Polymer Bulletin 43, 121–128 (1999)

Polymer Bulletin

Coupling and linking reactions of living polyisobutylene by allylsilanes

Savvas Hadjikyriacou, Rudolf Faust

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

Received: 16 May 1999/Revised version: 1 September 1999/Accepted: 1 September 1999

Abstract

The reactions of living polyisobutylene (PIB^+) with different allylsilanes, as potential linking and coupling agents, have been studied. Quantitative monoaddition of 2-Phenylallyltrimethylsilane to living PIB^+ yielded macromonomer (I), however coupling was absent. Rapid and quantitative coupling has been observed with 1,3-*bis*[2-(3-trimethylsilyl)-propenyl]benzene (bTPB). Using 1-(2-propenyl)-3-[2-(3-trimethylsilyl)-propenyl]benzene (PTPB) star polymers with an average of four arms have been prepared with high efficiency. The study of this linking reaction revealed that star formation takes place in two well separated steps. In the first step a macromonomer is formed *in situ* by the rapid reaction of PIB^+ with the allyltrimethylsilyl functionality. Subsequent reaction of this macromonomer with the remaining electrophilic PIB^+ ends followed by interchain reactions results in the formation of star polymers.

Introduction

Coupling and linking reactions of living ionic polymers are important in the preparation of telechelic polymers and linear or star block copolymers. While coupling using simple, efficient and readily available coupling agents is routinely practiced in living anionic polymerization, effective coupling agents have not been reported for living cationic polymers until recently. We have reported on a facile and quantitative process for the synthesis of telechelic PIBs by coupling of ω-isopropenyl functional PIB with catalytic amounts of triflic acid in hexanes at -80 °C (1). We have also disclosed a more general approach based on methodologies of using non-(homo)polymerizable monomers in living cationic polymerization, the living coupling reaction of living cationic polymers. We have achieved rapid and quantitative coupling of both low (M_n~1,000) and high (M_n~50,000) molecular weight living PIB using *bis*-diphenylethylene (*bis*-DPE) compounds such as 2,2-*bis*[4-(1-phenylethenyl)phenyl]propane (BDPEP), where two DPE moieties are separated by a spacer group (2,3). Kinetic studies revealed that the coupling reaction of living PIB by BDPEP is a consecutive reaction where the second addition is much faster than the first one. As a result, high coupling efficiency was also observed with excess BDPEP. Very recently we extended this concept to *bis*-furanyl derivatives and accomplished rapid and quantitative coupling of living PIB by 2,5-*bis*[1-(2-furanyl)-1-

methylethyl]-furan in hexanes/CH_3Cl (60/40 or 40/60, v/v) solvent mixtures at -80 °C in conjunction with $TiCl_4$, as well as in CH_3Cl at -40 °C with BCl_3 as Lewis acid (4).

In addition to the above publications in US 5,665,837 we disclosed coupling of living cationic polymers by unsaturated organosilicon compounds such as *bis*-(trimethylsilyl)ethylene or *bis*-(trimethylsilyl)cyclopentadiene. The use of these coupling agent was a rational extension of the finding that allyl functional PIB can be prepared by the quantitative reaction of living PIB with allyltrimethylsilane (5,6). However the coupling efficiency was lower than 100 %. Subsequently Storey and Maggio reported on a similar approach, coupling of living PIB with 1,1-*bis*(trimethylsilylmethyl)ethylene (7). This coupling reaction was also not quantitative, as the M_n increased only by ~70 %.
We have continued our search for an efficient coupling agent, and in this publication we report on successful developments of allylsilane based coupling and linking agents.

