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Capping of Living Polystyryl Cations with Ditolylethylene: Model Reactions with Dimeric Cations

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ABSTRACT: The addition reaction of 1,1-di-*p*-tolylethylene (DTE) to dimeric styryl living ends (diSt$^+$) in conjunction with $TiCl_4$ was investigated in 70:30 $CHCl_3-CH_2Cl_2$ (v:v) at −75 °C using on-line visible spectroscopy. This solvent composition and temperature was shown to be well suited for the polymerization of styrene since termination and chain transfer reactions could not be detected up to close to complete monomer conversion. The monoaddition of DTE to diSt$^+$ (i.e., capping) was found to be relatively fast and quantitative. The absorption maximum and the molar extinction coefficient of the DTE capped dimeric styryl cation (diStDTE$^+$) were determined to be $\lambda_{max} = 467$ nm and $\epsilon_{max} = 47\,000$ M^{-1} cm^{-1} respectively. Although operational, direct initiation is much slower than capping, and the kinetics of capping is unaffected. The apparent rate constant for capping was determined to be 152 M^{-3} s^{-1}. Retroaddition was not observed when the temperature was raised to −50 °C. However, at −50 °C, the diStDTE$^+$ underwent a slow decomposition by proton elimination.

Introduction

We have recently introduced the foundation and methodology of using non-(homo)polymerizable monomers, such as 1,1-diphenylethylene (DPE) and 1,1-di-*p*-tolylethylene (DTE) in carbocationic macromolecular engineering. By the intermediate capping reaction of the living polyisobutylene cation (PIB$^+$) with DPE and its derivatives, the dormant (chloro) end of the polymer is quantitatively transformed into a stable carbenium ion which has been shown to react quantitatively with a variety of nucleophiles such as CH_3OH,[1] NH_3,[2] silyl ketene acetals,[1] and silyl enol ethers[1] to yield end-functional PIBs. The stable carbenium ion formed upon capping with DPE or DTE is also well suited for the controlled initiation of a second monomer such as *p*-methylstyrene,[3] α-methylstyrene,[4] isobutyl vinyl ether,[5] and methyl vinyl ether.[6] Recently, bis-DPE compounds have been evaluated as “living” coupling agents,[7] and 2,2-bis[4-(1-phenylethenyl)phenyl]propane, which has two DPE moieties separated by a spacer group, was successfully used for the synthesis of A_2B_2 heteroarm star block copolymers.[8]

The successful synthesis of novel functional polymers and block copolymers outlined above is invariably based on quantitative monoaddition of a non- (homo-) polymerizable monomer such as DPE and its derivatives to living cationic chain ends. While monoaddition to living PIB$^+$ has been shown even when large excess of DPE was used, quantitative capping could be obtained only under selected conditions. We have reported that capping reactions of living PIB cation with diarylethylenes are equilibrium reactions that can be shifted toward completion by increasing Lewis acidity, solvent polarity, electron-donating ability of para substituents, concentration of reactants, or by decreasing the reaction temperature.[9] The corresponding kinetic and thermodynamic parameters have also been determined.[10]

While the concept of using non- (homo-) polymerizable monomers in carbocationic macromolecular engineering should be theoretically applicable to other living cationic polymers, so far there are no reports with living cationic polymers other than PIB$^+$. The aim of the research, which led to the results reported herein, was to broaden the scope of this concept to polymers of styrene and styrene derivatives. In this paper the kinetics and mechanism of capping dimeric styryl cation (as a model for the corresponding polystyryl living cationic end) with DTE in 70:30 $CHCl_3-CH_2Cl_2$ (v:v) using $TiCl_4$ as the co-initiator at −75 °C are reported.

Experimental Section

Materials. Styrene (St) was purified as described previously.[11] Reagent grade chloroform ($CHCl_3$) (1% ethanol stabilized) and methylene chloride (CH_2Cl_2) were washed with aqueous sodium hydroxide (10 wt %) solution and then with deionized water at least 3 times or until neutral. The solvents were then dried at least 24 h over anhydrous sodium sulfate and subsequently distilled from calcium hydride and phosphorus pentoxide. $CHCl_3$ and CH_2Cl_2 were distilled a maximum of 16 h prior to use, and stored at −80 °C. (*Caution!* When heated $CHCl_3$ may produce toxic fumes. In the presence of strong bases it may also form explosive compounds.) Titanium tetrachloride, ($TiCl_4$, 99.9%, Aldrich Chemicals) was used as received. 2,6-Di-*tert*-butylpyridine (DTBP) (Maybridge Chemical Co.) was vacuum distilled from calcium hydride prior to use. 1,1-Di-*p*-tolylethylene (DTE) and 1,1-bis(4-methoxyphenyl) ethylene (DMODPE) were synthesized by a method previously described.[12]

1,3-Diphenyl-1-butene (exo olefinic styrene dimer, diSt) was prepared according to a procedure outlined by Rosen.[13]

