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INITIATION VIA HALOBORATION IN LIVING CATIONIC POLYMERIZATION. 5. FACILE SYNTHESIS OF *SEC*-AMINE FUNCTIONAL POLYISOBUTYLENES

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INITIATION VIA HALOBORATION IN LIVING CATIONIC POLYMERIZATION. 5. FACILE SYNTHESIS OF *SEC*-AMINE FUNCTIONAL POLYISOBUTYLENES

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Key Words: PIB, Telechelic, Haloboration-Initiation, Dichloroborane, Azide, *Sec*-amine, NMR

ABSTRACT

The synthesis of *sec*-amine terminated telechelic polyisobutylene (PIB) has been accomplished by reacting *n*-butyl azide with the dichloroboron head group of PIB obtained by polymerization of isobutylene (IB) via haloboration-initiation. The facile, one-pot reaction resulted in complete conversion of the PIB dichloroboron head groups into butyl amino termini even at room temperature. The reaction is rapid and can be further accelerated by increasing the concentrations and/or the solvent polarity. The applicability of this head functionalization in the synthesis of asymmetric telechelic polymers is demonstrated through the synthesis of α-*sec*-amino-ω-*tert*-chloro and α-*sec*-amino-ω-methoxy-carbonyl PIB's. Telechelic α,ω-di-*sec*-amino PIB was also prepared by the combination of haloboration-initiation and living coupling reaction with 2,2-bis[4-(1-tolylethenyl)phenyl]-propane (BDTEP).

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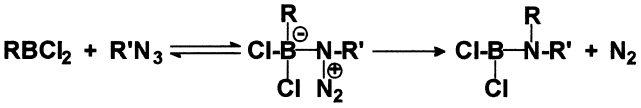
INTRODUCTION

End functional polymers are valuable intermediates for a variety of applications including chain extension and crosslinking reactions. They usually have low molecular weight and are, therefore, easily processable. The terminal functional groups can also be used to modify the properties of low molecular weight polymers, which can then be used as dispersants, for instance. Some of the most important functional groups are hydroxyl, carboxyl, and amine functionalities, which readily undergo several reactions involved in the applications of the telechelics or can initiate polymerization of a second monomer. In anionic polymerization, a number of techniques have been elaborated for the quantitative or nearly quantitative synthesis of polymers with such end groups, including the use of functional initiators [1] or chlorosilane terminating agents [2, 3] with protected groups. In cationic polymerization vinyl ethers and the more reactive styrene derivatives can be readily functionalized [4, 5], however, it is more difficult to obtain the previously mentioned functional groups, with less reactive monomers such as IB. The various methods that have been reported usually involve a number of steps and are rather cumbersome [6]. This is due to the fact that end quenching the living PIB chain end with nucleophiles usually results in a *tert*-chloro group. Functionalization by end quenching was recently accomplished via the application of non(homo)polymerizable monomers. We have recently reported the synthesis of functional PIBs by capping living PIB with 1,1-diphenylethylene followed by end quenching with a variety of nucleophiles, such as dry ammonia which has been shown to give quantitatively primary amine end group [7]. The drawback of this procedure is that it requires an intermediate capping reaction and it gives a somewhat sterically hindered amine.

In recent publications, direct initiation of the living polymerization of IB by BX_3 (X=Cl, Br) alone (in the absence of separately added cationogen) has been reported [8-10]. The polymerizations proceed in polar solvents in the presence of a proton trap to prevent initiation by protic impurities. The products are asymmetric telechelic PIB's with controlled molecular weight and relatively narrow molecular weight distribution, carrying X_2B- head groups and *tert*-halide tails. Synthetic applications of these valuable intermediates to obtain asymmetric telechelics of practical utility have also been demonstrated. One of the most important transformations of the head functionality is quantitative oxidation with H_2O_2 that yields primary hydroxyl group [9]. The facile synthesis of α-hydroxyl-ω-methoxycarbonyl as well as α-hydroxyl-ω-carboxyl telechelic PIB's has



Scheme 1. Reaction of alkyl dichloroboranes with alkyl azides.

also provided an important example for the versatility of haloboration-initiation for the preparation of asymmetric telechelic PIB's that are difficult to obtain by conventional methods [11, 12].

