Living Cationic Polymerization of p -Chloro-α-methylstyrene and Its Sequential Block Copolymerization with Isobutylene

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Living Cationic Polymerization of *p*-Chloro-α-methylstyrene and Its Sequential Block Copolymerization with Isobutylene

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ABSTRACT: The homopolymerization of *p*-chloro-α-methylstyrene (pClαMeSt) and its sequential block copolymerization with isobutylene (IB) initiated by 1,3-dimethyl-1,3-diphenyl-1-chlorobutane (DiαMeSt· HCl) in conjunction with BCl_3 was investigated in methylcyclohexane/methyl chloride (60/40, v/v) at −80 °C. The homopolymers exhibited close to theoretical M_n's, and the diagnostic M_n−conversion and first-order ($\ln[M]_0/[M]$−time) plots were linear; thus, chain transfer and termination were not detected. The propagating chain end of poly(pClαMeSt) was exceptionally stable; no decomposition could be detected even after 5 h under monomer-starved conditions. According to the ^{1}H NMR spectrum of homopoly-(pClαMeSt), the polymer is 94% syndiotactic; however, the precipitated polymer exhibited only a glass transition at 198 °C. Recrystallization from methylcyclohexane−methyl ethyl ketone solvent mixture yielded a semicrystalline polymer with T_m = 229 °C. Sequential block copolymerization of pClαMeSt with IB was also carried out by the addition of IB to the solution of living poly(pClαMeSt), followed by the addition of $TiCl_4$. By gel permeation chromatography, the crossover efficiency was ∼100%, and no homopolymer contamination was detected.

Introduction

One of the most important aspects of living polymerization is the ability to prepare block copolymers by sequential monomer addition. This ability has been utilized in living carbocationic polymerization to synthesize a wide variety of linear and star-branched block copolymers, mainly with polyisobutylene (PIB) as the rubbery block segment and plastic segments based on styrene,[1,2] α-methylstyrene,[3,4] indene,[5] and *p*-methyl-,[6] *p-tert*-butyl-,[7] *p*-chloro-, and *p*-fluorostyrene.[8] Triblock copolymers having a PIB central block segment and the above plastic end segments are useful thermoplastic elastomers. A comprehensive review on the subject is available.[9] The syntheses of PIB block copolymers with a crystalline (mainly polyester) block segment so far involved a much more difficult, multistep, site transformation process. Sequential monomer addition has not been reported for this type of block copolymer due to limitations in the availability of monomers that undergo living cationic polymerization and give rise to crystalline polymers. Polymer crystallinity is usually the consequence of a (stereo)regular macromolecular structure, which is conducive to packing in the crystalline lattice. Most of the above styrenic monomers, however, give rise to atactic polymers. Cationic polymerization of α-methylstyrene (αMeSt) yields a mostly syndiotactic polymer, which, however, does not crystallize even when the syndiotactic content is higher than 90%.[3] Polymers of *p*-methyl- and *p*-chloro-substituted αMeSt (pClαMeSt) have been reported to be crystalline with high T_g (∼140−175 °C) and T_m (∼210−220 °C).[10] Due to our interest in PIB based block copolymers, we were attracted to pClαMeSt, whose reactivity should be closer to IB than *p*-methyl-substituted αMeSt.

Lenz has reported on the polymerization of para-substituted αMeSt monomers at −78 °C using various Friedel−Crafts acids (in conjunction with adventitious protons) and solvents.[11] Poly(pClαMeSt) synthesized with $TiCl_4$ in methylene chloride at −78 °C exhibited M_n = 1.71 × 10^5 and PDI = 2.4. The solvent polarity strongly influenced the tacticity; polar solvent favored the formation of highly syndiotactic polymers (up to 96%). The influence of Friedel−Crafts acid was less important in polar solvent but was quite substantial in hexane. The polymerization of pClαMeSt by the 2-chloro-2,4,4-trimethylpentane/$TiCl_4$ initiating system in CH_3-Cl (MeCl)/methylcyclohexane (MeChx) (40/60, v/v) at −80 °C has also been reported by Chakraborty et al.[12] The syndiotactic diad fraction of the polymer (M_n = 2.0 × 10^4 and PDI = 3.4) was 0.8. Information on the crystallinity was not reported.[12] More recently the electropolymerization of pClαMeSt was investigated.[13] The polymers were reportedly crystalline, but details were not provided.

