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Kinetic Treatment of Slow Initiation in Living Carbocationic Polymerization and Investigation of Benzyl Halides as Initiators for the Polymerization of Isobutylene

Daniela Held, Béla Iván,*,† and Axel H. E. Müller*

Institut für Physikalische Chemie, Universität Mainz, Welderweg 15, D-55099 Mainz, Germany

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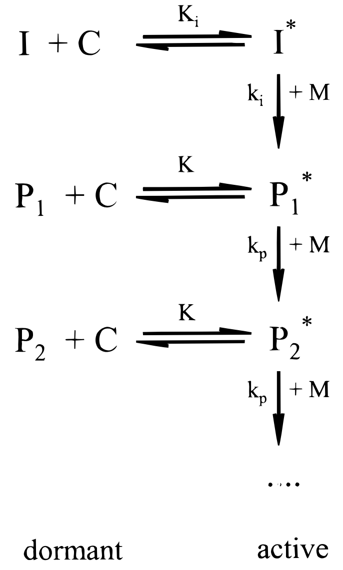
ABSTRACT: In contrast to earlier conclusions it is demonstrated that kinetic analysis of incremental monomer addition (IMA) experiments for living carbocationic polymerizations with slow initiation leads only to the ratio of *apparent* rate constants of initiation and propagation. The apparent rate constants depend on the true (bimolecular) rate constants and on the positions of the equilibria between dormant and active states of initiator and polymer chain ends, respectively. The same considerations are true for other living processes involving dormant species, e.g., group transfer polymerization or controlled radical polymerization. Slow initiation of living carbocationic polymerization of isobutylene (IB) was found with benzyl halide initiators, such as 4-methylbenzyl bromide, 4-methylbenzyl chloride, and 2,4,6-trimethylbenzyl chloride (TMBC), in conjunction with $TiCl_4$ as co-initiator in the presence of *N*,*N*-dimethylacetamide in 40:60 v/v CH_2Cl_2/hexane solvent mixture at −78 °C. The obtained ratio of apparent rate constant of initiation and propagation is compared to other initiators. TMBC led to a new asymmetric telechelic polyisobutylene (PIB) with tertiary chlorine and 2,4,6-trimethylbenzyl end groups, which can be further derivatized.

Introduction

Living carbocationic polymerization (LCCP) has developed rapidly during the past decade (see refs 1−5 for reviews). Due to its advantageous properties, polyisobutylene (PIB) obtained by LCCP of isobutylene (IB) has attracted significant interest worldwide. LCCP of IB can be carried out with a variety of initiators, such as tertiary esters,[6] ethers,[7] chlorides,[8] alcohols,[9] and peroxides[10] in conjunction with BCl_3 and $TiCl_4$ co-initiators. However, it was found that certain initiating systems, e.g., dicumyl chloride/BCl_3,[8] 1-methoxy-1-methylcyclohexane/$TiCl_4$,[11,12] *trans*-2,5-diacetoxy-2,5-dimethyl-3-hexene (DMHDiOAc)/BCl_3,[11,13] 2,6-diacetoxy-2,4,4,6-tetramethylheptane (DATMH)/$TiCl_4$,[14] and *tert*-butoxybenzene/$TiCl_4$[15] combinations, result in LCCP of IB with slow initiation. This process can be described by the slow addition of the first monomer to the initiator, followed by rapid propagation, and the ratios of rate constants of initiation and propagation were determined for some systems.[11−13]

Nucleophilic additives, for instance, esters,[1,14,16,17] amides,[1,18−20] amines,[21] pyridine,[21,22] 2,6-di-*tert*-butylpyridine (proton trap),[23,24] dimethyl sulfoxide (DMSO),[18,25,26] chelating agents,[27] inhiders (*inhi*bitor + retar*der*)[28] and tetrabutylammonium salts,[29,30] lead to much better process control, high initiating efficiencies, and PIBs with narrow molecular weight distribution (MWD) in LCCP of IB. It was found that the initiating efficiency can be increased to quantitative initiation in the case of the otherwise slow initiating system DMHDiOAc/BCl_3 in the presence of a nucleophile, such as DMSO[26] on one hand. Addition of ethyl acetate to the DATMH/$TiCl_4$ system yielded a 2 order of magnitude higher ratio for the rate constants of initiation and propagation,[14] indicating that nucleophilic additives can lead to an advantageous effect in LCCP by increasing the rate of initiation relative to propagation.

