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Influence of Chain Length on the Electrophilic Reactivity of Carbocations

Herbert Mayr* and Holger Schimmel

Department Chemie, Ludwig-Maximilians-Universität, Butenandtstr. 5-13, D-81377 München, Germany

Shinjiro Kobayashi,* Masashi Kotani, and T. R. Prabakaran

IFOC, Kyushu University, Higashi-ku, Fukuoka 812 Japan

Laszlo Sipos and Rudolf Faust*

Polymer Science Program, Department of Chemistry, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854

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ABSTRACT: The electrophilic reactivities of the bis(*p*-methylphenyl)carbenium ion **1b**⁺ and its macromolecular analogue **1a**⁺ have been compared in slow reactions with allylsilanes and in fast reactions with silyl enol ethers. Treatment of **1b-Cl** with TiCl₄ or GaCl₃ and of **1a-Cl** with GaCl₃ in CH₂Cl₂ at −70 °C gave solutions of the carbocations **1b**⁺ and **1a**⁺, the concentration of which was measured photometrically. Addition of allylsilanes led to the exponential decay of the benzhydryl cation concentrations, from which the second-order rate constants have been derived. The rate constants determined for the reactions of **1a**⁺ or **1b**⁺ with allyltriphenylsilane and with allylchlorodimethylsilane, respectively, agree within experimental error. Laser flash photolyses of **1a-Cl** and **1b-Cl** in acetonitrile/dichloromethane mixtures yielded the corresponding benzhydryl cations, which showed pseudo-first-order decay in the presence of variable concentrations of 1-trimethylsiloxy cyclohexene or 1-trimethylsiloxy cyclopentene. The second-order rate constants ranged from 1 × 10⁸ to 5 × 10⁸ L mol^{−1} s^{−1} but differed for **1a**⁺ and **1b**⁺ by less than 30%. It is concluded, therefore, that macromolecular carbocations and their low molecular weight analogues have the same reactivity.

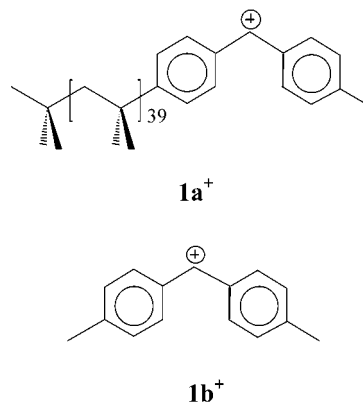
Introduction

The rate constants of carbocationic polymerizations are still the topic of substantial controversy.¹ For the propagation step of the cationic polymerization of isobutylene, values from 6 × 10³ to 7 × 10⁸ L mol^{−1} s^{−1} have been reported (Table 1).² For the carbocationic polymerization of styrene the published rate constants are ~10³ L mol^{−1} s^{−1}.⁴ There is evidence, however, that these numbers may underestimate the real *k_p* values by as much as 6 orders of magnitude.^{2e} Since solvent polarity has a large influence on ionization and dissociation equilibria⁵ but not on the rate of attack of carbocations on olefins or other neutral nucleophiles,^{6,7} and temperature has only a small effect on the rates of fast bimolecular reactions,⁸ the huge differences in the reported *k_p* cannot be due to the different reaction conditions employed.

Plesch has recently attempted to explain the discrepancies in propagation rate constants by monomer solvation of the propagating carbocation at high monomer concentration (>4 M).^{1b} The diffusion clock method,⁹ however, yielded virtually identical propagation rate constants with that recently reported by one of us for [IB] = 1–2.5 M^{2e} at higher IB concentrations up to 6 M in hexanes/methyl chloride 60/40 (v/v) at −80 °C.¹⁰