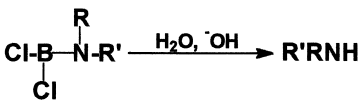
In addition to oxidation to obtain HO- functionality, other transformations of alkyl dichloroboranes are also known. One such transformation of practical importance is the conversion into a secondary amine. H. C. Brown and his coworkers reported that alkyl- and aryl dichloroboranes undergo a facile reaction with organic azides that yield secondary amines in excellent yields [13]. The mechanism of the reaction [14], shown in Scheme 1, has also been established.

The course of reaction can be monitored by measuring the evolved nitrogen. The amine is obtained upon subsequent hydrolysis (Scheme 2).

Since alkyl dichloroboranes rapidly hydrolyze, exposure to moisture must be avoided. The stability can be improved by using the dimethyl sulfide complex. This complex can similarly be subjected to the reaction with organic azides, although somewhat lower yields have been reported [15].

The synthetic value of this scheme for polymeric materials has been recognized. Shiono *et al.* synthesized *sec*-amine functional polypropylenes using a similar method in 1993 [16]. The vinylidene end groups of low molecular weight polypropylenes were converted to alkyl dichloroborane in several steps, including hydroboration and disproportionation with boron trichloride, followed by reaction with *n*-butyl azide. The reaction was carried out at high temperatures, and gave ~ 85% conversion as evidenced by ^{1}H and ^{13}C NMR.

In contrast to a route carried out through several intermediates in order to obtain an amine functional polymer, haloboration-initiation yields an alkyl dichloroborane. Thus, it provides a potential for the one-pot synthesis of the *sec*-amine functional polymers that can be prepared by haloboration-initiation, such



Scheme 2. Hydrolysis of the intermediate formed between an alkyl dichloroborane and an alkyl azide.

as PIB and polymers of styrene and its derivatives. The derivatization involves practically only two steps: polymerization and reaction with an organic azide.

EXPERIMENTAL

Materials

IB (Matheson) was dried by passing the gas through in-line gas purifier columns packed with BaO/Drierite and condensed in the cold bath of the glove box prior to polymerization. Methylene chloride (CH_2Cl_2) was extracted three times with 10 w% aqueous NaOH solution, then with deionized water until neutral, and dried over anhydrous sodium sulfate. The dried CH_2Cl_2 and xylene were refluxed for 24 hours on CaH_2 and freshly distilled under a nitrogen atmosphere. Di-*tert*-butyl pyridine (DTBP, Maybridge Chemical Co., Trevillet, U.K., 94%) was distilled from CaH_2. 1,1-Diphenylethylene (DPE, 99%), BCl_3 (99.9%), and titanium(IV) chloride ($TiCl_4$, 99.9%) were used as received from Aldrich. 1-Methoxy-1-trimethylsiloxy-2-methyl propene (MTSMP, United Chemical Technologies, Inc.) was also used as received. *n*-Butyl azide was synthesized according to the Reference [17]. The synthesis of BDTEP has been reported elsewhere [18].

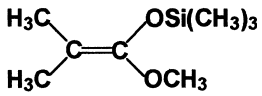
Polymerization

The polymerization of IB was carried out with BCl_3 at –40˚C in CH_2Cl_2 in the presence of DTBP [12] in an MBraun 150M stainless steel glove box (Innovative Technology, Inc.) equipped with a gas purification system (15 lb molecular sieves and 11 lb copper catalyst) which provides a dry nitrogen atmosphere (H_2O and O_2 less than 1 ppm).

Effect of Reaction Conditions on the Conversion of Alkyl Dichloroborane into Amine

After complete monomer conversion, the solvent and BCl_3 were removed under reduced pressure on a rotary evaporator. The polymer was dissolved in xylene or CH_2Cl_2, and *n*-butyl azide was added under a nitrogen atmosphere. The polymer was protected from moisture throughout this procedure in order to prevent hydrolysis of the dichloroboron head group. After the desired reaction time, the solution was quenched with ammoniacal methanol (10% aque-

ous ammonia in methanol). Finally, it was purified by repeated precipitation from hexane into methanol.