This publication reports on the living cationic polymerization of pClαMeSt and on the synthesis of poly-(pClαMeSt-*b*-IB) block copolymer by living cationic sequential block copolymerization.

Experimental Section

Materials. 1,3-Dimethyl-1,3-diphenyl-1-chlorobutane (DiαMeSt· HCl) was synthesized by the hydrochlorination of 2,4-diphenyl-4-methyl-1-pentene (αMeSt dimer, Aldrich, 99%) as described before.[14] *p*-Chloro-α-methylstyrene (pClαMeSt, Aldrich, 98%) was mixed with a small amount of dibutylmagnesium (1.0 M heptane solution) and distilled under vacuum before use. Methyl chloride (MeCl) and IB 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. Methylcyclohexane (MeChx, Aldrich, 99%) was refluxed for 24 h with concentrated sulfuric acid, washed with 5% NaOH solution then neutral with distilled water, dried on Na_2SO_4, and distilled from CaH_2 under nitrogen before use. Titanium tetrachloride (Aldrich, 99.9%), 2,6-di-*tert*-butylpyridine (DTBP, Aldrich, 97%), and boron trichloride (Aldrich, 99.9%) were used as received.

Polymerization. All polymerizations were carried out under a dry nitrogen atmosphere in an Mbraun 150-M glovebox (Innovative Technology Inc., Newburyport, MA). Large (75 mL) culture tubes were used as polymerization reactors. The total volume of the reaction mixture was 25 mL.

The polymerization of pClαMeSt was carried out using the following concentrations: [DiαMeSt·HCl] = 0.002 M, [BCl$_3$] = 0.006 M, [pClαMeSt] = 0.282 M, [DTBP] = 0.0035 M, unless noted otherwise. The order of addition was MeChx, MeCl, proton trap, diαMeSt·HCl, BCl$_3$, and the monomer. The polymerization mixture was quenched with prechilled methanol, and then the polymer was precipitated into 50 mL of methanol containing 100 ppm of 2,6-di-*tert*-butyl-4-methylphenol as an antioxidant. After decanting the solvent, the polymer was washed again with methanol and dried.

The polymer was crystallized in a MeChx−methyl ethyl ketone solvent mixture. Polymer (1.2 g) was suspended in 200 mL of MeChx, and then methyl ethyl ketone was added until the entire polymer dissolved (∼20 mL). The solution was left in an uncovered beaker for 3 days. The remaining material was dried in a vacuum at 130 °C for 1 day.

Synthesis of PpClαMeSt−PIB Diblock Copolymer. To synthesize PpClαMeSt, 10.4 mL of MeChx, 6.6 mL of MeCl, 1.0 mL of DTBP solution in MeChx (0.15 M), 1.075 g (7 mmol) of pClαMeSt, 1.0 mL of DiαMeSt·HCl solution in MeCl (0.05 M), and 1.0 mL of BCl$_3$ in a MeChx/MeCl 60/40 (v/v) mixture were added at −80 °C in this order. The polymerization was carried out for 20 min. An aliquot was then taken and quenched with prechilled methanol to determine M_n = 2.1 × 10^4 and M_w/M_n = 1.30 for the first block segment. To the rest of the solution were added 3.0 mL (38.5 mmol) of IB and 1.0 mL of TiCl$_4$ solution (0.90 M). After 120 min the polymerization mixture was quenched with prechilled methanol, and then the polymer was precipitated into 50 mL of methanol. The overall monomer conversion was 99.5%. The block copolymer exhibited M_n = 6.2 × 10^4 and M_w/M_n = 1.21.