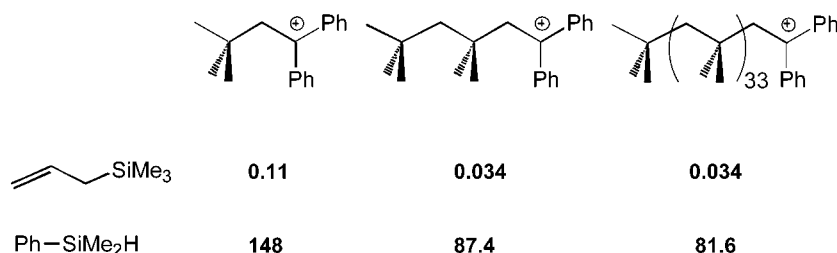
Alternatively, one might assume that macromolecular carbocations possess lower reactivity than low molecular weight model compounds. Two of us have shown, however, that the reactivity of 1,1-diphenylethylene-capped polyisobutylene carbocations toward various nucleophiles does not differ from that of the 3,3,5,5-tetramethyl-1,1-diphenyl-1-hexyl cation (Scheme 1).¹¹

The conclusion drawn from these experiments may be disputed, however, since the second-order rate constants in Scheme 1 are smaller than 10² L mol^{−1} s^{−1} whereas the retarding effect of a macromolecular backbone might only become effective in fast reactions, when diffusion processes become rate controlling. It was the goal of this work to compare the electrophilic reactivities of macromolecular carbocations (**1a**⁺) with those of their low molecular weight analogues (**1b**⁺), that can be photometrically detected, in fast reactions.



Experimental Section

Materials. Methyl chloride and isobutylene were dried in the gaseous state by passing them through in-line gas-purifier columns packed with BaO/Drierite. They were condensed in the cold bath of a glovebox prior to polymerization. 2,6-Di-*tert*-butylpyridine (DTBP, Aldrich, 97%), titanium tetrachloride

Scheme 1. Rate Constants ($\text{L mol}^{-1} \text{s}^{-1}$) of Addition of Silanes to Diphenylcarbenium Ions in CH_2Cl_2 at -70°C (Counterion: Ti_2Cl_9^-)**Table 1. Representative Propagation Rate Constants in the Cationic Polymerization of Isobutylene**

no.	solvent	$T/^\circ\text{C}$	$k_p/\text{L mol}^{-1} \text{s}^{-1}$	ref
1	CH_2Cl_2	-78°	9.1×10^3	2a
2	CH_3Cl	-48	1×10^{4a}	2b
3	heptane	-14	6×10^{3b}	2c
4	bulk	-78	1.5×10^8	2d
5	CH_2Cl_2	-78	6×10^8	2e
6	hexanes/ CH_3Cl 60/40 (v/v)	-80	7×10^8	2f

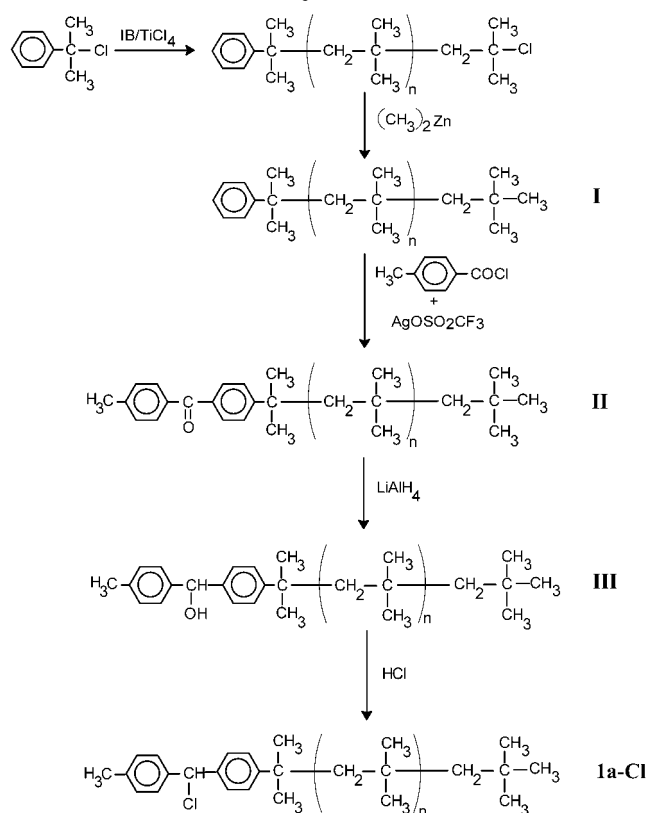
^a According to ref 1 this is probably k_p^+ . ^b According to ref 1 this is probably k_p^\pm .³