1-Methoxy-1-trimethylsiloxy-2-methyl propene (MTSMP)

α-*sec*-Amino-ω-*tert*-chloro Asymmetric Telechelic PIB

After polymerization of IB, the solvent and BCl_3 were removed under reduced pressure on a rotary evaporator at 0˚C. The polymer was dissolved in CH_2Cl_2, and then *n*-butyl azide was added. The solution was stirred at room temperature for 1 hour, after which it was cooled to 0˚C in an ice/water bath. Dry HCl gas was bubbled through the ice cold solution for 3 hours to rehydrochlorinate the olefinic chain ends. The solution was then poured into methanol containing 10% ammonium hydroxide. The product was purified by repeated precipitation from hexane into methanol.

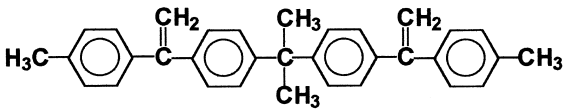
α-*sec*-Amino-ω-methoxycarbonyl Asymmetric Telechelic PIB

After polymerization of IB, the solvent and the BCl_3 were removed under reduced pressure on a rotary evaporator at 0˚C. The polymer was dissolved in CH_2Cl_2, followed by the addition of *n*-butyl azide. The solution was stirred at room temperature for 1 hour, and then cooled to 0˚C in an ice/water bath, and dry HCl gas was bubbled through it for 3 hours. Excess HCl was removed along with the solvent on a rotary evaporator under reduced pressure at 0˚C. The polymer was dissolved in a mixture of CH_2Cl_2 and Hex (60/40 v/v). The solution was cooled to –80˚C,and DTBP was added followed by the addition of $TiCl_4$ to ionize the *tert*-chloro chain ends. Capping was carried out by adding DPE ([DPE]/[chain end] ≈2.0). After 90 minutes, MTSMP was added and the reaction mixture was kept at –80˚C for 2 hours. After quenching with methanol containing 10% ammonium hydroxide, the product was dried and purified by repeated precipitation from hexane into methanol.

α,ω-Di-*sec*-Amino Symmetric Telechelic PIB

After polymerization of IB, the solvent and BCl_3 were removed under reduced pressure on a rotary evaporator at 0˚C. The polymer was dissolved in CH_2Cl_2, and *n*-butyl azide was added. The solution was stirred at room temper-

ature for 1 hour. After cooling the solution to 0˚C in an ice/water bath, dry HCl gas was bubbled through the ice cold solution for 3 hours. The excess HCl was removed along with the solvent on a rotary evaporator under reduced pressure at 0˚C. The polymer was dissolved in a mixture of CH_2Cl_2 and Hex (60/40 v/v). The solution was cooled to –80˚C, and DTBP was added followed by the addition of $TiCl_4$ to ionize the *tert*-chloro chain ends. Coupling was carried out by adding BDTEP ([BDTEP]/[chain end] ≈ 0.6). After 90 minutes at –80˚C, the reaction mixture was quenched with methanol containing 10% ammonium hydroxide. The product was dried and purified by repeated precipitation from hexane into methanol.



2,2-Bis[4-(1-tolylethenyl)phenyl]propane (BDTEP)

Characterization

Molecular weights were measured using a Vapor Pressure Osmometer calibrated with benzil in toluene. ^{1}H NMR spectra were recorded on Bruker 250 and 500 MHz instruments using deuterated chloroform (Aldrich, 99.8%, used as received). Functionalization was calculated by comparing the integrated peak areas corresponding to the head group with those of the end groups, and also with the main chain methylene peak.

RESULTS AND DISCUSSION

Investigation of the Transformation of Alkyl Dichloroboron Head Group into Amine Functionality

According to Scheme 1, first an adduct forms by the attack of the electron rich nitrogen of the azide on the electron deficient boron, followed by the migration of the alkyl group from the boron to the nitrogen with concomitant elimination of N_2. The reactivity increases in the order of trialkylborane<dialkyl chloroborane< alkyl dichloroborane, which is the order of increasing Lewis acidity (increasing electron deficiency, i.e. the driving force for the adduct formation). Boron trichloride is a much stronger Lewis acid than the organoborane

derivatives, thus the reaction between boron trichloride and alkyl azides is probably the fastest. When a PIB sample obtained via haloboration-initiation was subjected to the reaction with butyl azide under the same conditions without removal of BCl_3, amine formation was not detected. Haloboration-initiation is usually carried out at a relatively high concentration of the boron trihalide in order to obtain a reasonable polymerization rate. In CH_2Cl_2 at –40°C, the monomer conversion reaches ca. 95% in 2 hours at a BCl_3 concentration of 0.512 M. When the concentration is lowered to 0.103 M, complete polymerization of the monomer requires 14 hours. These concentrations are considerably higher than that of the polymer chains (~ $1.9x10^{-2}$ M). Thus, BCl_3 must be removed from the system before the addition of the azide. This can be accomplished by a simple distillation. To ensure the complete removal of BCl_3, the solvent is also distilled off and thus must be replenished. This process is, in fact, advantageous, since it aids in replacing the solvent or achieving higher concentrations for a more rapid reaction.

