Penultimate Effect in the Initiation of the Cationic Polymerization of Isobutylene: Kinetic Study of Initiation with (3-Chloro-1,1,3-trimethylbutyl)benzene[†]

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Introduction

The effect of a γ -substituent on the reactivity of the active center is well established in radical polymerization. That the reactivity of the propagating species may be affected by the next to the last or penultimate monomer unit is commonly referred to as penultimate behavior and necessitates the use of a modified copolymer composition equation with four reactivity ratios.¹ The effect of the penultimate monomer structure on the overall reactivity of the chain end in cationic polymerization has recently been demonstrated.² Compared to conventional radical copolymerization, living cationic copolymerization is complicated by the dynamic equilibrium between dormant and active centers. We have reported that the overall reactivity of ~CH₂CH(Ph)- $CH_2C(CH_3)_2$ -Cl (-St-IB-Cl) end structure is much lower than that of ~CH₂C(CH₃)₂-CH₂C(CH₃)₂-Cl (-IB-IB-Cl).² Because of the low reactivity of -St-IB-Cl ends, which arise in the living cationic synthesis of poly-(styrene-*b*-isobutylene) when IB is added at less than complete St conversion, coupling of the living diblock ends is not the preferred technique for the synthesis of poly(styrene-b-isobutylene-b-styrene) triblock copolymers.² The preferred simple and successful method involves difunctional initiation and sequential monomer addition.³ This method, however, is successful only when St is added after the complete polymerization of IB. When St is added at less than 100% IB conversion, the polymerization of St is much slower,^{3b} which again is due to the formation and low reactivity of -St-IB-Cl chain ends. For instance, when St is added after complete polymerization of IB, St polymerization is complete in 1 h. In contrast, when St is added at 94% IB conversion, St conversion reaches only \sim 50% in 1 h at otherwise identical conditions.⁴

A similar γ -substituent effect on the overall cationic reactivity has already been reported by Mayr et al.⁵ The rate of IB addition to (CH₃)₂C(Ph)CH₂C(CH₃)₂Cl (Cum–IB₁–Cl) was found to be 20–35 times lower than the rate of IB addition to Cum–IB₂–Cl, which changed little with further increase of *n* in Cum–IB_n–Cl. This may be ascribed to intramolecular solvation of the cationic center and/or to the negative inductive effect of the phenyl ring. In other words, the lower overall reactivity may be due to a lower reactivity of Cum–IB₁+ cations compared to Cum–IB_n⁺ cations, or it may be attributed to a lower equilibrium constant of ionization of Cum–IB₁–Cl.

It was the goal of this study to measure the rate constant of ionization (k_i) of Cum $-IB_1-Cl$ and compare it to that of 2-chloro-2,4,4-trimethylpentane (TMPCl) and to determine the rate constant of deactivation (reversible termination) (k_{-i}) and the rate constant of addition (k_c) of a reactive π -nucleophile (2-phenylfuran, 2-PhFu) for the corresponding Cum $-IB_1^+$ and TMP⁺ cations. The results were expected to identify the underlying reason(s) for the low overall reactivity of Cum $-IB_1-Cl$ and the similar -St-IB-Cl end structure.

Experimental Section

Materials. Synthesis of (3-Chloro-1,1,3-trimethylbutyl)benzene (Cum-IB1-Cl). Cum-IB1-Cl was prepared by a slightly different procedure than that already reported by Mayr and co-workers.⁵ Under a nitrogen atmosphere in a glovebox hexanes (Hex), methyl chloride (MeCl), cumyl chloride (0.02 M), DTBP (0.003 M), and IB (1.03 M) were added sequentially to a prechilled 400 mL round-bottom flask at -80°C. BCl₃ (0.06 M) dissolved in Hex/MeCl 60/40 (v/v) was added last. After 40 min, the reaction was terminated with prechilled methanol. The resulting solution was poured into NH4OH/ methanol to neutralize the reaction mixture. After evaporation of the solvent, the residue was dissolved in CH₂Cl₂, and the resulted solution was washed with water several times and with 1 M hydrochloric acid solution. The organic phase was dried over anhydrous magnesium sulfate and concentrated by evaporation followed by drying in a vacuum to afford quantitative yield of a colorless liquid.

¹H NMR: δ 7.30–7.07 (m, 5H, –C₆H₅), 2.30 (s, 2H, –CH₂–), 1.35 (s, 6H, –2(CH₃)), 1.21 (s, 6H, –2(CH₃)). ¹³C NMR: δ 148.7, 128.0, 125.9, 125.6, 71.7, 58.1, 38.4, 34.2, 30.9.