Scheme 1. Equilibria between Dormant and Propagating Initiator and Polymer Chain Ends



However, similar to other living and/or controlled systems, LCCP of vinyl monomers is a living polymerization process with equilibrium between active (propagating) cationic species and inactive (dormant) chains[1,32,33] (Scheme 1). In Scheme 1 the dissociation of the ion pairs formed into free ions is neglected.

In an early paper on the cationic polymerization of isobutylene initiated by organic halides and aluminum compounds, Kennedy and Gillham[34] qualitatively discussed that both the "ease of dissociation" of organic

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[†] Permanent address: Chemistry Institute, Chemical Research Center, Hungarian Academy of Sciences, H-1525 Budapest, Pusztaszeri u. 59-67, P.O. Box 17, Hungary.

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halides and the relative reactivity of the formed carbocations affect the "efficiency" of initiation in cationic polymerization. Mayr and Schneider[35] came to a similar conclusion by quantitatively determining the relative rates of initiation by various diarylmethyl chlorides in the presence of $SnCl_4$. However, later quantitative treatments of slow initiation using incremental monomer addition (IMA)[11−14] did not take into account the existence of these equilibria.

Since the applied initiators are not available from commercial sources and require sometimes even multistep synthesis, and some of them, e.g., cumyl chlorides have low stability and tend to eliminate HCl, it occurred to us to test certain commercially available benzyl halides as potential initiators for LCCP of IB in the presence of nucleophilic additives. This study deals with the slow initiation process by such initiators.

Experimental Section

4-Methylbenzyl chloride (Aldrich) was distilled under vacuum, and 4-methylbenzyl bromide (Aldrich) was recrystallized from hexane before use. Titanium tetrachloride, *N*,*N*-dimethylacetamide (DMA), 2,6-di-*tert*-butylpyridine (DtBP), and 2,4,6-trimethylbenzyl chloride (all from Aldrich) were used as received. Solvents and isobutylene (IB) were purified as described elsewhere.[31]

The polymerizations were carried out in a three-neck flask by conventional laboratory processes in 40:60 v/v CH_2Cl_2/hexane mixture at −78 °C under a dry nitrogen atmosphere as described.[31] First the solvents, the initiator, and additive were placed in the flask and cooled to −78 °C. Then monomer and prechilled $TiCl_4$ solution (in CH_2Cl_2) were added. Incremental monomer addition (IMA) and "all monomer in" (AMI) experiments were performed as reported in the literature.[6] In AMI experiments the polymerization times and the time of increments in IMA runs were 10 min. Polymerizations were quenched with prechilled methanol. After evaporation of the solvents the resulting polymer was dried to constant weight in vacuo at room temperature. Molecular weight averages and MWD were determined by GPC calibrated with PIB standards. ^{1}H NMR spectra were recorded on a Bruker AC-200 spectrometer in $CDCl_3$.

Results and Discussion

General Kinetic Analysis. For the similar case of group transfer polymerization, for which the same mechanism as given in Scheme 1 can be applied, it was derived earlier[36] that

$$\alpha = \frac{[P^*]}{[P] + [P^*]} = \frac{K}{1 + K[I]_0}[C]_0 \approx K[C]_0 \qquad (1)$$

$$\alpha_I = \frac{[I^*]}{[I] + [I^*]} = \frac{K_I}{1 + K_I[I]_0}[C]_0 \approx K_I[C]_0 \qquad (2)$$

α and α_I denote the fractions of active polymer chain ends and of active initiator molecules, respectively. $[I]_0$ and $[C]_0$ are the initial concentrations of initiator and co-initiator (MtX_n), respectively. The linear relation between α and $[C]_0$ is valid if the equilibria are shifted to the left-hand side ($\alpha \ll 1$, i.e., $K[I]_0 \ll 1$), which can be assumed in our case.[1,32−33,36−38]

