/40, v/v), reaction temperature (−70 °C), and reaction volume (200 mL) were held constant in all cases, and $TiCl_4$ was the final component added. The following was a typical polymerization procedure. The DiComp probe was fitted into a dry 250 mL four-necked round-bottomed flask equipped with a mechanical stirrer and RTD and immersed into the cold heptane bath (−70 °C) where it was allowed to thermally equilibrate prior to acquisition of a background spectrum (128 scans, 8 cm^{-1} resolution). To the chilled flask were added sequentially 1.64×10^{-3} mol (0.471 g) of bDCC and 188 mL of a stock solution prepared from 4.8×10^{-3} mol (1.08 mL) of D*t*BP, 6×10^{-4} mol (0.167 g) of *n*-Bu_4NCl, 676 mL of MCHex, and 450 mL of MeCl. The reaction mixture was stirred until it reached thermal equilibrium as indicated by the RTD. Subsequently, 0.10 mol (11.5 mL) of styrene (room temperature) was added, and the mixture was again allowed to reach thermal equilibrium. After stirring for an additional 5 min, 5.6×10^{-3} mol (0.61 mL) of $TiCl_4$, neat and at room temperature, was rapidly injected into the reactor.

The order of introduction of reactants in polymerizations using He_4NCl varied slightly from the above. A partial amount of the total $TiCl_4$ used (7.3×10^{-4} mol, 0.08 mL) was added to the stock solution to ensure common-ion formation prior to initiation. As expected, there was no polymerization upon introduction of the monomer to the reaction solution. To initiate the polymerization, the remaining volume of $TiCl_4$ (0.53 mL) was added to make a total concentration of 2.51×10^{-2} M (5×10^{-3} mol, 0.55 mL).

Reaction conversion was determined by monitoring the intensity of the absorbance (integrated peak area) centered around 907 and 887 cm^{-1} associated with the $=CH_2$ wag of styrene and IB, respectively. The rapid acquisition mode of the ReactIR 4000 was used to collect IR spectra of the reaction medium for 200 s (1.4 spectra/s, 2 scans/spectrum, 4 cm^{-1} resolution) prior to and after monomer addition to obtain solvent reference, A_r, and initial monomer concentration, A_0,

Table 1. bDCC-Initiated Styrene and IB Run Number and Molecular Weight Data[a]

$[bDCC]_0 \times 10^3$, M	$[M]_{RMC}$, M	RN	temp corr RN	conv, %	M_n(exp), g/mol	PDI	M_n(theor), g/mol	I_{eff}, %
				Styrene				
8.2	0.27	16.5	19.7	66	5110	1.52	4480	88
6.6	0.24	18.2	21.5	64	5700	1.49	5340	94
5.0	0.21	21.0	24.0	55	6570	1.47	6020	92
5.0	0.20	19.0	21.8	62	8030	1.31	6750	84
3.4	0.17	25.0	28.0	47	7970	1.40	7490	94
3.0	0.15	24.3	26.9	51	10400	1.30	9140	88
1.8	0.11	30.6	33.0	32	9950	1.40	9540	96
1.5	0.10	32.2	34.4	33	13700	1.30	11700	86
0.9	0.07	39.0	40.6	25	16200	1.27	14800	91
0.7	0.06	42.9	44.4	21	16600	1.28	15900	96
0.5	0.06	56.2		16	10100	1.41	16900	170
0.4	0.05	63.3		15	11200	1.41	20100	180
0.3	0.04	72.6			10500	1.44		
0.2	0.03	80.0		8	13600	1.43	21100	160
0.2	0.03	81.9		14	10700	1.48	36100	340
0.1	0.02	95.5		9	9260	1.66	45900	500
				IB				
14.6	0.11	3.8		72	1720	1.10	1670	97
13.0	0.11	4.1		70	1960	1.09	1800	92
12.0	0.12	4.9		65	1950	1.09	1760	90
11.4	0.10	4.3		64	2090	1.11	1860	89
9.8	0.09	4.5		58	2160	1.11	1950	90
9.0	0.07	3.9		49	2150	1.09	1780	83
8.2	0.08	4.6		54	2320	1.11	2130	92
6.6	0.06	4.6		46	2440	1.10	2240	92
5.0	0.04	4.1		36	2670	1.09	2190	82
3.5	0.03	4.7		27	2800	1.09	2290	82
2.0	0.02	4.9		18	3210	1.10	2810	88
0.9	0.01	4.4		8	3180	1.11	2780	87