Although the reaction is usually carried out in a nonpolar solvent, such as benzene or xylene, at elevated temperatures in order to drive the reaction to completion, according to our observation, the reaction can be conveniently carried out even at ambient temperatures. The results obtained in xylene are summarized in Table 1. The functionality was determined using ^1H NMR spectroscopy by comparing the integrated peak areas corresponding to the amine head group and those of the chain ends (*tert*-chloride, exo and endo olefin). The error of this method is about 10%. The results indicate that nearly quantitative functionalization can be obtained even at room temperature with a relatively short reaction time.

The reaction was also carried out in a polar solvent, namely CH_2Cl_2. Since the reaction takes place through ionic intermediates, higher rates and generally higher conversions can be expected. The results obtained in CH_2Cl_2 are shown in Table 2. Higher rates are obtained in CH_2Cl_2 under otherwise identical conditions (compare the last entry of Table 1 and the first entry of Table 2), in accord with the expected effect of solvent polarity. CH_2Cl_2 is also preferred for this reaction from a practical point of view; since the polymerization is carried out in CH_2Cl_2, there is no need for a second solvent. The second order kinetics of the reaction accounts for the observed higher rates at increased concentrations. As the results indicate, the reaction is complete in less than 30 minutes with appropriately high reactant concentrations (see entries 6 and 7 in Table 2). Importantly, the concentrations can be further increased to obtain an even faster reaction.

TABLE 1. Results of the Reaction of Cl_2B-PIB with *n*-Butyl Azide in Xylene

#	Temperature	[PIB] $Mx10^2$	[nBuN$_3$] $Mx10^2$	% Amine
1	Reflux[a]	3.8	15.8	89
2	110 °C[a]	"	"	100
3	RT[b]	"	"	89
4	110 °C[a]	"	128	97
5	RT[c]	1.6	6.3	16

[a]The solution was briefly brought to the temperature indicated.
[b]The solution was stirred for 1 hour.
[c]The solution was stirred for 30 min.

The presence and relative amount of the amine on the chain ends are evidenced by the ^{1}H NMR spectrum of the product (Figure 1). Two new peaks appear in the spectrum upon reaction with butyl azide. The triplet at 2.58 ppm (*a*) corresponds to the methylene protons adjacent to the nitrogen in the *n*-butyl group. The peak is split by the two adjacent methylene protons, and is not coupled with the proton on the nitrogen. On the other hand, the peak at 2.37 ppm (*b*) is a singlet, since the methylene protons that it represents are located in the PIB next to the nitrogen, which are not coupled because the adjacent carbon is a tertiary carbon with no protons. However, in an acidic medium the nitrogen becomes protonated. Characteristically to a salt of secondary amines, the protons on the carbons adjacent to the nitrogen exhibit a downfield shift due to a more electron-deficient environment. In addition, peak broadening of the methylene protons is observed due to the effect of the local medium or a different rate of exchange of the NH_2 protons.

TABLE 2. Results of the Reaction of Cl_2B-PIB with *n*-Butyl Azide in CH_2Cl_2 at Room Temperature

#	Reaction time, h	[PIB] $Mx10^2$	[*n*BuN$_3$] $Mx10^2$	M_n	% Amine[a]	% Amine[b]
1	0.5	1.6	6.3	3900	80	62
2	1	"	"	-	-	101
3	3	"	"	-	-	102
4	0.5	"	12.6	3700	104	103
5	1	"	"	-	-	101
6	0.25	3.1	12.6	4000	104	95
7	0.5	"	"	-	-	110
8	1	"	"	-	-	91
9	2	"	"	-	-	110

[a]Calculated by comparing the integrations of peaks *a* and *c* according to Figure 2 using the molecular weight.
[b]Calculated by comparing the integrations of peaks *a* and *e*.