Sources and purity of all other materials have been previously described. 6

General Reaction Procedure. All reactions were carried out at -80 °C under a dry nitrogen atmosphere using [Cum– IB₁-Cl] = 2.0×10^{-3} mol L⁻¹, [TiCl₄] = 1.6×10^{-2} mol L⁻¹, and [2,6-di-*tert*-butylpyridine, DTBP] = 3.0×10^{-3} mol L⁻¹ (unless otherwise noted). The solution of Cum–IB₁-Cl, TiCl₄, and DTBP in Hex/MeCl 60/40 (v/v) was kept for ~1 h to allow complex inorganic salts to precipitate. Then, the solution was filtered, and the reference spectrum was taken. Finally, the π -nucleophile was added, and the accumulation of the UV– vis spectra started.

UV–vis **Spectroscopy.** For the UV–vis spectroscopic measurements a quartz immersion probe 661.300-QX (Hellma, optical path 0.02 cm) connected to a fiber-optic visible (tungsten light source, Ocean Optics) and UV (AIS model UV-2, Analytical Instrument Systems, Inc.) light source and a Zeiss MMS 256 photodiode array detector was used. The latter was connected to a personal computer via a TEC5 interface, and the spectra were recorded using the "Aspect Plus" software (Zeiss).

Determination of the Rate and Equilibrium Constants via UV–vis Spectroscopy. For the calculation of the apparent rate constant of the capping reaction, the concentration of 5-(Cum–IB₁)-2-PhFu⁺ carbenium ions was derived from the measured absorbance at the absorption maximum $\lambda_{max} = 340$ nm and the corresponding molar adsorption coefficient $\epsilon_{max} =$ 30 000. A more detailed description of the procedure has been given.⁶

Characterization. ¹H NMR spectra were recorded on Bruker 250 MHz spectrometer using CDCl₃ as a solvent (Cambridge Isotope Laboratories, Inc.).

Results and Discussion

Kinetics of the Capping Reaction with 2-PhFu. We have previously reported on the addition reactions

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

10.1021/ma020189u CCC: \$22.00 © 2002 American Chemical Society Published on Web 05/24/2002 Scheme 1. Ionization Equilibrium of Cum $-IB_1-Cl$ ($K_i = k_i/k_{-i}$) and Capping with 2-PhFu





of non-(homo)polymerizable π -nucleophiles (π -Nu) 1,1bis(4-methylphenyl)ethylene (DTE), 1,1-bis(4-*tert*-butylphenyl)ethylene, and 2-PhFu to TMPCl and other hydrochlorinated isobutylene *n*-mers (n = 3, 36) in the presence of TiCl₄ in hexanes (Hex)/methyl chloride (MeCl) 60/40 (v/v) at -80 °C using on-line UV–vis spectroscopy.⁶ The apparent rate constants of capping, k_cK_i (where k_c is the rate constant of capping and K_i is the equilibrium constant of ionization), and the rate constant of ionization, k_i , have been determined using eq 1.

$$\frac{[\text{PIBCl}][\text{TiCl}_4]^2}{\frac{d}{dt}([\text{PIB}-\pi\text{-Nu}^+\text{Ti}_2\text{Cl}_9^-] + [\text{PIB}-\pi\text{Nu}^+])} = \frac{1}{\frac{1}{k_cK_i[\pi\text{-Nu}]} + \frac{1}{k_i}} (1)$$

The denominator on the left side of eq 1 contains the sum of the concentrations of capped ion pairs and free ions. The identical $k_c K_i$ values obtained with all three π -nucleophiles suggested diffusion-limited addition, and from the known value of diffusion-controlled second-order rate constant $k_c = 3 \times 10^9$ L mol⁻¹ s⁻¹, K_i and k_{-i} were calculated. We used the same methodology in the present research to determine k_i , K_i , and k_{-i} for Cum–IB₁–Cl. Scheme 1 describes the capping of Cum–IB₁–Cl with 2-PhFu as a reactive π -nucleophile.

Capping is a two-step process that involves the ionization of the chain end and subsequent addition of 2-PhFu. 2-PhFu was chosen as a reactive π -nucleophile because the nucleophilicity parameter N, which can be used to predict k_c based on the free energy relationship⁷ (eq 2, slope parameter, $s \approx 1$), is known for 2-PhFu (N = 3.6)⁸ but remains to be determined for 1,1-diarylethylenes.

$$\log k = s(N+E) \tag{2}$$

Based on N = 3.6 and the reported electrophilicity parameter of PIB⁺ (E = 7.5),⁹ $k_c \sim 10^{11}$ L mol⁻¹ s⁻¹ is calculated. The reactivity of Cum–IB₁–Cl is reportedly 20–35 times lower; however, even if the overall reactivity decrease is due solely to a decrease in the reactivity of Cum–IB₁⁺, $k_c \sim 4 \times 10^9$ L mol⁻¹ s⁻¹ is calculated; i.e., diffusion-limited addition of 2-PhFu is predicted. Thus, K_i and k_{-i} can be calculated from $k_c K_i$ values using $k_c = 3 \times 10^9$ L mol⁻¹ s⁻¹.

The reciprocal initial rate of capping vs 1/[2-PhFu] for the capping reaction of Cum $-IB_1-Cl$ in Hex/MeCl 60/40 (v/v) at -80 °C is shown in Figure 1. For comparison, the plot obtained with TMPCl and reported in ref 6 is also included.