(Aldrich, 99.9%), silver triflate (Aldrich, 99%), lithium aluminum hydride (Aldrich, 95%), and *p*-toluoyl chloride (Aldrich, 98%) were used as received. Dichloromethane (Doe & Ingalls) was distilled, then refluxed over CaH_2 , and distilled before use. HCl was generated from sodium chloride with concentrated sulfuric acid and passed through a column filled with drierite. Hexanes (Hex, mixture of hexane isomers plus methylcyclopentane, Aldrich, 99%) was refluxed for 24 h with concentrated sulfuric acid, washed with 5% NaOH solution and then with distilled water until neutral, dried on anhydrous Na_2SO_4 , and distilled from CaH_2 under nitrogen before use. Cumyl chloride was made by hydrochlorination of α -methylstyrene.

Polymerization of IB and Subsequent Methylation. The polymerization of IB was carried out under a dry nitrogen atmosphere ($[\text{H}_2\text{O}] < 1 \text{ ppm}$) in an MBraun 150 M stainless steel glovebox in hexanes/ CH_3Cl 60/40 (v/v) solvent at -80°C using the following concentrations: $[\text{cumyl chloride}] = 0.015 \text{ M}$, $[\text{IB}] = 0.493 \text{ M}$, $[\text{TiCl}_4] = 0.036 \text{ M}$, $[\text{DTBP}] = 0.006 \text{ M}$. The total volume of the polymerization mixture was 1 L. After 1.5 h polymerization time $(\text{CH}_3)_2\text{Zn}$ ($[(\text{CH}_3)_2\text{Zn}] = 0.144 \text{ M}$) was added, and the mixture was left to react overnight. The resulting polymer **I** (Scheme 2) exhibited $M_n = 2160$ and $M_w/M_n = 1.12$ determined by GPC.

Acylation of I with a Mixed Anhydride of *p*-Toluic Acid and Trifluoromethanesulfonic Acid. Into a 500 mL one-neck flask 8.48 g (33.0 mmol) of silver triflate was placed in an inert atmosphere glovebox. The material was suspended in 10 mL of CH_2Cl_2 , and 4.32 mL (32.7 mmol) of *p*-toluoyl chloride was added slowly under vigorous shaking. The blue suspension was mixed with 30 mL of CH_2Cl_2 solution of 13.84 g of polyisobutylene **I** (Scheme 2). The flask was closed and taken out of the glovebox. After stirring for 20 h at room temperature, the mixture was cooled in an ice bath, and $\sim 5 \text{ mL}$ of saturated aqueous NaCl solution was added dropwise. The suspension was filtered and taken up in 200 mL of hexanes. The organic phase was washed with 5% aqueous NaOH solution and then with water until neutral. The solution was dried on anhydrous Na_2SO_4 , and the solvent was evaporated to obtain 15.1 g of crude product. The product was purified on silica gel (100 g), by bonding it to the stationary phase, washing with 300 mL of hexanes, and eluting with 600 mL of hexanes/ CH_2Cl_2 50:50 v/v mixture. (On silica gel TLC plate the retention factor for starting polyisobutylene **I** and acylated polymer **II** were 0.92 and 0.05, respectively, with hexanes as eluent.) Yield: 13.79 g (93.7%). $M_n = 2490$ (GPC), $M_n = 2250$ (NMR).