Characterization. Molecular weights were measured using a Waters HPLC system equipped with a model 510 HPLC pump, a model 250 dual refractometer/viscometer detector (Viscotek), a model 486 UV/vis detector, a model 712 sample processor, and five ultra-Styragel GPC columns connected in the following series: 500, 10^3, 10^4, 10^5, and 100 Å. THF was used as eluent at a flow rate of 1.0 mL/min. The measurements were carried out at room temperature. The molecular weights and polydispersities were determined using the universal calibration curve and Viscotek TriSEC GPC software. The dn/dc values and therefore the M_n's of poly(pClαMeSt) and poly-(pClαMeSt-*b*-IB) diblock copolymers were calculated by assuming 100% recovery of the injected mass. ^{1}H NMR spectroscopy was carried out on a Bruker 250 MHz instrument.

Results and Discussion

Living Polymerization of pClαMeSt. We reported earlier[14] on the living cationic polymerization of αMeSt initiated by the hydrochlorinated olefinic αMeSt dimer (DiαMeSt·HCl)/BCl$_3$ initiating system in MeCl/hexanes (Hex) or MeCl/MeChx (40/60, v/v) mixtures at −60 to −80 °C. The polymerization of pClαMeSt was first investigated under identical conditions. In MeChx/MeCl 60/40 (v/v) at −80 °C the polymerization is slower than that of αMeSt, but still relatively rapid, and 100% conversion is reached in about 16 min. The M_n−conversion plot, shown in Figure 1, is linear and close to the theoretical line, indicating the absence of chain transfer to monomer. The M_w/M_n values decrease with increasing conversion and reach about 1.2 at complete monomer conversion. The M_w/M_n−conversion function is typical of slow exchange between active and dormant centers relative to the rate of propagation. Fitting of the M_w/M_n−conversion plot with eq 1,[15]

$$M_w/M_n \cong 1 + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \tag{1}$$

where x is the fractional conversion and β = (k_{-i})/(k_p[I]$_0$) (k_{-i} and k_p are the rate constants of deactivation and propagation, respectively, and [I]$_0$ is initiator
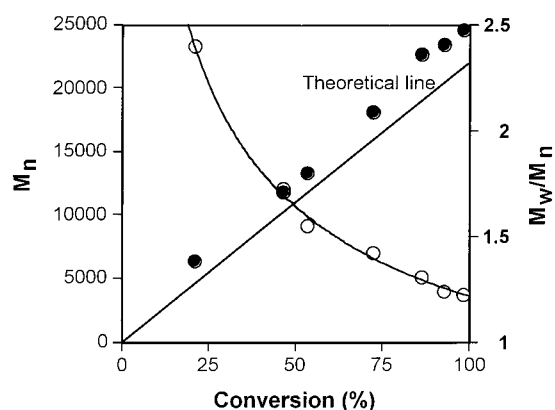

Figure 1. A M_n−conversion plot for the polymerization of pClαMeSt: filled symbols, M_n; open symbols, M_w/M_n. Reaction conditions: [DiαMeSt·HCl] = 0.002 M, [DTBP] = 0.0035 M, [BCl$_3$] = 0.006 M, [pClαMeSt] = 0.282 M, MeChx/MeCl 60/40 (v/v); temperature = −80 °C.
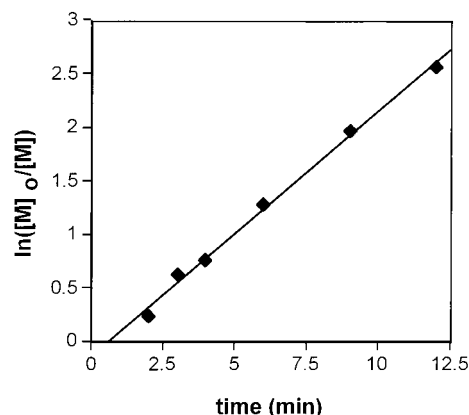

Figure 2. A ln[M]$_0$/[M]−time plot for the polymerization of pClαMeSt. Reaction conditions: [DiαMeSt·HCl] = 0.002 M, [DTBP] = 0.006 M, [BCl$_3$] = 0.006 M, [pClαMeSt] = 0.282 M, MeChx/MeCl 60/40 (v/v); temperature = −80 °C.

concentration) yielded a β value of 5.7. Thus, propagation is ∼88 times faster than deactivation, which results in broad molecular weight distributions, especially at low conversion. Interestingly, propagation is only 23 times faster than deactivation in the polymerization of αMeSt (β = 21.5 was calculated from the data of ref 14 for polymerizations carried out under the same conditions). Since k_{-i} is not expected to be lower for pClαMeSt (PpClαMeSt$^+$ should be less stable than PαMeSt$^+$), k_p(pClαMeSt) must be higher than k_p(αMeSt). Therefore, it seems that the effect of *p*-chloro substituent on cation reactivity is larger than its effect on monomer reactivity.