Cum-IB₁-PhFu⁺

Figure 1. Reciprocal initial rate of capping vs $1/[\pi$ -Nu] (\blacksquare , 2-PhFu; \bigcirc , DTE; \triangle , DBE) for the capping reaction of Cum–IB₁–Cl and TMPCl in Hex/MeCl 60/40 (v/v) at -80 °C.

Table 1. Kinetic and Thermodynamic Parameters for the Capping Reaction of PIBCl, TMPCl, and Cum–IB₁–Cl with 2-PhFu^a

initiator	$k_{ m c}K_{ m i}$ (L ³ mol ⁻³ s ⁻¹)	$k_{ m i}$ (L ² mol ⁻² s ⁻¹)	K _i (10 ⁻⁷ L ² mol ⁻²)	$k_{-i} (10^{-7} { m s}^{-1})$
PIBCl	1430	16.4	4.8	3.4
TMPCl	400	6.5	1.3	5.0
Cum-IB1-Cl	47	1.4	0.16	8.7

^{*a*} K_i and k_{-i} were calculated using $k_c = 3 \times 10^9$ L mol⁻¹ s⁻¹.

The $k_c K_i$ and k_i values determined from Figure 1 and the calculated K_i and k_{-i} values are shown in Table 1. In addition to values for Cum–IB₁–Cl, values reported for PIBCl and TMPCl⁶ are also included.

Capping of Cum-IB₁-Cl is 9 times slower than capping of TMPCl and 30 times slower than that of PIBCl. Since capping is diffusion-limited for all three, the difference is due to a difference in K_{i} . This in turn can be attributed mainly to a large difference in $k_{\rm i}$ values; i.e., the rate constant of ionization of Cum-IB1-Cl is about 5 and 12 times lower than that of TMPCl and PIBCl, respectively. Interestingly, for Cum-IB1-Cl the rate constant of deactivation k_{-i} is only 75% higher than that of TMPCl. This in turn suggests that the low overall reactivity of Cum-IB₁-Cl is due mainly to the low rate constant of ionization brought about by the electronic withdrawing effect of the phenyl ring. While intramolecular stabilization of the formed Cum- IB_1^+ by the phenyl ring cannot be ruled out, judged from the k_{-i} values, the reactivity of Cum $-IB_1^+$ is actually somewhat higher than the reactivity of the TMP⁺ cation. This relatively small reactivity difference, however, cannot compensate for the large decrease in the k_i value, and the overall effect is that Cum–IB₁–Cl is much less reactive than TMPCl or PIBCl.

Kinetics of the Capping Reaction with 1,1-Diphenylethylene (DPE). The reactivity of Cum $-IB_1^+$

Table 2. Rate Constants of Capping for the Capping Reaction of TMPCl and Cum–IB₁–Cl with DPE

initiator	$k_{\rm c}K_{\rm i}$ (L ³ mol ⁻³ s ⁻¹)	$k_{\rm c}$ (L mol ⁻¹ s ⁻¹)
TMPCl Cum–IB ₁ –Cl	24 4.7	$egin{array}{c} 1.9 imes10^8\ 2.9 imes10^8 \end{array}$

and TMP⁺ cations can also be compared in capping reactions using a non-(homo)polymerizable π -nucleophile, which adds slower than the diffusion limit. We have recently reported that capping of IB *n*-mers is approximately 15 times slower with DPE than with DTE or 2-PhFu, which was ascribed to a lower nucleophilicity of DPE compared to that of DTE and 2-PhFu.¹⁰ Therefore, we have determined the $k_c K_i$ value in the capping reaction of Cum–IB₁–Cl with DPE and compared it to values reported for TMPCl in ref 10. Using the K_i values listed in Table 1, we have calculated the k_c values, which are listed in Table 2. The rate constants of capping are not substantially different, indicating that the reactivities of Cum–IB₁⁺ and TMP⁺ cations are similar.

Conclusion

The nature of a γ -substituent may have a large effect on the rate of initiation in cationic polymerization. As initiation is a two-step process in cationic polymerization, ionization and cationation may be influenced to a different degree. Replacement of a methyl group in TMPCl with a phenyl group in Cum–IB₁–Cl results in an overall reactivity of Cum–IB₁–Cl that is close to an order of magnitude lower than that of TMPCl in cationic initiation. This can be explained by the much lower ionization rate and equilibrium constant of Cum–IB₁– Cl, attributed to the negative inductive effect of the phenyl ring, while the reactivity of Cum–IB₁⁺ is only slightly higher than that of TMP⁺. The penultimate effect found in the copolymerization of IB and St may be explained similarly. In this case, however, in addition to the negative inductive effect of the phenyl ring, a lower back strain (release of steric strain upon ionization) in -St-IB-Cl compared to -IB-IB-Cl may further decrease the rate end equilibrium constant of ionization.

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