[a] $[Styrene]_0 = [IB]_0 = 0.5$ M, $[TiCl_4] = 2.78 \times 10^{-2}$ M, $[DtBP] = 4.0 \times 10^{-3}$ M, $[n\text{-}Bu_4NCl] = 5.0 \times 10^{-4}$ M 60/40 MCHex/MeCl, −70 °C.

absorbance values. The value obtained for A_r was then reduced by 6%, which accounts for the volume dilution, and thus the solvent absorbance reduction, caused by subsequent addition of monomer and $TiCl_4$. A third set of spectra was acquired of the polymerization medium for 428 s, 1.4 spectra/s (2 scans/spectrum, 4 cm^{-1} resolution), and $TiCl_4$ was introduced at 50 s. Each spectrum was collected over the spectral ranges 4000−2200 and 1900−650 cm^{-1}. Monomer absorbance is known to decrease with increasing temperature by a factor of ∼0.42%/°C.[5] To account for reaction exotherm during the polymerization, a spectroscopic correction for temperature was made. Thus, absorbance data were converted to relative monomer concentrations using the following relationship

$$\frac{[M]_0}{[M]_t} = \frac{A_0 - A_r}{(A_t - A_r)(1 + 0.0042\Delta T)} \quad (3)$$

where $[M]_t$ and A_t are the monomer concentration and absorbance, respectively, at time t, and ΔT is the difference between the actual temperature of the reactor contents and the nominal temperature of the experiment. Temperature data were taken manually.

The concentration of monomer consumed during the RMC, $[M]_{RMC}$, was measured by calculating [M] at the point of intersection of the two linear regions observed in first-order kinetic plots, one of which occurs during RMC and one immediately thereafter, as shown in Figure 1.

Results and Discussion

Rapid Monomer Consumption. The RMC phenomenon affords a unique way to experimentally determine run number for a quasi-living polymerization. First-order kinetic plots show a well-defined point at which the initiator cations are exhausted, and the equilibrium concentration of chain end cations is established. This point is indicated by the sharp decrease in slope of the first-order plot for either monomer in Figure 1. Because of the relative infrequency of polymer chain end ionization, reported for IB as an average of one ionization event per chain per 49 s by Faust et al.[10] under typical polymerization conditions, we can assume that all initiating sites undergo one ionization−propagation−termination cycle before any significant number of second ionizations occur. Thus, this change in slope represents the end of the initiation process, and we conclude that the concentration of monomer consumed to this point, divided by the concentration of initiating sites, represents the run number of the first-formed bDCC cations. Therefore, RN is calculated as $[M]_{RMC}/[I]_0$, where $[M]_{RMC}$ is the concentration of monomer consumed during RMC and $[I]_0$ is the original concentration of initiating sites, which equals $2[bDCC]_0$ in the present case. Since the rate constant of reversible termination, k_{-i}, is the same regardless of whether the cation originated from bDCC or from R−Cl, in the absence of transfer reactions, $[M]_{RMC}/[I]_0$ is essentially the RN for the general polymerization process.