1-Bromo-1,3-diphenyl-butane (diSt·HBr) was synthesized by reacting 1,3-diphenyl-1-butene with 30% hydrogen bromide acetic acid solution ([HBr]/[diSt] = 3/1) for 16 h at 65 ± 5 °C.[14] The reaction mixture was cooled to room temperature and extracted three times with ethyl ether. The ethyl ether extract was then washed with aqueous sodium bicarbonate solution and then with deionized water until neutral (five times minimum). The ether extract was then dried for 24 h over anhydrous sodium sulfate. After evaporation of the ether under vacuum at 0 °C (with a minimum of light exposure), the product, a mixture of four isomers (two pairs of enantiomers) with a small amount of side products, was obtained. Purification was accomplished by column chromatography using a silica gel 60A column eluting first with hexanes and then with methylene chloride. The methylene chloride fraction was

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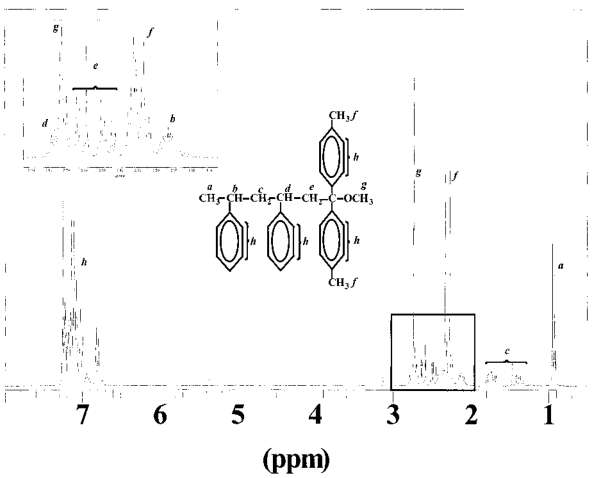


Figure 1. ^{1}H NMR spectrum of 1,1-bis(4′-methylphenyl)-3,5-diphenyl-1-methoxyhexane (diStDTE$-$OCH$_3$) in CDCl$_3$.

collected and the solvent evaporated. The product was further purified by recrystallization from hexanes at -5 °C. diSt·HBr exhibited a melting point of 50 °C and heat of fusion of 69 J/g.

1-Methoxy-1,1-bis(4-methylphenyl)-3,5-diphenylhexane (diStDTE$-$OCH$_3$) was prepared by mixing diSt·HBr (0.020 M) with DTE (0.022 M) in the presence of TiCl$_4$ (0.075M) as a co-initiator and DTBP (0.004 M) for 2 h at -75 °C in 70:30 CHCl$_3$:CH$_2$Cl$_2$ (v:v). The reaction mixture was quenched with prechilled methanol and poured into 10 vol % ammonical methanol. The solvent was evaporated, and the pure product was obtained by recrystallization from ethanol. Elemental analysis (Galbraith Lab. Inc.) confirmed the expected composition, C = 88.2 wt % (theoretical 88.4 wt %), O = 3.6 wt % (theoretical 3.6 wt %), and H = 7.9 wt % (theoretical 8.0 wt %). The ^{1}H NMR spectrum of the isolated product is shown in Figure 1.

To facilitate peak assignments, **1-*d*$_3$-methoxy-1,1-bis(4-methylphenyl)-3,5-diphenylhexane** (diStDTE$-$OCD$_3$) and **1-methoxy-1,1-bis(4-methylphenyl)-3-phenylbutane** (StDTE$-$OCH$_3$), were also prepared. diStDTE$-$OCD$_3$ was obtained by using CD$_3$OH instead of CH$_3$OH as quenching agent. StDTE$-$OCH$_3$ was prepared by a procedure similar to above by substituting 1-bromo-1-phenylethane St·HBr, (98%, Aldrich Chemical) for diSt·HBr. The ^{1}H NMR spectra for these compounds are included in the Supporting Information.

It is interesting to note that the methoxy peak of diStDTE$-$OCH$_3$ appears at 2.72 ppm, for StDTE$-$OCH$_3$ at 2.82 ppm and for PIBDTE$-$OCH$_3$ at 3.05 ppm.[12] The shift is most likely due to additional shielding of the methoxy protons by the 4-methylphenyl groups caused by conformational differences due to the St repeat units. The heat of fusion and melting points were 77 J/g and 77 °C for StDTE$-$OCH$_3$ and 69 J/g and 99 °C for diStDTE$-$OCH$_3$ respectively.

1,1-Bis(4-methylphenyl)-3,5-diphenyl-1-hexene was obtained by placing diStDTE$-$OCH$_3$ in CDCl$_3$ in a 5 mm NMR tube equipped with a poly(ethylene) cap. The CDCl$_3$ was then allowed to evaporate over approximately 14 days. The resultant material was then vacuum-dried for 24 h at 0.5 mmHg. The ^{1}H NMR spectrum for this compound is also included in the Supporting Information.