Experimental

1-(2-propenyl)-3-[2-(3-trimethylsilyl)-propenyl]benzene, (PTPB): In a 500 mL round bottom reaction flask a solution of 14.9 g (132 mmoles) of potassium tert.-butoxide dissolved in 150 mL of dried ethyl ether was cooled to -78 °C. Under stirring 53 mL of BuLi (2.5M in hexanes, 132 mmoles), cooled to -78 °C, was added. Precaution was taken to prevent the temperature to rise above -75 °C during addition. After the addition of BuLi, 11.0 mL of 1,3-diisopropenylbenzene (64 mmoles) was added dropwise while the temperature was maintained at -78 °C. The reaction was allowed to proceed for another 2 h and under N_2 the mixture was transferred to another flask containing a solution of 17.0 mL of chlorotrimethylsilane (134 mmoles) in 100 mL dried and distilled Et_2O, stirred at -78 °C. The reaction mixture was stirred for an additional 20 minutes and then was allowed to warm up to room temperature. It was poured into 500 mL of distilled water and the product was recovered by extractions with 2x100 mL hexanes. The organic phases were combined and washed with 2x200 mL distilled water and then with 300 mL saturated aqueous NaCl solution. It was left over anhydrous Na_2SO_4 overnight and the next day the solvent was evaporated on the rotavap. The crude product was purified by fractional distillation (yield = 30%). ^1H NMR spectrum: 0ppm (9H, s), 2.10ppm (2H, s), 2.20ppm (3H, s), 4.95ppm (1H, s), 5.15ppm (1H, s), 5.23ppm (1H, s), 5.45ppm (1H, s), 7.40ppm (3H, m), 7.60ppm (1H, s).

2-Phenylallyltrimethylsilane was synthesized in a process similar to that of PTPB by lithiating α-methylstyrene in tetrahydrofuran (THF). ^1H NMR spectrum: Oppm (9H, s), 2.1ppm (2H, s), 4.95ppm (1H, s), 5.25ppm (1H, s), 7.35ppm (3H, m), 7.60ppm (2H, m)

1,3-bis[2-(3-trimethylsilyl)-propenyl]benzene (bTPB): Into a 1L round bottom reaction flask equipped with an Ar inlet, an overhead stirrer, and a feeding funnel, $KOC(CH_3)_3$ (14.9 g, 0.133 moles) was suspended in 200 mL dried hexanes. The suspension was cooled to -78 °C in a dry ice-isopropanol mixture. Under stirring 55 mL, (0.133 moles) of nBuLi 2.5M in hexanes was added. The mixture was stirred for 15 minutes and then 21.1 mL (0.14 moles) of N,N,N',N'-tetramethylethylene diamine (TMEDA) was added dropwise. After the dropwise addition of 1,3-diisopropenylbenzene 11.0 mL, (0.063 moles) via a syringe, the reaction was allowed to proceed for 5 hours. During this time a deep red color developed. The reaction mixture was diluted with 100 mL precooled (-78

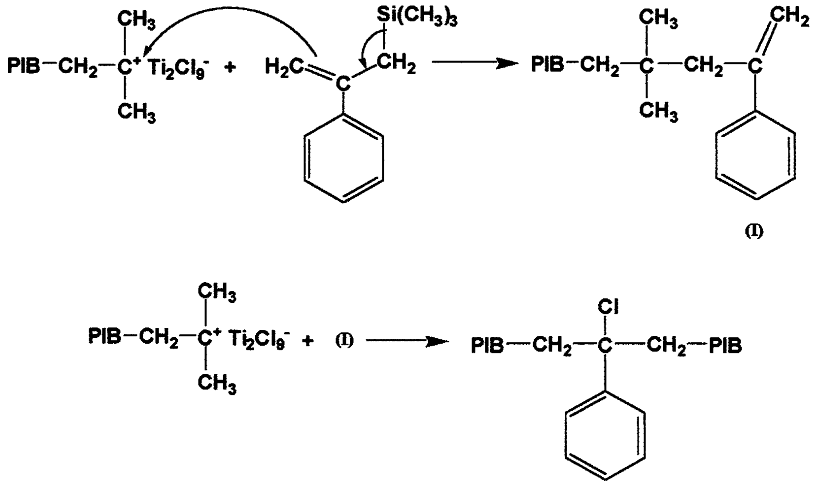
°C) THF. 17.0 mL of $(CH_3)_3SiCl$, (0.133 moles) dissolved in 100 mL THF was added dropwise and reacted at -78 °C for 10 minutes. The cooling bath was removed and the reaction mixture was allowed to warm up to room temperature. It was poured into 200 mL of distilled water and the aqueous phase was separated from the organic phase. The aqueous phase was washed twice with 100 mL hexanes. The organic phases were combined and washed 4 times with 200 mL distilled water and twice with 200 mL saturated aqueous NaCl solution to remove traces of TMEDA. The organic phase was left over anhydrous Na_2SO_4 overnight and the solvent was evaporated on the rotavap. The crude product was purified by fractional distillation. The overall yield was 20%. ^1H NMR spectrum: -0.03ppm (18H, s), 2.08ppm (4H, s), 4.90ppm (2H, s), 5.15ppm (2H, s), 7.30ppm (3H, m), 7.50ppm (1H, s).