Chain Transfer to Initiator. Equation 1 predicts no change in run number with changes in $[I]_0$ for a quasi-living polymerization. While searching for mild conditions for styrene and IB polymerizations that afford a small initial reaction exotherm, we found that decreasing $[I]_0$ was key to lowering the exotherm, keeping all other variables constant. For IB, as expected, the exotherm decreased by half when $[I]_0$ was halved. For styrene, however, the exotherm decreased by half only when $[I]_0$ was decreased by an order of magnitude. This indicated that for styrene an increase in $[I]_0$ did not produce a proportional increase in monomer conversion during RMC, suggesting that the run number was decreasing as $[I]_0$ was increased.

To better quantify these findings, a series of reactions with varying $[I]_0$ were carried out for styrene and IB, and the results are summarized in Table 1. Accompanying the reactions was an initial reaction exotherm. For

example, for $[bDCC]_0 = 8.2 \times 10^{-3}$ M the initial exotherm was 10.7 and 2.3 °C for styrene and IB, respectively. As the data in Table 1 show, the initial run number for IB is more or less unchanging with changes in $[I]_0$, in agreement with the theoretical prediction of eq 1. However, the initial run number for styrene is not only considerably larger than for IB, accounting for the larger exotherm, but also increases with decreasing $[I]_0$. This suggests that, for styrene, chain transfer to bDCC is occurring during the RMC period, thus causing a decrease in run number with increasing $[I]_0$.

Chain transfer to cumyl chlorides is a well-known phenomenon. Kennedy and Smith[13] reported chain transfer to *p*-dicumyl chloride (*p*-DCC) in isobutylene polymerizations co-initiated by BCl_3, and they coined the term "inifer" to describe *p*-DCC and its dual role as initiator and chain transfer agent. Further studies by Fehérvári et al.[14] found that chain transfer to initiator was a major process; they determined the chain transfer constant to initiator, $C_I = k_{tr,I}/k_p$, to be 0.3 for IB polymerizations co-initiated by BCl_3 using *p*-DCC as inifer in ~60/40 CH_2Cl_2/MCHex. The transfer activity of cumyl chlorides in styrene cationic polymerizations has apparently received little study.

It was conceivable that the initial reaction exotherm, which increases with increasing $[I]_0$, could cause a sudden rise in temperature that would increase k_{-i} sufficiently to account for the observed effect. To investigate this hypothesis and determine the effect of temperature on styrene RN and post-RMC apparent rate constant of propagation, a series of polymerizations were run in which the temperature was varied from −60 to −90 °C, with $[I]_0 = 2[bDCC]_0$ held constant at 8×10^{-4} M, which was the highest $[I]_0$ that could be used while still avoiding significant initial rises in temperature. The results are summarized in Table 2. The highest exotherm, observed at −91 °C, was 3 °C. An Arrhenius plot of ln(RN) vs T^{-1} was constructed, and the resulting apparent E_A was found to be −2.84 kcal/mol. This mild temperature dependence cannot explain the observed changes in RN with changes in $[I]_0$; however, this value for E_A was used to correct the RN data for styrene where large exotherms accompanied the polymerization. The corrected RNs are listed in Table 1 and were used for subsequent analyses. This apparent activation energy for run number is strictly only valid at $[I]_0 = 8 \times 10^{-4}$ M; however, it does provide a means for estimating the actual RN that would be obtained in the absence of a temperature rise.

Kennedy and Smith[13] introduced eq 4, by which the chain transfer constant to initiator, C_I, could be extracted from molecular weight data obtained at low monomer and inifer conversions.

$$\frac{2}{DP} = \frac{k_{-i}}{k_p[M]} + C_I\frac{[I]}{[M]} + C_M \qquad (4)$$

DP is the number-average degree of polymerization, C_M is the chain transfer constant to monomer (determined to be negligible for IB), and the factor of 2 accounts for a difunctional inifer. Equation 4 was derived with the assumption of low inifer and monomer conversions, which obviously does not apply in our case; thus, it cannot be used to quantify the occurrence of chain transfer. However, for $C_M = 0$, eq 4 is of the form $RN^{-1} = RN_0^{-1} + a[I]_0$, where $RN^{-1} = 2/DP$, RN_0 is the run number in the absence of chain transfer to the initiator, and *a* is an arbitrary constant. If monomer and inifer conversions were small, then *a* would assume the value of $C_I/[M]$. Thus, we may use eq 4 as a convenient means for extrapolating to RN_0; i.e., the RN that would prevail in the absence of inifering, in the limit of $[I]_0 = 0$. Thus, a plot of RN^{-1} vs $[I]_0$ yields a *y*-intercept equal to $k_{-i}/k_p[M]$, as given by eq 1.