1-Chloro-1-(4-methylphenyl) ethane (pMeSt·HCl) was prepared by hydrochlorination of of *p*-methylstyrene in CH$_2$Cl$_2$ (1:1 v:v) by bubbling dry HCl gas through the solution at -78 °C for 16 h. The product obtained after evaporation of CH$_2$Cl$_2$, contained oligomers and was purified by vacuum distillation over calcium hydride at 85 °C, 0.5 Torr. ^{1}H NMR spectrum: 7.29 (q), 5.12 (q), 2.39 (s), and 1.89 ppm (d).

Procedures. All capping reactions and polymerizations were carried out under a dry nitrogen atmosphere in a MBraun 150-M glovebox (Innovative Technology Inc.). The capping reactions were carried out in a 250 mL round-bottom flask equipped with a magnetic stirring bar. The rate of capping was studied in 70:30 CHCl$_3$$-CH_2Cl_2$ (v:v) in the presence of DTBP at -75 °C. The reaction components were added to the precooled solvent system in the following sequence: (1) TiCl$_4$; (2) DTBP; (3) diSt·HBr; (4) DTE.

Instrumentation. Scanning visible spectroscopic analysis was performed with a model 661.000 quartz immersion probe connected to a LS-1 fiber optic tungsten light source (Ocean Optics) and a Zeiss MMS photodiode array detector. The entire system was driven by a Tec 5 interface and Aspect Plus software (Zeiss).

Molecular weights were determined with a size exclusion chromatography system consisting of a Model 510 HPLC pump (Waters), a Model 486 tunable UV/visible detector (Waters) and a Model 250 RI/viscosity detector (Viscotek). Separation was achieved using five ultra-Styragel columns (Waters) of varying pore size connected in the following order: 500, 10^3, 10^4, 10^5, and 100 Å. Samples were eluted in THF at a flow rate of 1 mL/min and analyzed using Viscotek version 3.0 universal and conventional calibration software and a Digital 386-22 PC. The universal and conventional calibration curves were obtained with 15 narrow molecular weight polystyrene standards (Pressure Chemical Co.). ^{1}H NMR spectroscopy was performed on a Bruker 250 or 200 MHz spectrometer.

Melting points and heat of fusion measurements were made with a TA Instruments model 2910 differential scanning calorimeter (DSC). The data were processed with a model 2200 data station using version 4.0 of the standard DSC analysis program. Samples were run at 1.0 °C per minute per ASTM-E793 and E794.

Results and Discussion

The Polymerization of St. The living polymerization of St with organic halides as initiators has been reported in conjunction with SnCl$_4$,[11] TiCl$_3$(OR)[15] and TiCl$_4$,[16,17] as co-initiators. With SnCl$_4$ the polymerization is rather slow even at a relatively high temperature (~-15 °C); therefore we carried out preliminary polymerization and end-capping studies only in conjunction with TiCl$_3$(OEt) or TiCl$_4$ as co-initiators. The polymerization of St (0.7 M) was first examined using pMeSt·HCl (2.36×10^{-3} M) as initiator with mixed co-initiators TiCl$_4$ and Ti(OEt)$_4$ at concentrations of 2.81×10^{-2} and 1.31×10^{-2} M respectively, in the presence of DTBP in CH$_2$Cl$_2$ at -78 °C. The polymerization was rather slow with quantitative conversion being obtained in 4.5 h ($M_{\mathrm{n\ theo}} = 31\,000$, $M_{\mathrm{n\ exp}} = 30\,000$). Capping with DTE was even slower and incomplete after 16 h. Capping was also slow with the more reactive DMODPE; therefore, experimentation with TiCl$_3$(OEt) was discontinued.

The living polymerization of St with a relatively high polymerization rate has been reported using 2-chloro-2,4,4-trimethylpentane (TMPCl)/TiCl$_4$ in 40:60 CH$_3$Cl$-$methylcyclohexane v:v at -80 °C in the presence of proton trap.[16,17] The low temperature and the use of nonpolar solvent mixtures were necessary to minimize side reactions, such as direct initiation and intermolecular alkylation, and to obtain controlled M_{n}s. Even under those conditions the molecular weight distributions (MWDs) were rather broad ($M_{\mathrm{w}}/M_{\mathrm{n}} \sim 1.7$). In this study a 70:30 CHCl$_3$$-CH_2Cl_2$ (v:v) solvent mixture was employed as the polymers obtained with the pMeSt·HCl/TiCl$_4$ initiating system at -75 °C exhibited controlled M_{n}s and relatively narrow MWDs ($M_{\mathrm{w}}/M_{\mathrm{n}} \sim 1.3$). According to the first-order plot, shown in Figure 2, termination cannot be detected during the polymerization up to close to complete monomer conversions. Above ~95% conversion, however, the first-order plots are not reliable in diagnosing the presence or absence of ter-