If it is assumed that ionization and ion collapse are fast compared to initiation and propagation, the rates of initiation and polymerization, R_i and R_p, respectively, are given by the following equations:

$$R_i = -\frac{d[I]}{dt} = \frac{d[P]}{dt} = k_i\alpha_I[I][M] = k_i\alpha_I([I]_0 - [P])[M] \qquad (3)$$

$$R_p = -\frac{d[M]}{dt} = \frac{d[M]_{pol}}{dt} = k_i\alpha_I[I][M] = k_i\alpha_I([I]_0 - [P])[M] \qquad (4)$$

where $[I]_0$, $[I]$, $[M]$, $[P]$, and $[M]_{pol} = [M]_0 - [M]$ are the initial concentration of initiator, the concentration of initiator, monomer, polymer chains, and monomer consumed in polymer chains, respectively. Dividing eq 4 by eq 3 gives

$$\frac{d[M]_{pol}}{d[P]} = \frac{\alpha k_p}{\alpha_I k_i}\frac{[P]}{[I]_0 - [P]} + 1 \qquad (5)$$

Assuming that α_I and α are independent of $[M]_{pol}$ and $[P]$, integration of this differential equation yields

$$[M]_{pol} = \frac{\alpha k_p}{\alpha_I k_i}[I]_0\{-\ln([I]_0 - [P]) - [P]\} + [P] \qquad (6)$$

Considering that the initiating efficiency is

$$f = \frac{[P]}{[I]_0} \qquad (7)$$

similar to earlier calculations, the following relation can be obtained between the initiating efficiency and the weight of polymer formed in IMA experiments

$$-\ln(1 - f_i) - f_i = \frac{\alpha_I k_i}{\alpha k_p}\frac{m_p}{M_{mon}V[I]_0} = \frac{k_{i,app}}{k_{p,app}}\frac{m_p}{M_{mon}V[I]_0} \qquad (8)$$

where m_p, M_{mon}, and V are the weight of polymer, the molecular weight of monomer, and the volume of the polymerization system, respectively. Equation 8 clearly indicates that in the case of equilibrium between active and dormant species in living polymerizations, the slope of $-\ln(1 - f) - f$ versus weight of polymer plot gives only the ratio of *apparent* rate constants of initiation and propagation $k_{i,app}/k_{p,app} = k_iK_I/(k_pK)$, since

$$k_{i,app} = \alpha_I k_i \approx K_I k_i[C]_0 \qquad (9)$$

$$k_{p,app} = \alpha k_p \approx K k_p[C]_0 \qquad (10)$$

On the basis of this analysis it can also be concluded that the initiating efficiency in living polymerizations is a function of not only the rate constants of initiation and propagation but also the corresponding equilibrium constants of initiation and polymer chain ends. This means that, without affecting k_i and k_p, changing the position of the active-dormant equilibrium can lead to changes of the initiating efficiency. Only when α_I and α are equal or if both equilibria are shifted to the right-hand side (α_I, $\alpha \approx 1$), the expression derived earlier[13] for slow initiation in LCCP can be applied. However, at least for IB polymerization it is known that $\alpha \ll 1$.

It should be noted that the derivation above should also be applied to other living or controlled systems where dormant species are present, e.g., group transfer polymerization or controlled radical polymerization.

Table 1. Yield, x_P, Number-Average Molecular Weights, $\bar{M}_n$, Polydispersity Index, $\bar{M}_w/\bar{M}_n$, and Initiator Efficiency, *f*, in Polymerization of Isobutylene in CH_2Cl_2/Hexane (40/60) at −78 °C by Different Benzyl Halide Initiators; $[I]_0 = [Additive] = [TiCl_4]/16 = 9 \times 10^{-3}$ M, $[IB]_0 = 0.77$ M

initiator	additive	x_P (%)	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	*f* (%)
TMBC		100	0.92	3.62	52[a]
TMBC	DtBP	91	3.31	1.26	14
TMBC[b]	DtBP	98	3.86	1.27	12
TMBC	DMA	97	2.76	1.28	17
MBB	DMA	68	3.82	2.24	13
MBC	DMA	88	3.19	1.71	15

[a] Apparent initiator efficiency (see text). [b] TMBC/$TiCl_4$/DtBP mixture aged for 10 min before monomer addition.