Table 2. Run Number and Apparent Propagation Rate Constant Data for Styrene as a Function of Temperature[a]

temperature, °C	RN	$k_{app} \times 10^4$, s^{-1}
−91	100	3.24
−80	66	1.65
−70	45	0.99
−59	31	0.68

[a] $[Styrene]_0 = 0.5$ M, $[bDCC]_0 = 4.0 \times 10^{-4}$ M, $[TiCl_4] = 2.78 \times 10^{-2}$ M, [D*t*BP] $= 4.0 \times 10^{-3}$ M, [*n*-Bu_4NCl] $= 5.0 \times 10^{-4}$ M, 60/40 MCHex/MeCl, −70 °C.

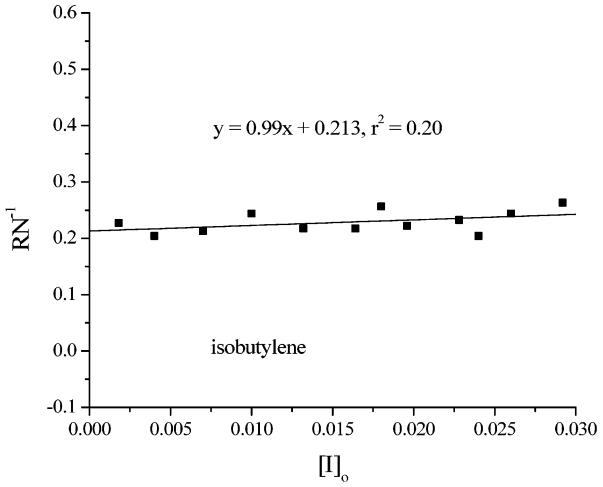

Figure 2. RN^{-1} vs $[I]_0$ for isobutylene polymerizations initiated by bDCC. $[TiCl_4] = 2.78 \times 10^{-2}$ M; $[IB]_0 = 0.5$ M; $[bDCC]_0 = (0.9-15) \times 10^{-3}$ M; [D*t*BP] $= 4.0 \times 10^{-3}$ M; [*n*-Bu_4NCl] $= 5.0 \times 10^{-4}$ M; 60/40 MCHex/MeCl cosolvents (v/v), −70 °C.

Figures 2 and 3 show plots of RN^{-1} vs $[I]_0$ for IB and styrene, respectively, constructed from the temperature-corrected RN data in Table 1. A linear fit was applied to the data for IB in Figure 2, but the correlation was poor ($r^2 = 0.20$). We concluded that the RN for IB is essentially constant, somewhere between 4 and 5 under these conditions, regardless of $[I]_0$, and the variation in the data represents the uncertainty of the measurement. The average RN for IB was 4.4, and this was very close to the RN of 4.7 obtained from the linear extrapolation in Figure 2. We accepted the latter value to account for any minor occurrence of chain transfer to the initiator and from it calculated a value of k_p/k_{-i} for IB of 9.4 M^{-1}.