Reduction of II with LiAlH_4 . 11.7 g of **II** (Scheme 2) in 200 mL of dry THF, freshly distilled from LiAlH_4 , was reacted

Scheme 2. Synthesis of 1a-Cl

with $\sim 0.5 \text{ g}$ of LiAlH_4 at room temperature for 3 h. Then the excess LiAlH_4 was destroyed at 0°C by the dropwise addition of ethyl acetate. The solution was mixed with 200 mL of hexanes and washed with aqueous HCl solution (0.5 M) and then with water. The organic phase was dried on anhydrous Na_2SO_4 , and the solvent was evaporated to yield 12.0 g of crude **III**. The product was purified on silica gel (130 g) with hexanes/ CH_2Cl_2 50:50 v/v mixture. Yield: 10.8 g (92.5%). $M_n = 2570$ (GPC), $M_n = 2410$ (^1H NMR).

Hydrochlorination of III. **1a-Cl** was finally obtained by the hydrochlorination of **III** with HCl gas in CH_2Cl_2 at 0°C .

Characterization. Molecular weights and molecular weight distributions were measured at room temperature, using a Waters HPLC system equipped with a model 510 pump, a model 486 tunable UV/vis detector, a model 250 dual refractometer/viscometer detector (Viscotek), a model 712 sample processor, and five Ultrastaygel GPC columns connected in the following series: 500, 10^3 , 10^4 , 10^5 , and 100 \AA . The flow rate of THF, which was used as an eluent, was 1.0 mL/min . NMR spectra were recorded on Bruker 250 MHz spectrometer with CDCl_3 as a solvent (Cambridge Isotope Laboratories, Inc.).

Synthesis of 1b-Cl. Bis(*p*-tolyl)methyl chloride, **1b-Cl**, was synthesized analogously from bis(*p*-tolyl)methanol,^{5b} which was either purchased or prepared from *p*-methylbenzophenone and *p*-methylphenylmagnesium bromide.

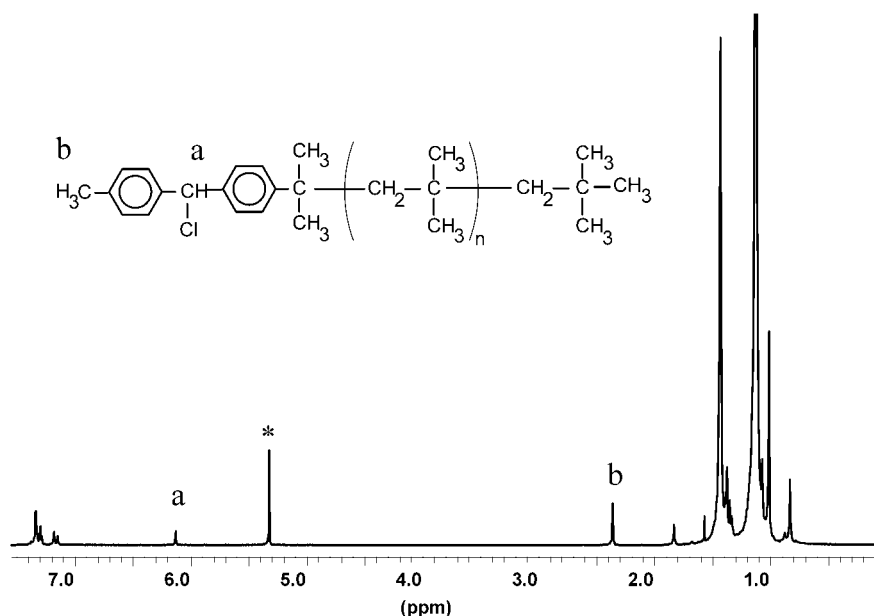


Figure 1. ^1H NMR spectrum of **1a-Cl**.

Kinetic Investigation of the Slow Reactions. The kinetics of the reactions of **1a** $^+$ and **1b** $^+$ with allyltriphenylsilane and with allylchlorodimethylsilane were determined in CH_2Cl_2 solution by means of the working station described previously.^{6a} Details of the individual kinetic experiments (concentrations, rates at variable temperature) are given in Tables S1–S4 of the Supporting Information.