Slow Initiation with Benzyl Halides. In the course of our studies, the polymerization of isobutylene was investigated with benzyl halides as potential new initiators since effective initiation has only been reported with cumyl compounds,[1−5,18,22,24] DMHDiOAc,[26] and 2-chloro-2,4,4-trimethylpentane (TMPCl).[18,23,25] Successful initiation with the latter compound is most likely due to the loss of steric strain in this molecule upon cationization.[1] Orienting experiments with different benzyl halides were carried out by the “all monomer in” (AMI)[6] technique. As shown in Table 1, there is nearly quantitative conversion of IB when 2,4,6-trimethylbenzyl chloride (TMBC) is used as initiator both in the absence or presence of DtBP or DMA. In the absence of additive this initiator leads to relatively high apparent initiating efficiency, but to broad and multimodal MWD. This indicates the presence of uncontrolled initiation, most likely by protic impurities, and chain transfer to monomer. This is supported by the fact that relatively low yields were observed in control experiments, i.e., in the presence of additives and absence of initiator. The MWD of polyisobutylene (PIB) is much narrower and monomodal when the polymerization of IB was induced with benzyl halides in the presence of either DtBP or DMA. However, the initiating efficiencies are rather low in the range of 12−17%. Aging of the TMBC initiator in the presence of $TiCl_4$ and DtBP does not result in higher initiating efficiency. Monosubstituted benzyl halides, such as 4-methylbenzyl bromide (MBB) and 4-methylbenzyl chloride (MBC), lead to relatively low yields and initiating efficiencies of 13% and 15%, respectively, and the resulting PIBs showed broad MWDs. Interestingly, TMBC leads only to a slightly higher initiating efficiency than that observed with MBC although the formation of a somewhat more stable carbocation is expected in the case of TMBC.

Since the most promising results in terms of initiating efficiencies and MWD were obtained by using TMBC as initiator in the presence of DMA, further systematic experiments were carried out with this system by the IMA method. From the synthetic point of view it is noteworthy that the methyl-substituted benzyl halides yield new asymmetric telechelic PIBs. This was proven by ^{1}H NMR spectroscopy of PIBs obtained by TMBC. Integration of peaks characteristic for the aromatic and methyl protons of the initiator (6.82 and 2.26 ppm) and the methylene protons at 1.94 ppm next to the tertiary chlorine end group indicate the formation of exact α-trimethylbenzyl-*ω*-*tert*-chlorine polyisobutylene chains.

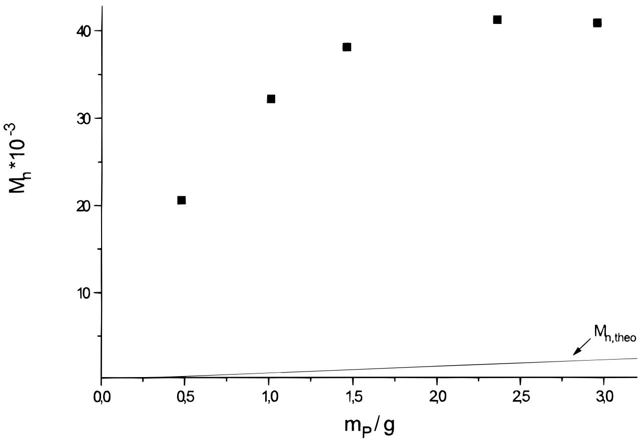

Figure 1. Number-average molecular weight as a function monomer concentration consumed in incremental monomer addition of isobutylene to TMBC initiator (see Table 2 for experimental details).

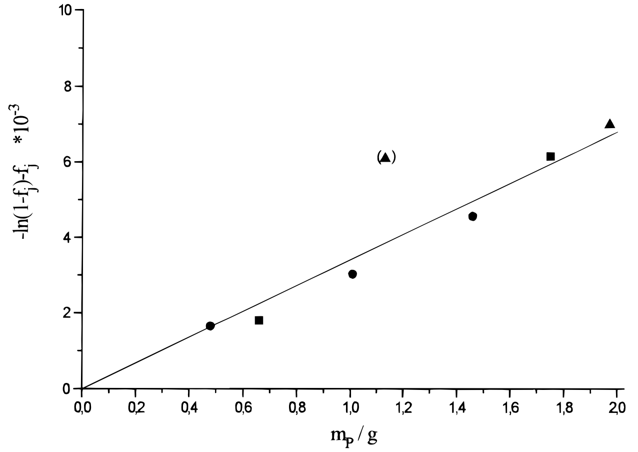

Figure 2. Plot of initiating efficiency as a nonlinear function of weight of polymer (m_P) in polymerization of isobutylene by TMBC initiator (see Table 2 for experimental details).