The plot for styrene (Figure 3, filled squares) shows a dramatic dependence of RN on $[I]_0$, but the data form a curve rather than a line, suggesting an additional complication. From the initiator efficiency (I_{eff}%) data in Table 1, it is apparent that additional sources of initiation become significant in the styrene systems as [b-DCC] falls below about 10^{-3} M. Since a proton trap was present, the additional initiation is probably direct initiation by $TiCl_4$, which has been previously reported for styrene under these conditions.[15] It is important, however, that the extrapolation used to determine RN_0^{-1} exclude any points for which initiation is poorly

Table 3. Styrene Run Number and Molecular Weight Data in the Presence of He_4NCl[a]

$[bDCC]_0 \times 10^3$, M	$[M]_{RMC}$, M	RN	temp corr RN	conv, %	M_n(exp), g/mol	PDI	M_n(theor), g/mol	I_{eff}, %
8.2	0.28	17.8	21.5	62	4700	1.53	4220	90
6.6	0.25	18.9	22.5	54	5100	1.48	4550	89
5.0	0.22	22.1	25.7	48	6450	1.36	5290	82
3.4	0.17	26.0	29.3	37	6900	1.42	5950	86

[a] $[Styrene]_0 = 0.5$ M, $[TiCl_4] = 2.51 \times 10^{-2}$ M, $[DtBP] = 4.0 \times 10^{-3}$ M, $[He_4NCl] = 5.8 \times 10^{-4}$ M, 60/40 MCHex/MeCl, −70 °C.

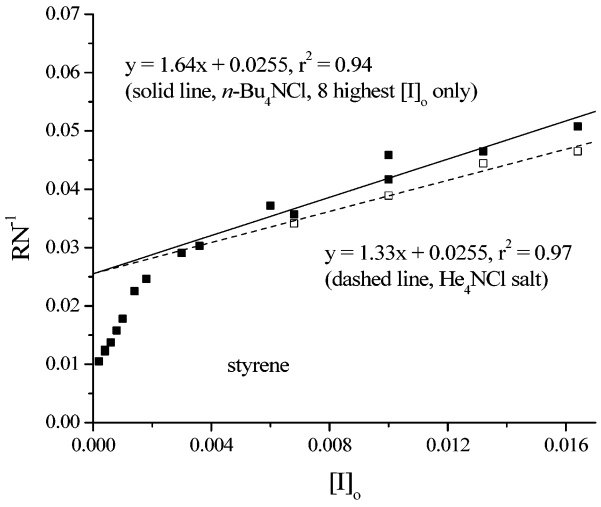

Figure 3. RN^{-1} vs $[I]_0$ for styrene polymerizations initiated by bDCC. $[styrene]_0 = 0.5$ M; $[DtBP] = 4.0 \times 10^{-3}$ M; 60/40 MCHex/MeCl cosolvents (v/v), −70 °C. Solid squares: $[TiCl_4] = 2.78 \times 10^{-2}$ M; $[n\text{-}Bu_4NCl] = 5.0 \times 10^{-4}$ M; $[bDCC]_0 = (0.1-8.2) \times 10^{-3}$ M; solid line is linear fit performed for $[bDCC]_0 = (1.5-8.2) \times 10^{-3}$ M only. Open squares: $[TiCl_4] = 2.51 \times 10^{-2}$ M; $[n\text{-}He_4NCl] = 5.8 \times 10^{-4}$ M; $[bDCC]_0 = 3.4-8.2 \times 10^{-3}$ M; dashed line is linear fit.

controlled. Thus, for the styrene data in Figure 3, we applied linear regression to the eight highest $[I]_0$ only ($\geq 3.0 \times 10^{-3}$ M), yielding a good fit ($r^2 = 0.94$) represented by the solid line in the plot. From the intercept we calculated a value of k_p/k_{-i} for styrene of 78 M^{-1}. From the data in Figures 2 and 3, we concluded that inifering is negligible in IB polymerizations but appears to be a significant process in styrene polymerizations under these conditions.