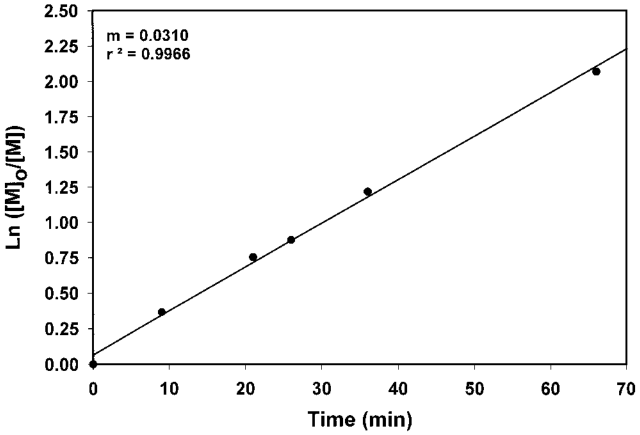


Figure 2. First-order plot for the polymerization of St in 70:30 $CHCl_3-CH_2Cl_2$ (v:v) at −75 °C. $[TiCl_4] = 3.0 \times 10^{-2}$ M, $[pMeSt \cdot HCl] = 2.36 \times 10^{-3}$ M, [styrene] = 0.70 M, and $[DTBP] = 4.0 \times 10^{-3}$ M.

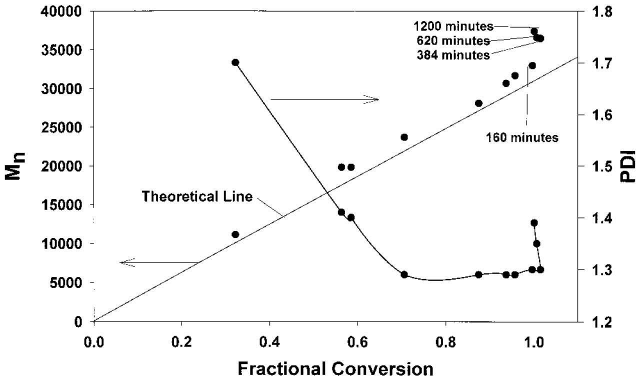


Figure 3. M_n and PDI vs Conversion Plot for the Polymerization of St in $CHCl_3$:CH_2Cl_2 70:30 (v:v) at −75 °C. $[TiCl_4] = 3.0 \times 10^{-2}$M, $[pMeSt \cdot HCl] = 2.36 \times 10^{-3}$M, [Styrene] = 0.70M, $[DTBP] = 4.0 \times 10^{-3}$M.

mination unless conversion measurements are much more accurate than ours (∼1%). From the first-order plot the apparent rate constant of propagation ($k_{app} = k_p[M_n^+]$, where k_p is the absolute propagation rate constant and $[M_n^+]$ is the active chain end concentration) was determined to be 5.1×10^{-4} s^{-1}. The M_n vs conversion plot, shown in Figure 3, is linear, thus chain transfer is also absent. At extended times, intermolecular alkylation is observed, as the M_n increases with time. This reaction is very slow, as the last four points represent samples quenched after reaction times of 160, 384, 619, and 1200 min.

Polymerizations were also carried out in the absence of initiator. Under these conditions, 65% monomer conversion was obtained after 13 h. Thus, direct initiation is operational but slow compared to initiation with pMeSt·HCl. Direct initiation of St has been observed with other solvent systems, utilizing $TiCl_4$ as the coinitiator,[16,18] although the mechanism has not yet been determined.

Capping of diSt$^+$ with DTE. The end-capping of living polystyryl cations with DTE was studied using the hydrobrominated St dimer, diSt·HBr, as a model compound. To confirm that side reactions such as β-proton elimination and inter- or intramolecular alkylation are absent in the studied time frame of end-capping, St polymerizations were initiated by the aged diSt·HBr/$TiCl_4$ initiating system. Thus, diSt·HBr, $TiCl_4$, and DTBP were premixed and after various aging

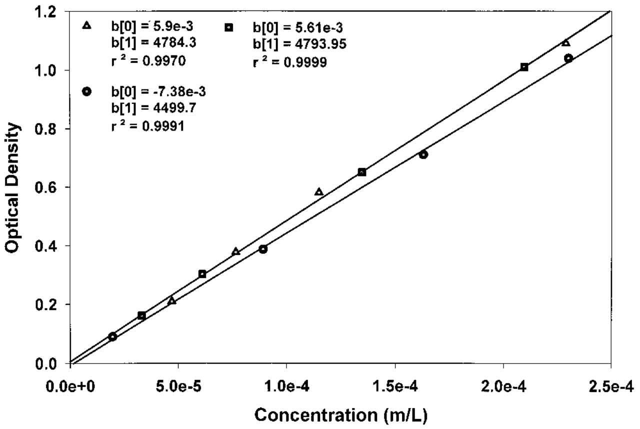


Figure 4. Optical Density vs Concentration of diStDTE$^+$. Path Length = 0.1 cm, $[TiCl_4] = 5.0 \times 10^{-2}$M, $[DTBP] = 4.0 \times 10^{-3}$M.