Table 2. Weight of Polymer, m_P, Number-Average Molecular Weights. $\bar{M}_n$, Polydispersity Index, $\bar{M}_w/\bar{M}_n$, and Initiating Efficiency, *f*, in Incremental Monomer Addition (IMA) Experiments in IB Polymerization; $[TMBC] = [DMA] = [TiCl_4]/16 = 9 \times 10^{-3}$ M, $[IB]_0 = 0.77$ M

m_P (g)	$10^{-4}\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	*f* (%)
0.47	2.05	1.20	5.6
1.01	3.22	1.27	7.6
1.46	3.81	1.27	9.2
2.36	4.12	1.38	13.8
2.96	4.08	1.42	17.5

Figure 1 shows number-average molecular weights, $\bar{M}_n$, as a function of the concentration of total monomers consumed in a series of three parallel IMA experiments. It is seen that the molecular weights are significantly higher than the theoretical values, indicating slow initiation. The reproducibility of these experiments up to about 1.5 M IB is quite satisfactory, and larger scatter of data can be seen only above this concentration. When the initiating efficiency is plotted as $-\ln(1 - f_j) - f_j$ versus weight of polymer (m_p),[11,13] significant deviations were observed from the expected straight lines above 1−1.5 M. This is most likely due to changes in the polarity of the polymerization system caused by the addition of the nonpolar monomer. Therefore, for further analysis only data points with less than 1 M IB were taken into account (Figure 2).

Table 2 shows the results of a series of IMA experiments. These data clearly indicate that the molecular weight and the initiating efficiency increase with addition of monomer, and PIBs with relatively narrow MWD can be obtained. Plotting the data obtained with less than 1 M according to the equation derived for IMA experiments assuming slow initiation in living cationic polymerization[11,13] yields a straight line starting from the origin, as shown in Figure 2. This finding indicates that polymerization of IB by TMBC as initiator occurs by slow initiation, irreversible termination and chain transfer being absent.

The diagnostic plot in Figure 2 gives $k_{i,app}/k_{p,app} = 8.6 \times 10^{-5}$ with TMBC initiator. In a similar experiment with 1-chloro-1-phenylethane as initiator, the ratio of the apparent rate constants was found to be 2 orders of magnitude higher,[39] whereas cumyl chloride was reported to lead to fast initiation.[25] Mayr[40] discussed the relative stabilities of carbocations, determined as the rate constants of S_N1 solvolysis. The stabilities increase in the order benzyl$^+$ < 1-phenylethyl$^+$ < 1,1,3,3-tetramethylpentyl$^+$ (TMP$^+$) < cumyl$^+$. The TMP cation can serve as a model for the PIB cation. The cation stabilities should be reflected in the corresponding ionization equilibrium constants, K_i or K, and, inversely, in the their reactivity toward addition of alkenes, k_i and k_p, and one might assume that the two effects should cancel each other. Since the order of $k_{i,app}/k_{p,app}$ values is the same as the one for the stabilities, we can conclude that the ionization equilibrium constant is the determining factor for slow initiation in IB polymerization. However, as suggested by Mayr and Schneider,[35] the relative rate constants of initiation of various initiators may become the determining factor when their ionization equilibria are strongly shifted to the right-hand side (e.g., some diarylalkyl halides in the presence of strong Lewis acids).

Benzyl halides in conjunction with Et_2AlCl were reported[34,41] to be effective initiators for IB polymerization, reflecting the importance of the equilibrium constant, i.e., the right selection of co-initiator for effective initiation. However, conditions for living polymerization of IB with Et_2AlCl due to undesired chain breaking events (termination and chain transfer) have not been reported yet.

As discussed in this study, benzyl halide/$TiCl_4$ combinations lead to living polymerization of IB with slow initiation in the presence of nucleophilic additives, and this process results in new asymmetric telechelic PIB with exact chain end functionalities, which can be further derivatized, e.g., by metalation or halogenation of the substituted phenyl groups.

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