Synthesis of α-*sec*-Amino-ω-*tert*-chloro Asymmetric Telechelic PIB

PIB obtained by living cationic polymerization of IB ususally carries a *tert*-chloro end group. This can then be used for the synthesis of various functional groups by organic transformation reactions directly or via the exo olefinic end that is obtained by dehydrochlorination. The endo double bond, the product of an uncontrolled elimination, is undesirable due to its low reactivity. The elimination of HCl from the chain end of *tert*-chlorine terminated PIB's is catalyzed

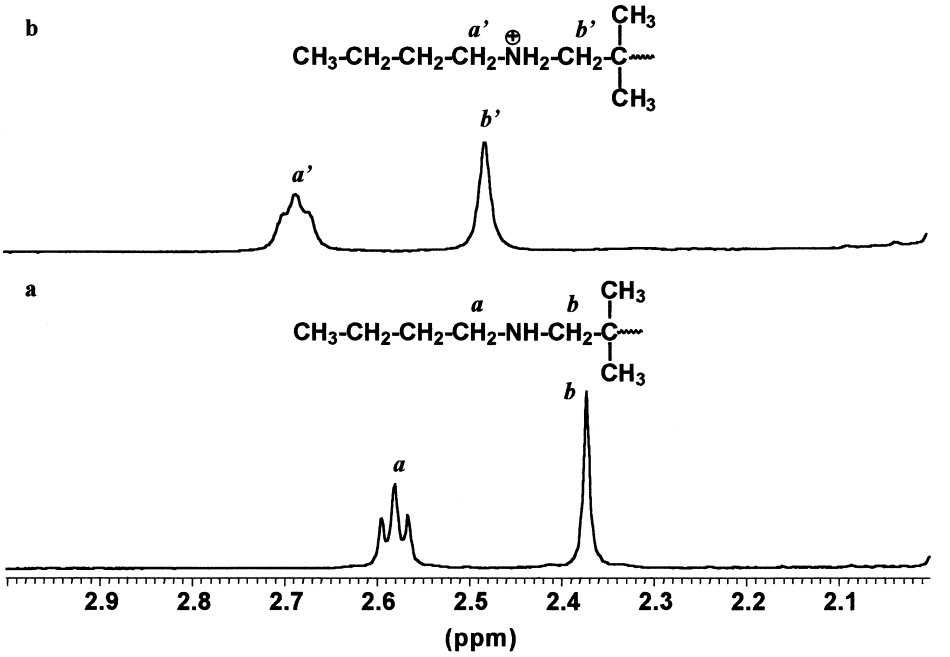


Figure 1. 500 MHz ^{1}H NMR spectra of *n*-butyl amine terminated PIB showing the peaks corresponding to protons on the carbons adjacent to the amino nitrogen in *a*. the free amine, and *b*. the protonated amine.

by acids. Usually, the rapid reaction of the Lewis acids with methanol (or water) upon quenching efficiently suppresses elimination and allows the clean synthesis of *tert*-chloro functional PIB's. Such reaction, however, should be avoided before reacting the head group with an azide due to the similarly high reactivity of alkyl dichloroboranes toward methanolysis (or hydrolysis) that would destroy the reacting site. Therefore, BCl_3 should be removed without quenching under anhydrous conditions. During this process, the polymer solution becomes more concentrated in the Lewis acid, which catalyzes the elimination at room temperature. As a result, 30-40% elimination was observed when BCl_3 was distilled off along with the solvent at room temperature (entry 1, Table 3). The rate of elimination can be reduced at lower temperatures. Removal of the Lewis acid at 0˚C to–10˚C reduces the degree of elimination to 7-8% (entries 2 and 3). When the removal of BCl_3 was attempted at –40˚C (entry 4), elimination was not observed, however the reaction between the dichloroborane head group and the azide did not take place even when longer reaction times were used. This indicates that the removal of the Lewis acid at –40˚C was not complete under the conditions

TABLE 3. End Functionalities of α-Amino-ω-chloro PIB's Prepared under Different Conditions