Table 1. Polymerization of St with Aged DiSt·HBr/$TiCl_4$ Initiating System in 70:30 $CHCl_3-CH_2Cl_2$ (v:v) at −75 °C in the Presence of DTBP ($[diSt \cdot HBr]_o = 1.00 \times 10^{-3}$ M, $[TiCl_4] = 5.0 \times 10^{-2}$ M, [St] = 0.30 M)

DiSt·HBr aging time prior to St addition (min)	calcd chain end concn[19] (M)
13	1.10×10^{-3}
59	1.08×10^{-3}
118	1.03×10^{-3}
234	1.07×10^{-3}

times St was added. Samples were quenched after 90 min polymerization time with prechilled methanol. Conversion and molecular weight were measured and the chain end concentration calculated[19] (see Table 1). Inspection of Table 1 reveals that the active chain end concentration remained constant and equals [diSt·HBr] independently of the aging time.

After it is established that side reactions are absent, capping reactions were studied using the diSt·HBr model compound. First the absorption maximum (λ_{max} = 467 nm) and the molar extinction coefficient of the diStDTE$^+$ cation (ϵ_{max} = 47 000 M^{-1} cm^{-1}) were determined by mixing various concentrations of diStDTE−OCH_3 (2.5×10^{-4} to 2×10^{-5}M) with a large excess of $TiCl_4$ ($[TiCl_4] = 5.0 \times 10^{-2}$M) in the presence of proton trap (Figure 4). The linearity of the Beer−Lambert plot at constant $[TiCl_4]$ also verifies that the chain ends are completely ionized at all concentrations tested. An identical molar absorption coefficient (ϵ_{max} = 47 000 M^{-1} cm^{-1}) was calculated for StDTE$^+$. For the 1,1-(di-p-tolyl)ethyl$^+$ cation in aqueous sulfuric acid at 25 °C, Deno et al.,[20] reported ϵ_{max} = 63 100 M^{-1} cm^{-1} at λ_{max} = 458 nm. Compared to the molar extinction coefficient reported by Deno[20] the lower ϵ of diStDTE$^+$ is somewhat surprising and could possibly be due to solvent or steric factors[21] but may also be due to a space polarization effect[22,23] caused by the phenyl ring alignment. The latter, however, is usually accompanied by a bathochromic shift. Our observed ϵ_{max} and λ_{max} values for diStDTE$^+$ and StDTE$^+$ are in good agreement with ϵ_{max} = 44 000 M^{-1} cm^{-1} at λ_{max} = 463 nm found for the 3,3,5,5-tetramethyl-1,1-ditolylhexyl cation (TMPDTE$^+$)[24] and ϵ = 45 000 M^{-1} cm^{-1} at λ_{max} = 440 nm obtained for the 3,3,5,5-tetramethyl-1,1-diphenylhexyl cation (TMPDPE$^+$)[10] in 40:60 CH_3Cl−hexane (v:v) at −80 °C.

Capping experiments were performed using $[diSt \cdot HBr] = 1.5 \times 10^{-3}$ and $[DTE] = 3.0 \times 10^{-3}$ at $[TiCl_4] = 5.0 \times 10^{-2}$ M and 3.0×10^{-2} M concentrations. The

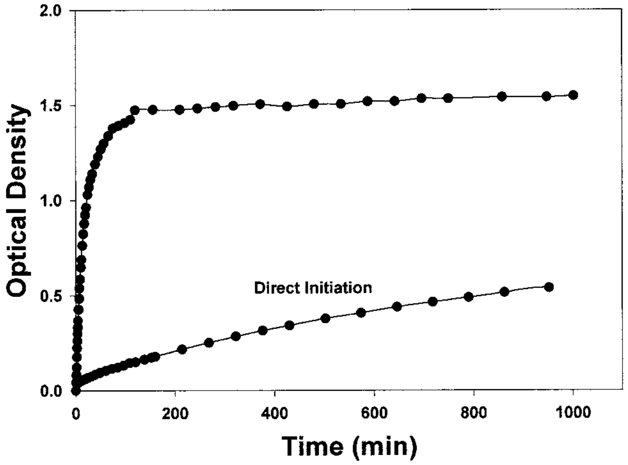
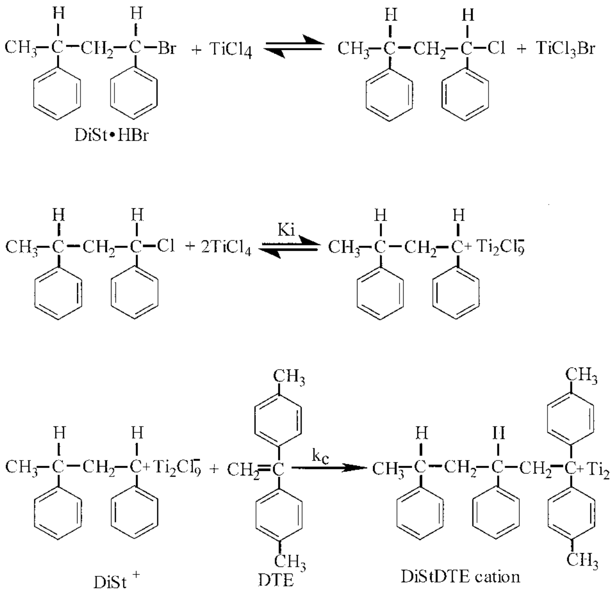


Figure 5. Absorbance vs Time for the Capping Reaction and for the Control Experiment in $CHCl_3$:CH_2Cl_2 70:30 (v:v) at −75 °C. $[TiCl_4] = 5.0 \times 10^{-2}$M, [diSt·HBr] $= 1.5 \times 10^{-3}$M [DTE] $= 3.0 \times 10^{-3}$M, [DTBP] $= 4.0 \times 10^{-3}$M.