Polymerization procedures, sources, purification and characterization of all other materials have already been described (8). To facilitate identification of the end groups by ^1H NMR spectroscopy, isobutylene (IB) was polymerized to yield low molecular weight PIB (Mn~2500). Coupling or linking was effected by introducing the corresponding agent in a solution using the solvent employed for the polymerization. At predetermined times, samples were quenched with methanol. Details are provided in the legends of the Figures.

Results and Discussion

Coupling reactions

In the first set of experiments α-trimethylsilylmethyl-styrene was tested as a potential coupling agent. The coupling reaction was envisioned to take place according to Scheme 1.



Scheme 1: The envisioned coupling reaction of living PIB with 2–Phenylallyltrimethylsilane

Using the 2-Phenylallyltrimethylsilane/chain end ratio of 0.5, a macromonomer would be generated in situ in the first step, that subsequently reacts with the remaining living PIB^+ chain ends to yield the coupled product. Addition of 2-Phenylallyltrimethylsilane to living PIB and the quantitative formation of macromonomer (I) was indeed observed within 5 minutes. However even after 2h in hexanes/CH_3Cl 60/40 (v/v) at -80 °C, coupling was only 15 % as determined by ^1H NMR spectroscopy. By increasing the solvent polarity of the reaction mixture to hexanes/CH_3Cl 40/60 (v/v), the coupling efficiency increased only moderately to 33 % in 6h. Apparently the reactivity of the macromonomer is very low in the envisioned coupling reaction, possibly due to steric hindrance. Although 2-Phenytallyltrimethylsilane failed as a coupling agent we have recognized its importance for the facile synthesis of a PIB macromonomer. Using a 2-Phenylallyltrimethylsilane/chain end ratio of 2.8 we have succeeded in the quantitative functionalization of living PIB obtained with TMPCl as well as 5-tert.-butyl-1,3-dicumyl chloride (tBu-DiCumCl). The ^1H NMR spectrum of the corresponding α,ω-telechelic macromonomer, is shown in Figure 1.