#	Conditions (after the polymerization of IB)	% -Cl	% -NH-
1	Solvent and BCl_3 evaporated at RT. Polymer dissolved in CH_2Cl_2 and stirred for 1 hr at RT after the addition of BuN_3.	66	104
2	Solvent and BCl_3 evaporated at 0°C. Polymer dissolved in CH_2Cl_2 and stirred for 0.5 hrs at RT after the addition of BuN_3.	92	50
3	Solvent and BCl_3 evaporated at 0°C. Polymer dissolved in CH_2Cl_2 and stirred for 5 hrs at 0°C after the addition of BuN_3.	93	108
4	BCl_3 evaporated at –40°C (?). Solution allowed to warm to RT. BuN_3 added and solution stirred for 2 hrs at RT.	100	0
5	Solvent and BCl_3 evaporated at RT. Polymer dissolved in CH_2Cl_2 and HCl bubbled through it for 3 hrs at 0°C. Excess HCl evaporated at 0°C. Solution stirred for 0.5 hr after the addition of BuN_3.	100	0
6	Solvent and BCl_3 evaporated at RT. Polymer dissolved in CH_2Cl_2 and BuN_3 added. HCl bubbled through it for 3 hrs at 0°C.	100	52
7	Solvent and BCl_3 evaporated at 0°C. Polymer dissolved in CH_2Cl_2 and BuN_3 added. Stirred at RT for 1 hr. HCl bubbled through it for 3 hrs at 0°C.	100	100

used. The fact that the elimination mainly occurs during the concentration of the polymer solution is further evidenced by a similar degree of elimination when the diluted solution was stirred at 0˚C (entry 3) or at room temperature (entry 2) for a relatively long period of time after the removal of BCl_3 (no further elimination was observed).

When the removal was carried out at reduced temperatures (0 to –10˚C) the rate of reaction with the azide was lower than when higher temperatures were used. Only 50% of the chains carried an amine head group after 30 minutes (entry 2), which would otherwise be a sufficiently long time for the completion of the reaction. This is probably due to an incomplete removal of the BCl_3; thus, the concentration of the active butyl azide is lower than calculated, which in turn results in a lower reaction rate.

Since the elimination of HCl from the ω chain end seems to be difficult to avoid without using very high vacuum, rehydrochlorination following the removal of BCl_3 is inevitable for a successful synthesis of the α-*sec*-amino-ω-*tert*-chloro PIB. The reaction sequence proved to be important. Amine functionality was not observed when the reaction with the azide was carried out after rehydrochlorination (entry 5), probably due to remaining HCl dissolved in the medium. When the reaction with the azide was carried out simultaneously with the rehydrochlorination,the yield was 52% (entry 6). This presumably took place during the early stages of the rehydrochlorination, when negligible amount of HCl was present in the solution. Apparently, the presence of HCl can not be permitted during the reaction of the dichloroborane with the azide. Thus, we carried out this reaction first, and then the rehydrochlorination as a separate step. This reaction sequence proved to be successful, giving nearly complete functionalization both on the head group and the end group (entry 7). The presence of acids after the formation of the reaction intermediate between the dichloroborane and the azide did not result in a reduced yield of the amine. This may be attributed to the stability of the intermediate (Scheme 1).

The ^{1}H NMR spectrum of the product is shown in Figure 2. The absence of the characteristic peaks at 4.58, 4.78 (exo double bond), and 5.09 ppm (endo double bond) indicates 100% *tert*-chloro end functionality. The peak integrations for the amine and the chloride termini are also in excellent agreement.

Synthesis of α-*sec*-Amino-ω-methoxycarbonyl Asymmetric Telechelic PIB

It has been demonstrated that the boron containing head group obtained by haloboration-initiation is a useful precursor for the synthesis of various head