Scheme 1



capping reaction for diSt·HBr is shown in Scheme 1. In Scheme 1 we assumed that in the first step the bromo ends of diSt·HBr are rapidly exchanged by chloro ends. This seems to be a reasonable assumption given the large excess of $TiCl_4$ and the reversible nature of ionization.

The capping reaction was followed by measuring the absorption at $\lambda = 467$ nm. A kinetic plot of absorbance vs time for $[TiCl_4] = 5.0 \times 10^{-2}$ is shown in Figure 5. According to the plot, capping is relatively fast and quantitative (capping efficiency = 105−110% using $\epsilon = 47\,000$).

It is important to point out that the visible spectrum observed in the kinetic studies, where excess DTE was used ([DTE]/[diSt·HBr] = 2), is identical with the spectra of $diStDTE^+$ and $StDTE^+$ cations, which were obtained by ionization of the corresponding methoxy model compounds (i.e., in the absence of free DTE). This indicates that solvation effects caused by residual DTE as noted by Sigwalt[22] for DPE (although at much higher concentrations) are absent.

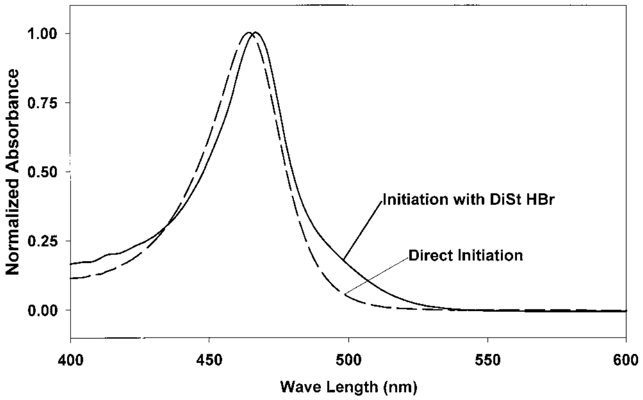


Figure 6. Normalized visible spectra of the products of capping and direct initiation.

Control experiments were also carried out in the absence of diSt·HBr but under otherwise identical conditions as capping reactions. The results indicate that when DTE (3.0×10^{-3} M) is mixed with $TiCl_4$ (5.0×10^{-3} or 3.0×10^{-3} M) in the presence of DTBP (3.0×10^{-3} or 6.0×10^{-3}M) in 70:30 $CHCl_3-CH_2Cl_2$ (v:v) at −75 °C, a colored species is slowly generated (see Figure 5). The visible spectra observed in the capping reaction and in the control experiment shown in Figure 6 are very similar. In the control experiment, $\lambda_{max} = 464$ nm which is very similar to $\lambda_{max} = 467$ nm observed for the $diStDTE^+$ cation. Because protic initiation does not occur in the presence of proton trap, it was postulated that this species is due to direct initiation by $TiCl_4$. The control experiments, which were run in duplicate at $TiCl_4$ concentrations of 3.0×10^{-2} and 5.0×10^{-2} M, were quenched with methanol and poured into ammonical methanol. The ^1H NMR spectra of the product (not shown) exhibited peaks at 5.35 (s), 2.35 (s), 3.10 (s), 1.81 (s), and 7.25 (m) ppm. The peak at 5.35 ppm was assigned to unreacted DTE. Peak intensities at 1.81 and 3.10 ppm were always identical which led us to the assumption that these peaks are the methyl and methoxy protons of 1-methoxy-1,1-di-*p*-tolylethane ($HDTE-OCH_3$), respectively. This is the product expected from direct initiation after quenching with methanol (see Scheme 2). This is substantiated by the observation that the ratio of intensities of the 1.81 and 3.10 ppm peaks changed to 3.0/2.1 when CH_3OD was used for quenching.

The ratio of $diStDTE^+$ to cations formed in direct initiation was determined by ^1H NMR spectra of the quenched reaction mixtures assuming 100% capping efficiency. On the basis of this assumption, approximately 10% and 5% of the cationic species were produced by direct initiation at $[TiCl_4] = 5.0 \times 10^{-2}$ and 3.0×10^{-2} M concentrations, respectively.