Kinetic Investigation of the Fast Reactions. For the laser experiments, the solutions (optical densities/cm were 0.5–1.5) were photolyzed by 6 ns pulses (30 mJ) of 266 nm from a Continuum Powerlite 9010 Nd:YAG laser with fourth harmonic generator. The signals of the photomultiplier were digitized by a Tektronix TDS744A oscilloscope. The rate constants were determined by plotting the observed rates (at five different concentration of 1-trimethylsiloxy-cyclohexene or 1-trimethylsiloxy-cyclopentene) as a function of the concentration of the nucleophile. These plots were all linear with $R > 0.99$.

Results and Discussion

Choice of Systems. Laser flash photolytic generation of carbocations has been used for investigating fast reactions of carbocations with nucleophiles.¹² While photolyses of benzhydryl halides and *p*-cyanophenolates have been reported to proceed with homolytic and heterolytic cleavage of the C–X bond to give benzhydryl radicals and cations, respectively, photolysis of benzhydryl acetate and diphenylmethanol was found to give homolytic cleavage exclusively.¹³ Since the carbocations obtained by capping of polyisobutylene with 1,1-diphenylethylene do not form stable adducts with halides or phenolates,¹⁴ we could not synthesize suitable precursors for the photolytic generation of the carbocations shown in Scheme 1. For that reason we have decided to investigate benzhydryl cations linked to a polyisobutylene chain. The synthetic strategy for the precursor benzhydryl chloride linked to polyisobutylene is shown in Scheme 2.

First, isobutylene was polymerized by the cumyl chloride/ TiCl_4 initiating system in a hexanes/ CH_3Cl 60/40 (v/v) solvent mixture at -80°C . After complete conversion $(\text{CH}_3)_2\text{Zn}$ was added to methylate quantitatively the ω -end.¹⁵ Friedel–Crafts acylation of the aromatic headgroup of the methylated polymer was attempted with toluoyl chloride and AlCl_3 in CS_2 at

reflux temperature and in CH_2Cl_2 at -25°C (which was the lowest temperature at which both the polymer and the AlCl_3 –*p*-toluoyl chloride complex dissolved completely) for 20 h. In both cases ^1H NMR spectroscopy indicated incomplete acylation. Furthermore, degradation was a severe side reaction according to a comparison of the GPC traces of the starting material and the products. Acylation was also attempted at -80°C in a hexanes/ CH_2Cl_2 50/50 (v/v) solvent mixture for 20 h. In this system the polymer dissolved, but the AlCl_3 –toluoyl chloride complex precipitated. It was not surprising, therefore, that neither acylation nor degradation occurred under these conditions.

Complete acylation was finally achieved with the mixed anhydride of *p*-toluic acid and trifluoromethanesulfonic acid, synthesized in situ from silver triflate and *p*-toluoyl chloride, at room temperature in CH_2Cl_2 solvent.¹⁶ Acylation is clearly evident from the ^1H (Figure S1 in Supporting Information) and ^{13}C (Figure S2) NMR spectra of the acylated PIB, which showed the resonance signals for CH_3 –Ph– protons at $\delta = 2.47$ and the carbonyl ^{13}C signal at $\delta = 196.6$. By comparing the integrals for the methyl protons in the repeating unit of polyisobutylene and the methyl protons in the CH_3 –Ph– headgroup in the ^1H NMR spectrum, $M_n = 2250$ was calculated. This value is in good agreement with $M_n = 2490$ measured by GPC and virtually identical to the $M_n = 2170$ determined for the precursor polymer **I** by ^1H NMR spectroscopy.

The reduction of the acylated polyisobutylene was carried out with LiAlH_4 in dry THF. The doublet at $\delta = 5.82$ in the ^1H NMR spectrum of the product can be attributed to the CH group formed in the reduction, and the doublet at $\delta = 2.12$ corresponds to the OH group (Figure S3). In the ^{13}C NMR spectrum the carbonyl ^{13}C signal absent and a new resonance signal appeared at $\delta = 76.3$ (Figure S4).