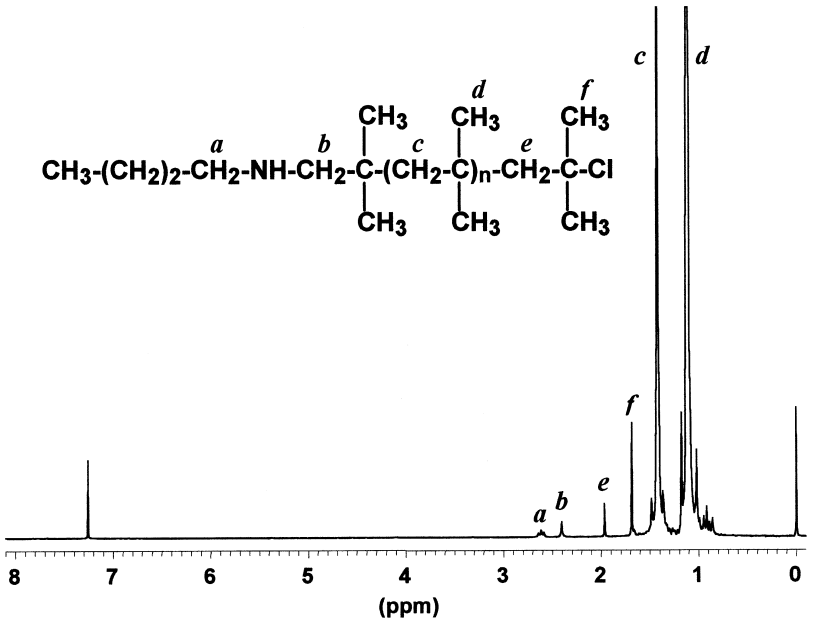
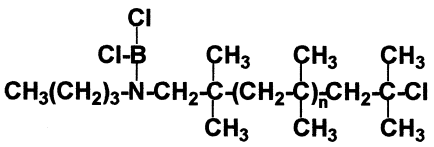


Figure 2. 250 MHz ^{1}H NMR spectrum of α-*sec*-amino-ω-*tert*-chloro asymmetric telechelic PIB.

functionalized polymers and allows independent end functionalization. We have recently accomplished the capping of living PIB chain end, obtained by direct initiation using BCl_3, with DPE. Using this technique we have already reported the synthesis of α-hydroxyl-ω-methoxycarbonyl and α-hydroxyl-ω-carboxyl PIB's [12]. Since end quenching with silyl ketene acetals does not influence the dichloroboron head group, it occured to us that its transformation into a *sec*-amine could also be carried out. However, the capping reaction requires a relatively high $TiCl_4$ concentration. This Lewis acid should also be removed before the addition of the azide. Our attempts to remove the high boiling $TiCl_4$ without affecting the dichloroborane head group remained unsuccessful. Extended evacuation (overnight) even at elevated temperatures (60°C) did not completely remove $TiCl_4$. Tetrabutyl ammonium salts, such as tetrabutyl ammonium chloride, have been used in similar systems to deactivate $TiCl_4$ [19]. Unfortunately, a similar attempt failed in this case probably due to the formation of a complex with the alkyl dichloroborane head group.

We finally succeeded in the synthesis of α-*sec*-amino-ω-*tert*-chloro PIB by using a different reaction sequence. After the polymerization of IB, BCl_3 was removed and the dichloroboron head group was reacted with butyl azide. It has been shown for the synthesis of α-*sec*-amino-ω-*tert*-chloro PIB that significant

HCl elimination takes place during elimination of BCl_3. Consequently, the polymer chain ends must be rehydrochlorinated before capping with DPE. Thus, first an intermediate for α-*sec*-amino-ω-*tert*-chloro PIB was prepared. The excess HCl was removed under vacuum. After transferring the PIB back to the glove box and dissolving it in a CH_2Cl_2/Hex (60/40) solvent mixture, capping was carried out, followed by functionalization with MTSMP. The ^{1}H NMR spectrum of the product is shown in Figure 3. According to the integration of the peak areas, nearly quantitative head and end group functionalization has been achieved.



Intermediate formed between PIB dichloroboranе and butyl azide

Synthesis of α,ω-di-*sec*-Amino Symmetric Telechelic PIB

The convenient transformation of the dichloroboron head group into *sec*-amine also allows the synthesis of symmetric telechelic polymers, by coupling