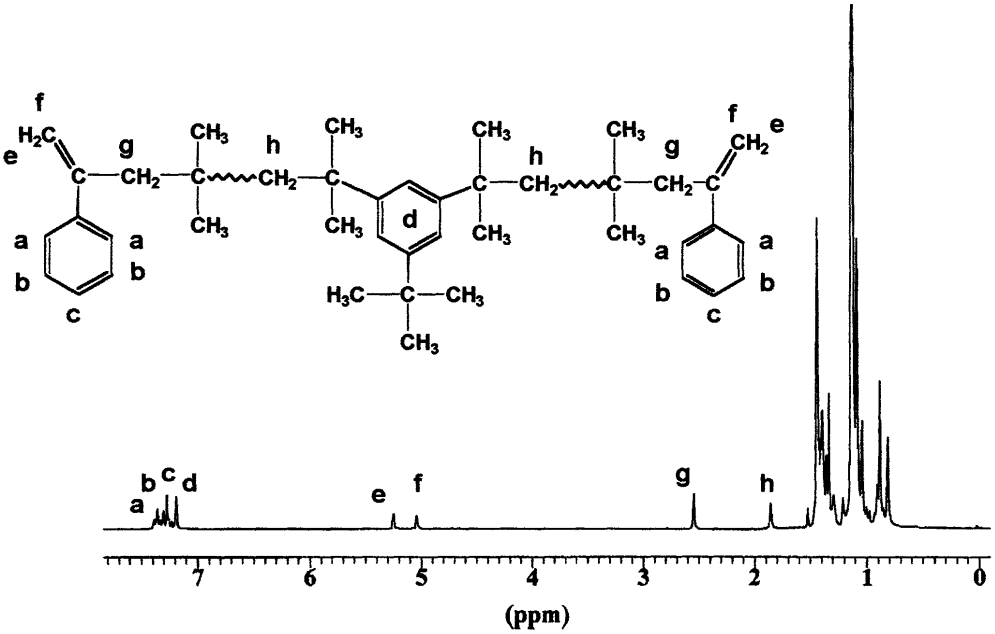


Figure 1: The ^1H NMR spectrum of the telechelic macromonomer. Reaction conditions: [tBu-DiCumCl]=$1x10^{-2}$ M, [DTBP]=$3x10^{-3}$ M, [$TiCl_4$]=$6x10^{-2}$ M, [IB]=0.36 M, [2–Phenylallyltrimethylsilane]=$2.2x10^{-2}$ M, Solvent: hexanes/CH_3Cl 60/40 (v/v), T=-80 °C.

The low coupling efficiency in the above described experiments incited us to test di-allyltrimethylsilyl-derivatives such as 1,3-bis[2-(3-trimethylsilyl)-propenyl]benzene, (bTPB) as coupling agents. With bTPB rapid and quantitative coupling of living PIB was achieved as determined by ^1H NMR spectroscopy (Figure 2) and GPC Chromatography (Figure 3). According to GPC the product exhibited doubled M_n. The absence of unreacted PIB-Cl and monoadded product is indicated by the smooth shift of the RI traces to higher molecular weight without tailing as well as by the absence of the corresponding resonances in the ^1H NMR spectrum.

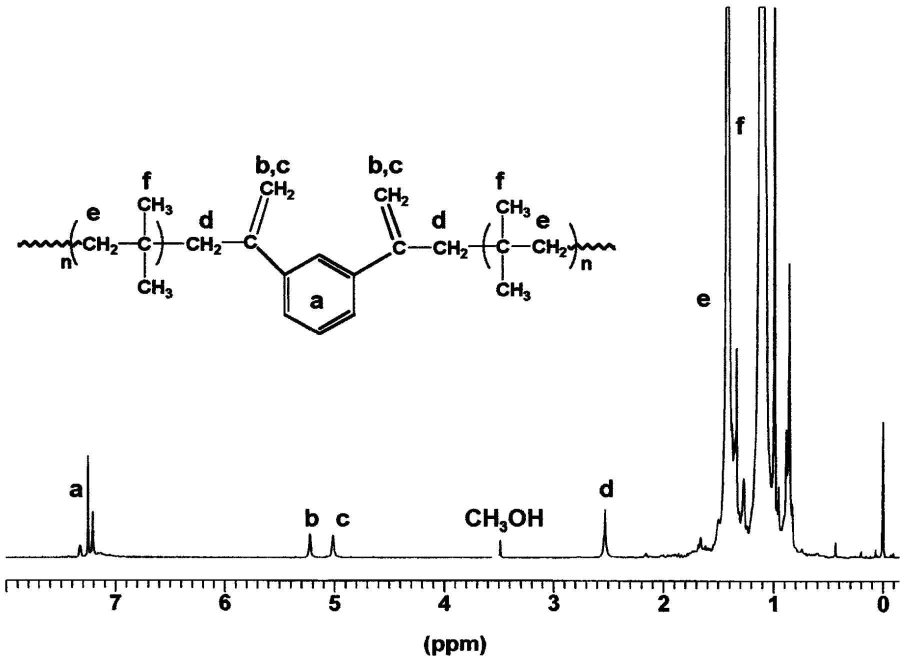


Figure 2: The ^{1}H NMR spectrum of the coupled PIB. Reaction conditions: [TMPCl]=2×10^{-2} M, [DTBP]=3×10^{-3} M, [$TiCl_4$]=8×10^{-2} M, [IB]=0.71 M, [bTPB]=1.05×10^{-2} M,