The first-order (ln[M]$_0$/[M]−time) plot, shown in Figure 2, is also linear starting at close to the origin, and thus termination is not detected. Therefore, we conclude that the polymerization of pClαMeSt in conjunction with BCl$_3$ in MeChx/MeCl (60/40 v/v) at −80 °C is living.

The lifetime of the propagating chain end of poly-(pClαMeSt) was measured in a separate experiment. First, a low molecular weight polymer (M_n = 5.4 × 10^3) was prepared, and the polymerization mixture was left under monomer-starved conditions for different times. After a given time, a second monomer increment was added (0.334 M, $M_{n\text{total}}$(theoretical) = 2.55 × 10^4) and polymerized for 30 min. Table 1 lists the total conversions and the M_n and M_w/M_n values.

Table 1. Characteristics of Poly(pClαMeSt) after a Second Monomer Addition[a]

time of addition of second monomer increment (min)	conv (%)	$M_n \times 10^{-3}$	M_w/M_n
original	87.4	5.4	1.51
90	90.8	24.2	1.19
180	84.4	22.2	1.22
240	82.4	21.2	1.26
300	89.8	23.6	1.21

[a] Reaction conditions: $[Di\alpha MeSt \cdot HCl]_0 = 0.002$ M, $[DTBP] = 0.006$ M, $[BCl_3] = 0.006$ M, $[pCl\alpha MeSt]_1 = 0.0521$ M, $[pCl\alpha MeSt]_2 = 0.334$ M; $M_n(100\%$ conversion$) = 2.55 \times 10^4$. Polymerization time for original sample: 30 min.
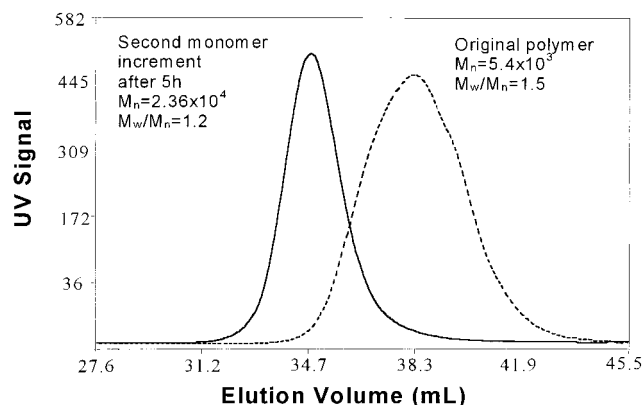
Figure 3. GPC chromatograms (UV traces) of the starting polymer and the final polymer obtained by adding the second portion of pClαMeSt after 5 h monomer starvation. Reaction conditions are given in Table 1.

Figure 4. ^{1}H NMR spectrum of poly(pClαMeSt) ($M_n = 2.55 \times 10^4$, $M_w/M_n = 1.23$).

Figure 5. DSC thermogram of poly(pClαMeSt) ($M_n = 2.4 \times 10^4$). The scanning rate is 10 °C/min.