The apparent larger role of inifering, based on observed changes in run number with varying $[I]_0$, in styrene polymerizations suggested to us the possible participation of free ions during RMC, despite the presence of D*t*BP and the common ion salt precursor, *n*-Bu_4NCl. Thus, we speculated that the production of common ions might be slower for styrene systems relative to those of IB. Were ion-pair dissociation occurring during RMC, it would result in a decreasing run number with increasing $[I]_0$, as observed, since the only kinetically significant termination event for free ions during RMC would be chain transfer to initiator. If free ions were significantly contributing to propagation, the resulting value of k_{-i} for styrene, calculated with the assumption that only ion pairs were propagating, would be too low. It would appear as though the chain end remained ionized for a longer period of time, allowing more monomer units to add.

To counter the possibility that common ion generation might be slower in styrene systems, a new series of styrene polymerizations were run using a more soluble common ion precursor, tetraheptylammonium chloride. In addition, a small fraction of the $TiCl_4$ was prereacted with the salt, so that $Ti_2Cl_9^-$ ions would be available to the system immediately. The run number data of this experiment are shown in Table 3 and Figure 3 (open squares). It is noteworthy that the extrapolated value for RN_0^{-1} (Figure 3, He_4NCl) was identical to and thus strongly validated the previous result (*n*-Bu_4NCl). We concluded that all reasonable measures had been taken to ensure the suppression of ion-pair dissociation and that the kinetic parameters we had calculated represented those for paired ions only.

Tables 1 and 3 list the molecular weights and polydispersity indices for the final polymer samples. The PDIs for styrene were close to the most probable distribution for difunctional chains ($M_w/M_n = 1.5$), consistent with the significant contribution of transfer toward chain breaking. As expected, they first trended downward with decreasing $[I]_0$, as the importance of transfer to initiator diminished; then they rose again at very low $[I]_0$, as I_{eff} began to rise. For IB, the PDIs were narrow and essentially invariant with $[I]_0$.

Determination of Rate Constants. According to the data in Tables 1 and 3, the RN for styrene is at least 4−5 times that for IB at any $[I]_0$ used in this study and is only shortened by the process of chain transfer to initiator. The reciprocal intercepts of the plots in Figures 2 and 3 yielded values of RN for each monomer in the absence of inifering; these values are 39 and 4.7 for 0.5 M styrene and IB, respectively. These numbers result in k_p/k_{-i} values of 78 and 9.4 M^{-1} for styrene and isobutylene, respectively. Faust et al.[10] reported that $k_p[M]/k_{-i}$ for IB (at 1 M) was 20 at −80 °C under similar conditions, which agrees well with our IB data at −70 °C considering that RN decreases with increasing temperature.[5] Faust[16] has also reported a k_p/k_{-i} value for styrene at −70 °C of 19 M^{-1}; this value is significantly lower than our value of 78 M^{-1}. If we assume that the k_p value reported for IB by Faust et al. at −80 °C (7×10^8 M^{-1} s^{-1}) is not much different at −70 °C, then we calculate a value of k_{-i} for IB at −70 °C of 7.5×10^7 s^{-1}, which is a bit larger than the value reported by these authors at −80 °C, as it should be at the warmer temperature. If we also assume a k_p value for styrene found by Faust et al.[16] of 1.5×10^9 M^{-1} s^{-1} at −70 °C, we obtain k_{-i} for styrene at −70 °C of 1.9×10^7 s^{-1}. Thus, $k_{-i}^{IB}/k_{-i}^{S} = 3.9$, and we conclude then that the rate constant of ion-pair collapse is smaller for styrene than it is for IB.

As Figure 1 shows, under identical conditions the post-RMC slope of the first-order plot is higher for IB than for styrene, and we can conclude that $k_p k_i/k_{-i}$ for the PIB chain end is greater than that for the PS chain end under these conditions. Past studies comparing styrene and IB polymerization rates have concluded that IB is a "faster"[17] and a "slower"[18] monomer than styrene. This confusion can be readily understood by examining Figure 1. Even though the slope of the first-order plot is higher for IB than for styrene, i.e., the propagation rate of IB is higher, the monomer conversion at moderate reaction times is higher for styrene due to its larger run number and larger degree of RMC.