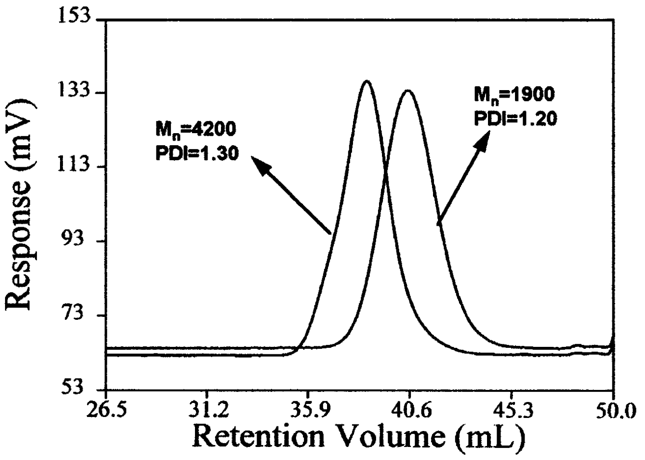


Figure 3: Overlaid chromatograms of starting and coupled PIBs.

Coupling of living PIB with bTPB was also attempted in conjunction with BCl_3 in CH_3Cl at -40 °C. However coupling was absent even after 6h. This finding is in line with earlier reports that allyl functional PIB cannot be prepared by the reaction of PIB-Cl with allyltrimethylsilane in conjunction with BCl_3 (9).

Linking reactions

The above results that i) macromonomer (I) was found to possess low reactivity toward living PIB and that ii) bTPB induced quantitative and rapid coupling of living PIB, inspired us to design a novel and efficient linking agent for the synthesis of star-branched

PIBs by the arm first - core last method. Similarly to its use in anionic polymerization, divinylbenzene have already been shown to be an efficient linking agent, however linking is relatively slow (10). 1,3 and 1,4-diisopropenylbenzene are more reactive than divinylbenzene, however they are reportedly ineffective for the synthesis of multiarm star PIBs (11, 12). This was confirmed by us in experiments where we attempted to employ 1,3-diisopropenylbenzene in linking reactions. The efficiency of star polymer formation however was very low and the majority of the PIB-Cl chains ends remained unreacted as indicated by ^{1}H NMR spectroscopy. This may be ascribed to the low overall addition rate of 1,3-disopropenylbenzene to PIB-Cl ends compared to the very high homopolymerization rate of 1,3-disopropenylbenzene. This problem may be circumvented by utilizing 1-(2-propenyl)-3-[2-(3-trimethylsilyl)-propenyl]benzene, (PTPB), a molecule with dual (i.e., allyltrimethylsilyl and a vinylic) functionality. Since the allyltrimethylsilyl functionality is about 1000 times more reactive than the vinylic functionality, it was expected that the allylsilyl functionality will react rapidly with the electrophilic PIB$^+$ chain ends and form macromonomers in situ that are not sterically hindered as opposed to (I). The GPC RI traces of the starting PIB and the products after various linking reaction times are shown in Figure 4. Upon linking the M_n has quadrupled, corresponding to an average number of four chains linked together to form a four arm star polymer within 2h. The star polymer architecture was also suggested by ^{1}H NMR spectroscopy. The formation of a rigid core is indicated by the broadening of the signals from the linking agent, that were almost indiscernible in the spectrum.