Hydrochlorination of the alcohol yielded the final product **1a-Cl**. The peak assigned to the methine proton moved downfield from $\delta = 5.83$ to 6.13 in the ^1H NMR spectrum (Figure 1), and the carbon resonance shifted from $\delta = 76.3$ to 64.66 in the ^{13}C NMR spectrum (Figure 2). Importantly, the molecular weight and molecular

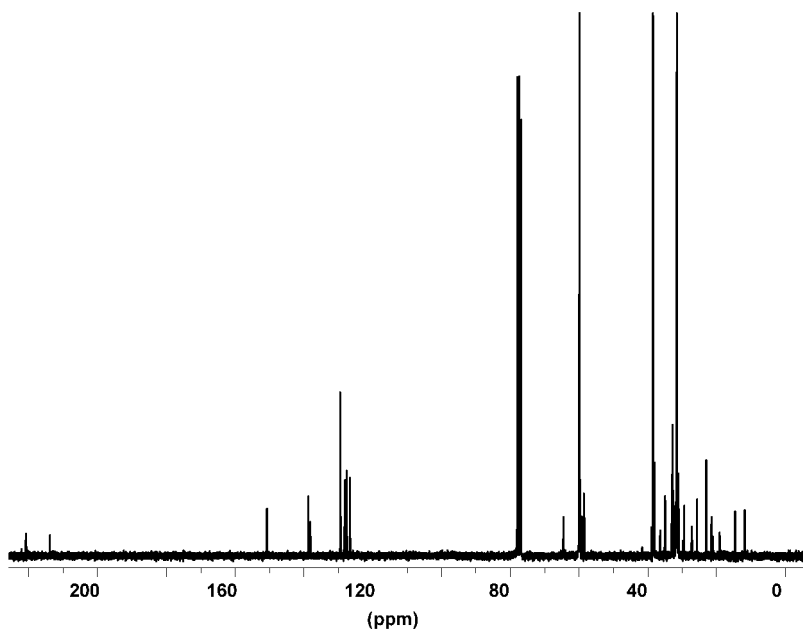


Figure 2. ^{13}C NMR spectrum of **1a-Cl**.

Table 2. Characteristics of the Polymers at Different Steps of the Synthesis

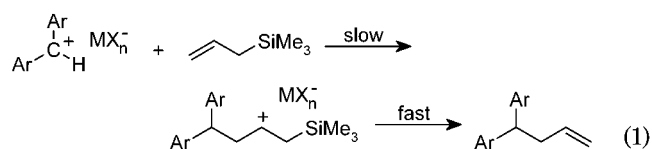
compd	yield ^a (%)	M_n (GPC)	M_w/M_n	M_n (NMR)
I	94.6	2360	1.12	2170
II	93.7	2490	1.09	2250
III	92.5	2570	1.07	2410
1a-Cl	100.0	2540	1.07	2430

^a Purified product.

weight distribution remained constant during the four steps of the synthesis (Table 2).

Kinetic Investigations with Long-Lived Carbocations. Treatment of **1b-Cl** with TiCl_4 or GaCl_3 in CH_2Cl_2 gave solutions of the carbocation **1b**⁺, the concentration of which was detected photometrically using fiber optics and the working station described previously.¹¹ While the ionization of **1a-Cl** with TiCl_4 caused problems, the reaction with GaCl_3 led to the quantitative formation of **1a**⁺. Addition of 5–120 equiv of the allylsilanes led to the exponential decay of the benzhydryl cations, from which the second-order rate constants have been derived.

Table 3 shows that the rate constants (−70 °C) determined for **1a**⁺ and **1b**⁺ with both allylsilanes agree within experimental error, indicating that replacement of a *p*-methyl group of **1b**⁺ by a polyisobutylene group does not change the electrophilicities of the benzhydryl cations. Similar rate constants obtained with different counterions GaCl_4^- (or Ga_2Cl_7^-) and Ti_2Cl_9^- are in accord with rate-determining formation of the carbon–carbon bond followed by a rapid desilylation step (eq 1).