Upon addition of the second monomer increment a smooth polymerization takes place, apparently with the same rate as the first increment. The molecular weight distributions of the products remain constant ($M_w/M_n = 1.2$), independent of the time of the second monomer addition. Interestingly, the polymer obtained by adding the second monomer increment even after 5 h exhibited a monomodal GPC chromatogram without any trace of dead polymer (see Figure 3). Thus, the chain end is very stable and much more stable than living PαMeSt, which starts to decompose after ~30–40 min under monomer-starved conditions; living PαMeSt has a half-life of ~3 h under identical conditions.[16] Since intramolecular backbiting (indanyl ring formation) is the most important side reaction in the polymerization of αMeSt, the exceptional stability of the PpClαMeSt living end suggests a very low rate of intramolecular alkylation. In the absence of steric hindrance the reactivity (stability) of the polymer cation and the reactivity of the aromatic ring determine the rate of intramolecular alkylation. Cumyl chloride hydrolyzes 5 times faster than *p*-chloro-substituted cumyl chloride,[17] which indicates the lower stability of the *p*-chloro-substituted cumyl cation. The higher reactivity of the PpClαMeSt$^+$ chain end, however, is most likely compensated by the lower equilibrium constant of ionization. This is suggested by a comparison of the overall polymerization rates (the polymerization αMeSt is about 3 times faster than that of pClαMeSt under identical conditions) and monomer reactivities (the reactivity of of αMeSt is estimated[18] to be about 3 times higher than that of pClαMeSt). In other words, the lower rate of pClαMeSt polymerization can be accounted for mainly by the lower monomer reactivity due to the *p*-chloro substituent. This leads us to conclude that the stability of the living PpClαMeSt is
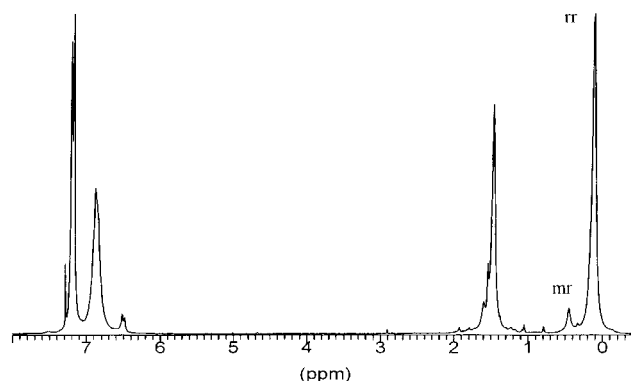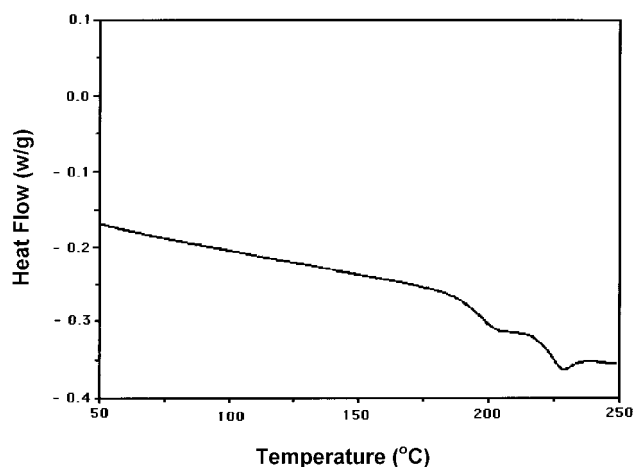
due to the much lower reactivity of the aromatic ring in intramolecular alkylation because of the *p*-chloro substituent. It is known that halogens deactivate the aromatic ring in Friedel–Crafts alkylation, but since they are ortho–para orienting, the deactivation of the meta position is much larger. For instance, the partial rate factors for nitration of chlorobenzene are 0.28 (para), 0.028 (ortho), and 0.001 (meta).[19] A large 65-fold difference in the alkylation rate of toluene and *p*-chloro-substituted toluene with allyldichlorosilane in the presence of AlCl$_3$ as catalyst[20] is also in line with our conclusion.

Tacticity and Thermal Behavior of PpClαMeSt. According to the ^{1}H NMR spectrum of homopoly-(pClαMeSt) (Figure 4), the polymer is 94% syndiotactic. Despite this high syndiotacticity, the DSC thermogram of the precipitated polymer does not show any melting point; i.e., the polymer is completely amorphous. After crystallization from methylcyclohexane–methyl ethyl ketone solvent mixture a distinct melting point shows up at 229 °C ($T_g = 198$ °C at 10 °C/min scanning rate) (Figure 5). Thermal gravimetric analysis revealed that above the melting point the polymer begins to decompose; therefore, the baseline drift after T_m in Figure 5 is attributed to this decomposition.