The kinetics for the capping reaction were derived as follows:

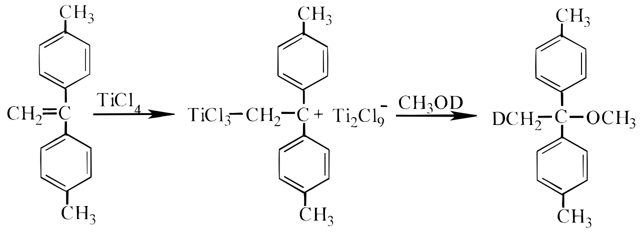
$$K_i = \frac{[\mathrm{DiSt}^+\mathrm{Ti}_2\mathrm{Cl}_9^-]}{[\mathrm{TiCl}_4]^2[\mathrm{DiSt{\cdot}HCl}]} \tag{1}$$

$$-\frac{\mathrm{d[DTE]}}{\mathrm{d}t} = k_c[\mathrm{DTE}][\mathrm{DiSt}^+\mathrm{Ti}_2\mathrm{Cl}_9^-] \tag{2}$$

Substituting eq 1 into eq 2 and assuming K_i is $\ll 1$ and $[TiCl_4] = [TiCl_4]_o$

$$-\frac{\mathrm{d[DTE]}}{\mathrm{d}t} = K_i k_c[\mathrm{TiCl}_4]_o^2[\mathrm{DTE}][\mathrm{DiSt{\cdot}HCl}] \tag{3}$$

Scheme 2



If we use the following relationship

$$[\mathrm{DiSt{\cdot}HCl}] = [\mathrm{DTE}] - \frac{[\mathrm{DTE}]_o}{2} \qquad (4)$$

Substituting eq 4 into eq 3 and rearranging

$$\frac{-\mathrm{d}\,[\mathrm{DTE}]}{[\mathrm{DTE}]([\mathrm{DTE}]-0.5[\mathrm{DTE}]_o)} = k_c K_i [\mathrm{TiCl_4}]_o^{\,2}\,\mathrm{d}t \qquad (5)$$

Integrating and rearranging

$$\frac{2}{[\mathrm{DTE}]_o}\ln\left[\frac{[\mathrm{DTE}]_o}{2[\mathrm{DTE}]-[\mathrm{DTE}]_o}\right] = K_i k_c [\mathrm{TiCl_4}]_o^{\,2} t \qquad (6)$$

Figure 7 is a plot of the kinetic data at $[\mathrm{TiCl_4}] = 5.0 \times 10^{-2}$ and 3.0×10^{-2} M in the form the linear relationship of eq 6. The plot deviates slightly from linearity at about 85% capping. This could be due to direct initiation, small inaccuracies in measurements or the assumption that $TiCl_4$ concentration remains constant. The apparent rate constant (k_cK_i) for this reaction is determined to be 152 M^{-3} s^{-1}.

It is known that the capping of PIB with diphenylethylene (DPE) is an equilibrium reaction, and that this equilibrium is shifted toward completion by increasing Lewis acidity, solvent polarity, electron-donating ability of *p*-substituents, concentration of reactants such as DPE and Lewis acid, or by decreasing the reaction temperature.[9,25,26] The effect of temperature was found to be rather significant; i.e., it is exceedingly difficult to achieve complete capping of living PIB^+ at −40 °C. This can be explained by the unfavorable thermodynamics of the capping reaction at higher temperature, most probably due to steric hindrance. It is well documented, that DPE adds to poly(styryllithium) quantitatively even at room temperature; thus, the free energy change must be negative. Therefore, it was expected that capping of living poly(styrene) cation is irreversible up to room temperature. To prove this presumption, diStDTE−OCH_3 (2.0×10^{-4} M) was ionized with $TiCl_4$ (1.0×10^{-2} M) in the presence of proton trap at −75 °C, and then the temperature was increased to −50 °C. The visible spectrum was monitored for any significant change in the cation concentration assuming a constant molar extinction coefficient ($\epsilon_{\max} = 47\,000$ M^{-1} cm^{-1}). At −50 °C, the cation concentration first decreased sharply and then slowly until after 15 h at −50 °C the cation concentration was 37% of its original concentration. The sample was quenched with CH_3OH at −50 °C and analyzed by ^1H NMR spectroscopy. The ^1H NMR spectrum (not shown) exhibited a split doublet at 6.15 ppm which was assigned to the olefinic proton of 1,1-bis(4′-methylphenyl)-3,5-diphenyl-1-hexene. The ratio of the peak at 6.15 ppm to the methoxy protons at 2.72 ppm (diStDTE−OCH_3) was calculated to be 0.17/1. This ratio corresponds to a 34% decrease in original cation concentration, which is in good agreement with the concentration determined from the visible spectrum. From these results it was hypothesized that at −50 °C ionization is not complete and thus termination by chlorination occurred initially, followed by a slow decomposition by elimination.