Kinetic Investigations of Laser Flash Photolytically Generated Carbocations. Previous work has shown that photolysis of benzhydryl chlorides in dichloromethane resulted in exclusive homolytic cleavage of

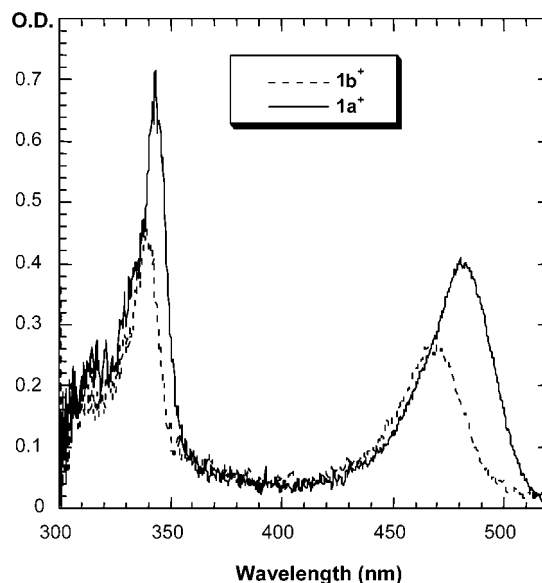


Figure 3. Electronic spectra of benzhydryl cations **1a**⁺, **1b**⁺ in acetonitrile/ CH_2Cl_2 (3/1).

the C–Cl bond, while in acetonitrile homolytic and heterolytic cleavage occurred with simultaneous formation of benzhydryl radicals and cations, respectively.¹² Since **1a-Cl** turned out to be insoluble in acetonitrile, the laser flash photolyses were carried out in acetonitrile/ CH_2Cl_2 mixtures (v/v = 1/3). As shown in Figure 3, photolysis of **1b-Cl** gave a mixture of the radical **1b**[•] ($\lambda_{\text{max}} = 338 \text{ nm}$) and the cation **1b**⁺ ($\lambda_{\text{max}} = 469 \text{ nm}$) in accord with previous observations.¹³ From the molar absorption coefficients reported in ref 13 and the spectrum shown in Figure 3, one can derive a cation/radical ratio of $[\mathbf{1b}^+]/[\mathbf{1b}^\bullet] = 0.4$ compared to 0.67 in pure acetonitrile.¹³ While the absorption maxima of the radical **1a**[•] ($\lambda_{\text{max}} = 342 \text{ nm}$) and the carbocation **1a**⁺ ($\lambda_{\text{max}} = 482 \text{ nm}$) experience a slight bathochromic shift relative to **1b**[•] and **1b**⁺, respectively, Figure 3 indicates the formation of the same cation/radical ratio from both precursors **1a-Cl** and **1b-Cl**, when the two cations as

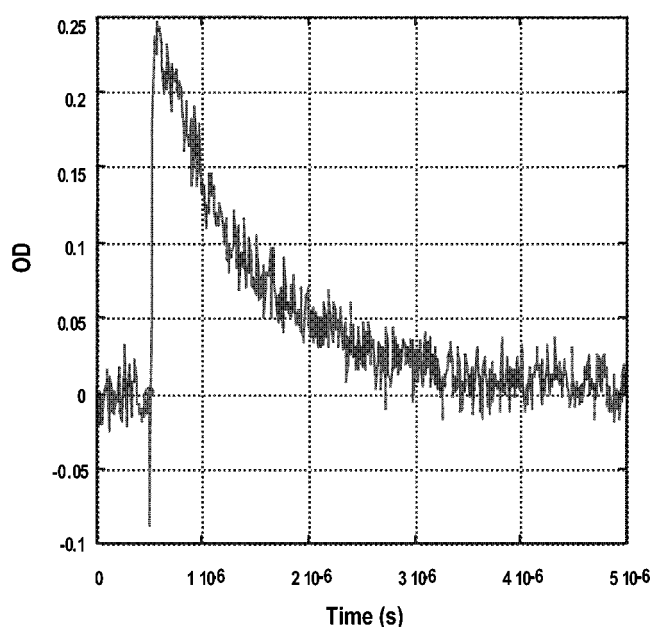
Table 3. Rate Constants and Activation Parameters for the Reactions of the Benzhydryl Cations $1a^+$, b^+ with Allylsilanes in CH_2Cl_2