Sequential Block Copolymerization of pClαMeSt with IB. To determine the crossover efficiency from living PpClαMeSt to IB, poly(pClαMeSt-*b*-IB) diblock copolymer was prepared by sequential monomer addition (see Experimental Section). Since BCl$_3$ is unable to ionize the poly(pClαMeSt)-IB$_n$-Cl ends (where n is
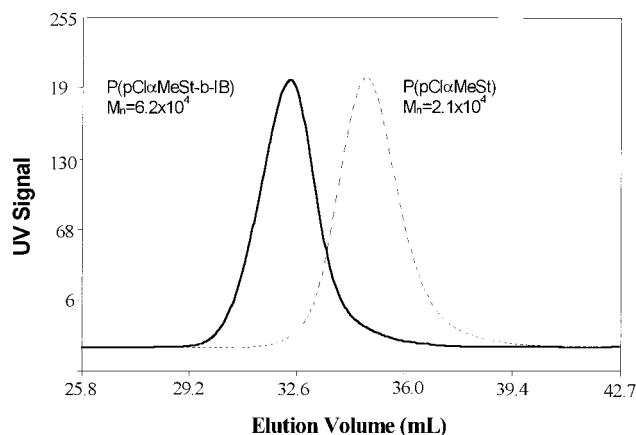
Figure 6. GPC chromatograms (UV traces) of the copolymer and the starting poly(pClαMeSt) Reaction conditions: [DiαMeSt·HCl]$_0$ = 0.002 M, [DTBP] = 0.006 M, [BCl$_3$] = 0.006 M, [pClαMeSt]$_0$ = 0.282 M, [TiCl$_4$] = 0.036 M, [IB]$_0$ = 1.54 M; M_n(poly(pClαMeSt)) = 2.1 × 10^4, M_n(poly{pClαMeSt−IB} diblock copolymer) = 6.2 × 10^4.

presumably 1)[16] that form upon addition of IB to the solution of living poly(pClαMeSt), addition of TiCl$_4$ is necessary to polymerize IB. Figure 6 shows the UV traces of the GPC chromatograms of the starting poly-(pClαMeSt) and the resulting poly(pClαMeSt-*b*-IB) diblock copolymer. The UV trace of the diblock copolymer smoothly moved to lower elution volumes (higher molecular weights) without any tailing, and the experimental M_n (= 6.2 × 10^4) is close to the theoretical M_n (= 6.4 × 10^4). On the basis of these observations, we conclude that the blocking efficiency is close to 100% and that there is no detectable homopolymer contamination. This is a major improvement over the ∼60% blocking efficiency obtained in the synthesis of poly-(αMeSt-*b*-IB) diblock copolymer under essentially identical conditions.[16] Since the low blocking efficiency was explained by intramolecular alkylation involving the poly(αMeSt)-IB$_1^+$ cation,[16] we attribute the essentially quantitative blocking observed in this work with poly-(pClαMeSt-*b*-IB) to the reduced tendency to form indanyl ring due to deactivation of the aromatic ring.

Conclusion

The living polymerization of pClαMeSt can be achieved using the 1,3-dimethyl-1,3-diphenyl-1-chlorobutane (DiαMeSt·HCl)/BCl$_3$ initiating system in methylcyclohexane/methyl chloride (60/40, v/v) at −80 °C. The highly stereoregular (94% syndiotactic) polymer is semicrystalline, exhibiting a T_g at 198 °C and T_m at 229 °C. Although the extent of crystallinity is presently unknown, it is most likely low considering the small entalpy of fusion (∼2 J/g). Therefore, the synthesis of

PIB block copolymers with a highly crystalline block segment involving a simple sequential monomer addition remains a challenge. The propagating chain end of poly(pClαMeSt) is exceptionally stable and in conjunction with TiCl$_4$ can efficiently initiate the sequential block copolymerization of IB. These attributes may be utilized for the efficient synthesis of triblock copolymers by coupling living diblock copolymers. This concept has recently been applied for the synthesis of a P(αMeSt-*b*-oligo(pClαMeSt)-*b*-IB-*b*-oligo(pClαMeSt)-*b*-αMeSt) thermoplastic elastomer reported elsewhere.[21]

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