Table 4. bDCC-Initiated Styrene and Isobutylene Rate Constant Data[a]

$[bDCC]_0 \times 10^3$, M	$k_{app} \times 10^4$, s^{-1}	$k_p k_i/k_{-i}$, $M^{-3}\ s^{-1}$	k_i, $M^{-2}\ s^{-1}$
	Styrene		
8.2	11.5	91	1.2
6.6	11.3	111	1.4
5.0	8.3	108	1.4
5.0	6.7	86	1.1
3.4	5.5	105	1.3
3.0	4.2	91	1.2
1.8	3.9	140	1.8
1.5	2.3	101	1.3
	IB		
14.6	36.8	163	17
13.0	36.4	181	19
12.0	18.6	100	11
11.4	30.0	170	18
9.8	26.2	173	18
9.0	14.4	104	11
8.2	22.5	177	19
6.6	16.9	165	18
5.0	8.2	106	11
3.5	5.5	101	11
2.0	3.5	113	12
0.9	1.5	108	11

[a] $[Styrene]_0 = [IB]_0 = 0.5$ M, $[TiCl_4] = 2.78 \times 10^{-2}$ M, $[DtBP] = 4.0 \times 10^{-3}$ M, $[n\text{-}Bu_4NCl] = 5.0 \times 10^{-4}$ M, 60/40 MCHex/MeCl, −70 °C.

Therefore, without real-time FTIR to see the details of initiation, it would appear as though IB were propagating more slowly than styrene, which would be inaccurate.

The apparent rate constant of propagation for quasi-living polymerizations is directly proportional to $k_pK_{eq} = k_pk_i/k_{-i}$, as shown in eq 2. Although Figure 1 shows that k_pK_{eq} for IB is larger than for styrene, its RN is considerably smaller. This indicates that k_i must be much larger for IB. Given accurate apparent rate constants of propagation, extracted from the slope of the first-order plot after the initial RMC period, we can independently calculate the apparent rate constant of ionization for both monomers assuming ion pairs are the sole reactive species. Apparent rate constants of propagation were calculated for styrene and IB from the post-RMC region of the first-order plots and are listed in Table 4. For styrene, these data were calculated only for $[bDCC] > 10^{-3}$ M due to the previously discussed lack of control over initiation at low [bDCC]. These k_{app}'s were corrected for the temperature rise caused by the polymerization exotherm according to the Arrhenius equation, given apparent activation energies for styrene of −3.8 kcal/mol, calculated from the data in Table 2, and for IB of −7.2 kcal/mol.[19] To confirm that measured rate constants were in accord with eq 2, $\ln(k_{app})$ vs ln[CE] plots were constructed for both monomers, as shown in Figure 4. As expected, the order of propagation with respect to bDCC initiator was close to unity for both monomers. Using the appropriate values for $[I]_0$ and $[TiCl_4] = 2.78 \times 10^{-2}$ M, we obtained values for k_pk_i/k_{-i} at −70 °C for the various experiments, which are also listed in Table 4. Combining the k_pk_i/k_{-i} values with values for k_{-i}/k_p, determined from the intercepts in Figures 2 and 3, yielded values for the apparent rate constant of chain end ionization, k_i, for styrene and IB as listed in Table 4. The average values of k_i are as follows:

$$k_i = 1.3\ M^{-2}\ s^{-1}\ \text{(for styrene)};$$
$$k_i = 15\ M^{-2}\ s^{-1}\ \text{(for IB)}$$