$Ar_2CH^+X^-$	nucleophile	$k(-70\text{ }^\circ\text{C})\text{ L mol}^{-1}\text{ s}^{-1}$	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J mol}^{-1}\text{ K}^{-1}$
1a $GaCl_4^-$	$H_2C=CH-CH_2-SiPh_3$	391 ± 23	20.26 ± 1.39	-92.4 ± 6.7
1b $GaCl_4^-$	$H_2C=CH-CH_2-SiPh_3$	385 ± 19	18.68 ± 0.89	-100.3 ± 4.2
1a $GaCl_4^-$	$H_2C=CH-CH_2-SiClMe_2$	24.6 ± 2.3	16.83 ± 1.38	-132.3 ± 6.4
1b $GaCl_4^-$	$H_2C=CH-CH_2-SiClMe_2$	25.6 ± 1.3	19.98 ± 0.57	-116.4 ± 2.6
1b $Ti_2Cl_6^-$	$H_2C=CH-CH_2-SiClMe_2$	19.9 ± 0.7	19.76 ± 0.61	-119.6 ± 2.7

Table 4. Rate Constants ($L\text{ mol}^{-1}\text{ s}^{-1}$) for the Reactions of the Benzhydryl Cations $1a^+$, b^+ with Silyl Enol Ethers in Acetonitrile and Acetonitrile/ CH_2Cl_2 (1/3 v/v)^a

	1a		1b	
	TMSOCP	TMSOCH	TMSOCP	TMSOCH
CH_3CN			4.23×10^8	1.15×10^8
CH_3CN/CH_2Cl_2	3.56×10^8	1.26×10^8	4.62×10^8	1.60×10^8
(<i>R</i>)	(0.997)	(0.9996)	(0.994)	(0.9996)

^a TMSOCP = 1-trimethylsilyloxycyclopentene; TMSOCH = 1-trimethylsilyloxycyclohexene.

**Figure 4.** A typical exponential decay of the benzhydryl cations in a reaction with silyl enol ethers (1-trimethylsilyloxycyclohexene ($[TMSOCH] = 7.451 \times 10^{-3}\text{ M}$)).

well as the two radicals are assumed to possess identical molar absorption coefficients, respectively.

The pseudo-first-order decay of the benzhydryl cation absorption in the presence of different concentration of 1-trimethylsilyloxycyclohexene and 1-trimethylsilyloxycyclopentene was observed; a typical decay plot is shown in Figure 4. These plots were fitted with an exponential function to determine the rate of reaction. The second-order rate constants listed in Table 4 were determined by plotting the observed rates (at five different concentration of 1-trimethylsilyloxycyclohexene or 1-trimethylsilyloxycyclopentene) as a function of the concentration of the nucleophile. In accordance with the results of previous investigations, the change from acetonitrile to acetonitrile/dichloromethane solvent had only little influence on the reactivity of the carbocation.⁵ More importantly, however, the rate constants determined for the ditolylcarbenium ion $1b^+$ differ from those of the analogous polymer-bound carbenium ion $1a^+$ by less

than 30%, even when the rate constants under consideration are greater than $10^8\text{ L mol}^{-1}\text{ s}^{-1}$. We can conclude, therefore, that macromolecular carbocations with $M_n \sim 2400$ and low molecular weight analogues do not differ in reactivity with the consequence that the high k_p values reported for the polymerization of isobutylene are real.

Supporting Information Available: 1H and ^{13}C NMR spectra of **II** and **III** and tables of rate constants for reactions of $1a^+$ and $1b^+$ with allylchlorodimethylsilane and allyltriphenylsilane in CH_2Cl_2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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