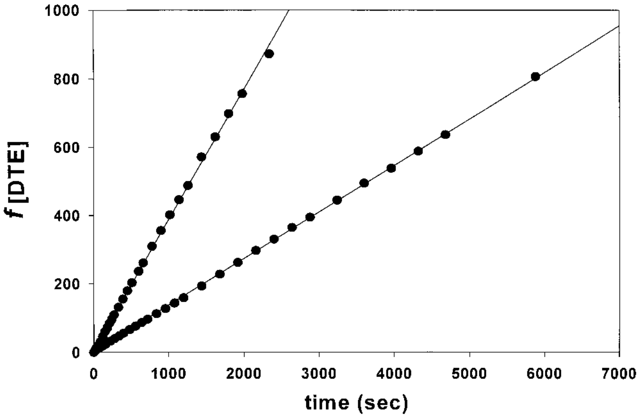


Figure 7. *f* [DTE] vs time where *f* [DTE] = left side of eq 6. The plot was made assuming $\epsilon = 47{,}000$ and no contribution from direct initiation. Conditions were $CHCl_3$:CH_2Cl_2 70:30 (v:v) at −75 °C, $[\mathrm{TiCl_4}] = 3.0$ and 5.0×10^{-2}M, $[\mathrm{diSt{\cdot}HBr}] = 1.5 \times 10^{-3}$M, $[\mathrm{DTE}] = 3.0 \times 10^{-3}$M, $[\mathrm{DTBP}] = 4.0 \times 10^{-3}$M.

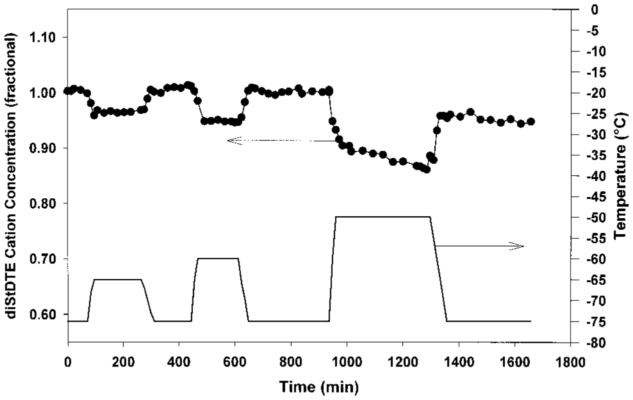


Figure 8. DiStDTE$^+$ cation concentration and Temperature vs Time. 70:30 (v:v) $CHCl_3$:CH_2Cl_2 at −75 °C, $[\mathrm{TiCl_4}] = 1.0 \times 10^{-2}$M, $[\mathrm{diStDTE{-}OCH_3}] = 2.0 \times 10^{-4}$ M, $[\mathrm{DTBP}] = 4.0 \times 10^{-3}$M.

To confirm this hypothesis another experiment was carried out under identical conditions except this time the temperature was modulated in the following order: −75 to −65 to −75 to −60 to −75 to −50 °C and then back to −75 °C. The results of these experiments are shown in Figure 8. When the temperature was increased quickly from −75 to −65 °C and from −75 to −60 °C the cation concentration decreased rapidly and remained constant at 1.93×10^{-4} and 1.90×10^{-4} M, respectively. When the temperatures were lowered back to −75 °C, the cation concentrations very quickly returned back to their original 2.00×10^{-4} M. The speed at which the absorbance returned back to the initial at −75 °C indicates a fast equilibrium between ionized and nonionized species relative to capping. Thus, as expected, the extent of ionization is higher at lower temperatures. When the temperature was increased from −75 to −50 °C, the cation concentration first decreased rapidly to 1.82×10^{-4} M. After the first rapid decrease in absorbance it continued decreasing slowly with time indicating decapping or decomposition. After 5 h at −50 °C, the temperature was again returned to

−75 °C. The absorbance never returned to its initial value and stabilized at an absorbance equal to a cation concentration of 1.90×10^{-4} M or at 95% of its original value. This indicated that 5% of the cation decomposed. The final sample was quenched at −75 °C, and the product was characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectrum (not shown) indicated the presence of 1,1-Bis-tolyl-3,5-diphenyl-1-hexene (split doublet at 6.15 ppm, olefinic proton) and diStDTE−OCH_3 (−$OC\mathbf{H}_3$ protons at 2.72 ppm). Integration of the two peaks at 6.15 and 2.72 ppm gave a ratio of 0.015/1. This ratio corresponds to a 4.3% decrease in model compound concentration, which is in good agreement with the spectroscopic finding.

Conclusions

The capping reaction of diSt$^+$ (as a model for the living polystyryl cation) with DTE in conjunction with $TiCl_4$ in 70:30 $CHCl_3$−CH_2Cl_2 (v:v) solvent mixture at −75 °C was studied by on line visible spectroscopy. Capping was found to be rapid and quantitative. Although operational, direct initiation is much slower than capping so that the kinetics of capping is unaffected. Importantly, retroaddition was not observed when the temperature was raised to −50 °C. However, at −50 °C the diStDTE$^+$ cation underwent a slow decomposition by proton elimination. In conclusion, the methodology of using non- (homo-) polymerizable monomers in carbocationic macromolecular engineering appears to be applicable to polystyrene.

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Supporting Information Available: ^{1}H NMR spectra of 1,1-bis(4′-dimethylphenyl)-3,5-diphenyl-1-d_3-methoxyhexane (diStDTE−OCD_3), 1,1-bis(4′-methylphenyl)-1-methoxy-3-phenylbutane (StDTE−OCH_3), and 1,1-bis(4′-methylphenyl)-3,5-diphenyl-1-hexene in $CDCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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