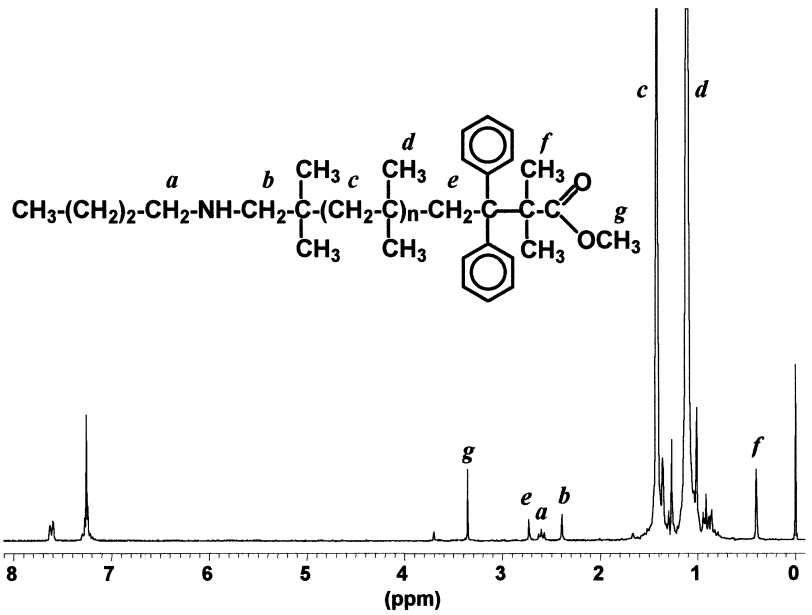


Figure 3. 250 MHz ^{1}H NMR spectrum of α-*sec*-amino-ω-methoxycarbonyl asymmetric telechelic PIB.

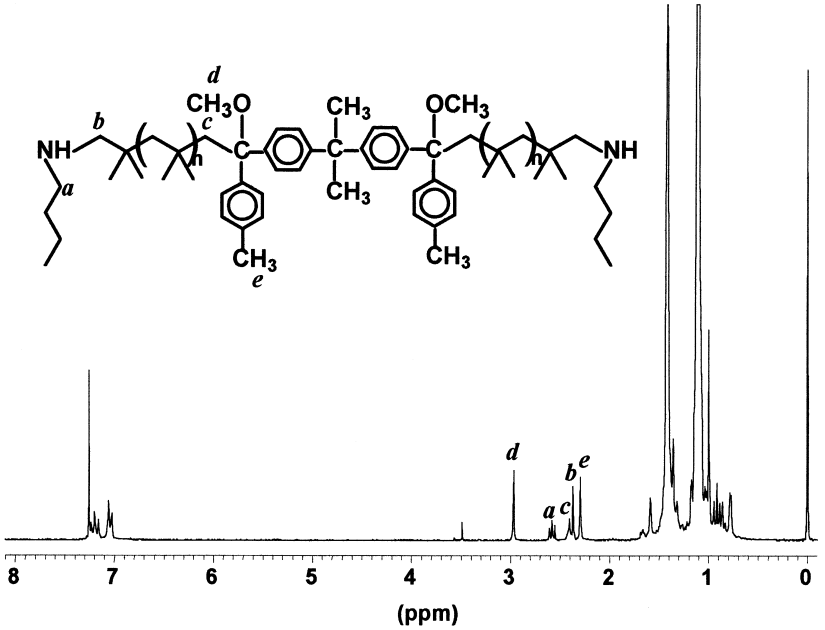


Figure 4. 250 MHz ^{1}H NMR spectrum of α,ω-di-*n*-butyl amino symmetric telechelic PIB.

of the living chain ends with bis-diphenylethylene derivatives [18]. These coupling agents require the presence of $TiCl_4$. Due to the difficulties of removing the $TiCl_4$ before the reaction with the azide, a reaction sequence similar to that applied for the capping was used. This procedure proved to be successful. Monoaddition was undetected and the head groups underwent quantitative transformation into *sec*-amine. The ^{1}H NMR spectrum of the product is shown in Figure 4. Molecular weight measurements carried out using VPO also support the observed nearly quantitative coupling. The M_n of the original PIB before coupling was 3800, that of the coupled product was found to be 7600.

CONCLUSION

A nearly quantitative one-pot synthesis of *sec*-amine functional asymmetric telechelic PIB has been elaborated. This facile method consists of two steps: living polymerization by haloboration-initiation and a rapid reaction with an organic azide under mild conditions after the removal of the Lewis acid. A similar synthetic strategy can be used to obtain amine terminated symmetric or

other asymmetric telechelic PIB's. Furthermore, the synthetic scheme may be used to obtain other *sec*-amine functional polymers, such as polystyrene and poly(α-methyl styrene) [9, 20, 21] that can be synthesized via haloboration-initiation. An advantage of the technique is that it involves only the head group leaving the possibility open for independent chain end functionalization.

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