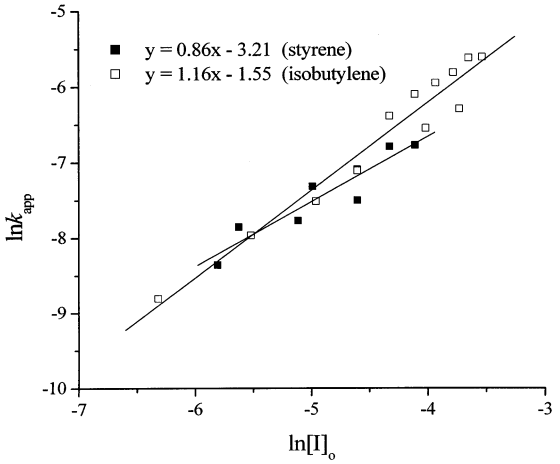

Figure 4. $\ln(k_{app})$ vs $\ln[I]_0$ for styrene and isobutylene polymerizations initiated by bDCC. $[TiCl_4] = 2.78 \times 10^{-2}$ M; $[styrene]_0 = [IB]_0 = 0.5$ M; $[bDCC]_0 = (0.9-15) \times 10^{-3}$ M; $[DtBP] = 4.0 \times 10^{-3}$ M; $[n\text{-}Bu_4NCl] = 5.0 \times 10^{-4}$ M; 60/40 MCHex/MeCl cosolvents (v/v), −70 °C.

We note that our value above for IB is in excellent agreement with the value reported by Faust et al.[10] of 16.4 $M^{-2}\ s^{-1}$ at −80 °C. As expected, the k_i value for IB is indeed considerably higher than that of styrene, by a factor of about 11. If we again assume a value for k_p of 1.5×10^9 $M^{-1}\ s^{-1}$ for styrene and 7×10^8 $M^{-1}\ s^{-1}$ for IB, we can calculate an average K_{eq} of 6.9×10^{-8} and 2.0×10^{-7} M^{-2} for styrene and IB, respectively.

Thus, because of a significantly smaller k_i and smaller k_{-i}, the polystyrene chain end is slower to ionize and slower to collapse, resulting in a slower propagation rate and a larger run number compared with those of IB. The time interval between consecutive ionization events is given by eq 5.[10] Under the conditions reported in this paper, the PS and PIB chain ends undergo one ionization cycle every 9.7×10^2 and 88 s, respectively.

$$\tau_i = \frac{1}{k_i[TiCl_4]^2} \tag{5}$$

This slow ionization and collapse for quasi-living styrene polymerization has been the cause of inefficient crossover when synthesizing PS−PIB−PS triblock copolymers of low end-block MW.[20] These copolymers are synthesized by sequential block copolymerization where styrene is introduced to the polymerization system after the IB polymerization has reached >99% conversion. For a typical block copolymer synthesis, the PIB−Cl chain end concentration is about 1.0×10^{-3} M and $[styrene]_0 = 0.12$ M. From our results we see that even at this low $[styrene]_0$ the run number for styrene would exceed 9 units. Given low target PS end-block MW, high run number increases the likelihood that some end blocks will be very short or nonexistent (no crossover). This causes the end of the elastomeric block to be not firmly anchored into the network.

Conclusions

Recognition and characterization of the RMC phenomenon in quasi-living cationic polymerization, using real-time FTIR, has afforded a more in-depth mechanistic view of initiation and propagation processes for styrene and IB polymerizations. Most importantly, it has provided an independent means of measuring run number for a quasi-living polymerization. Determina-

tion of run numbers by this method for styrene and IB led to the discovery of an "inifer" process during RMC, as predicted in past studies,[5] which was significant for styrene but not for IB under the present polymerization conditions. Calculation of RN in the limit of zero initiator concentration led to values for k_p/k_{-i} of 78 and 9.4 M^{-1} for styrene and IB, respectively. Analysis of this process resulted in the calculation of apparent rate constants of chain-end ionization of 1.3 and 15 M^{-2} s^{-1} and ion-pair collapse of 1.9×10^7 and 7.5×10^7 s^{-1} for styrene and IB, respectively. The former were calculated from k_{-i}/k_p and k_{app} ($=k_p k_i/k_{-i}$) and do not rely on an assumed value for k_p. For IB the k_i value agrees remarkably well with results recently generated using diffusion clock methods.[10]

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