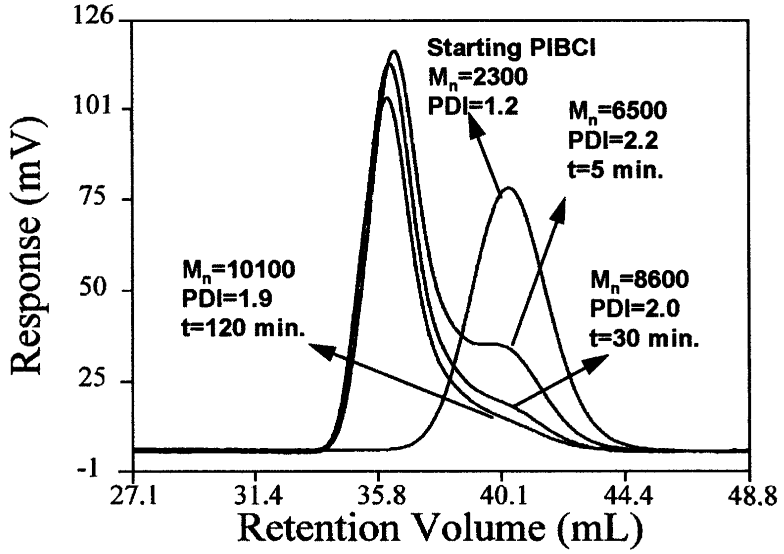


Figure 4: The overlaid GPC-RI traces of the starting and linked PIBs. Reaction conditions: [TMPCl]=2x10^{-2} M, [DTBP]=3x10^{-3} M, [TiCl$_4$]=8x10^{-2} M, [IB]=0.71 M, [PTPB]=1.05x10^{-2} M, solvent hexanes/CH$_3$Cl, T=-80 °C.

Characteristic resonance signals of the chloro-terminated PIB, ($\sim CH_2C(CH_3)_2C\mathit{H}_2C(C\mathit{H}_3)_2Cl$) i.e., the methylene and methyl protons next to the chloro group at 1.96 and 1.67 ppm were absent in the ^{1}H NMR spectrum. Deconvolution of the GPC Chromatogram of the product obtained after 2h reaction time however demonstrated that 7.5% of the PIB ends were not linked. This is probably due chains capped by the linking agent which did not participate in the linking reactions. This is also suggested by the observation that introducing additional linking agent after 2h failed to increase the linking efficiency.

The effect of the concentration of the linking agent on the M_n was investigated by varying the linking agent/PIB chain end ratio under identical conditions. The results are plotted in Figure 5.

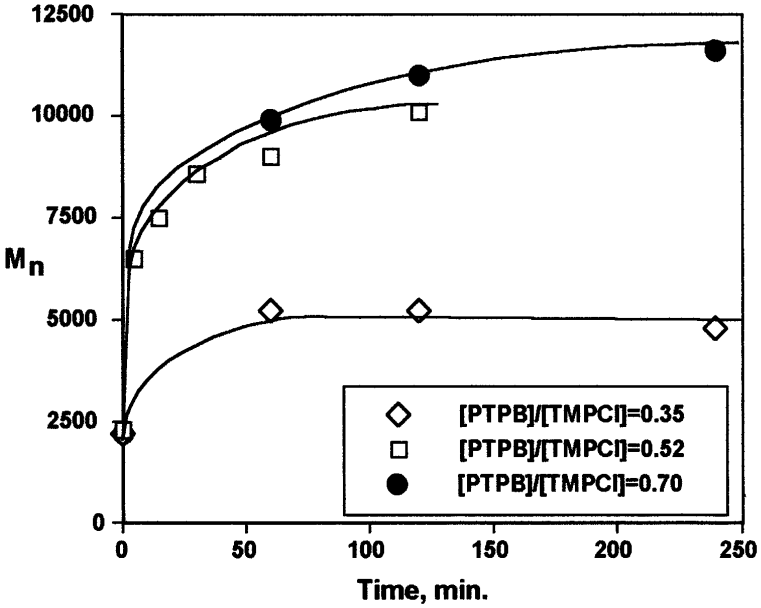


Figure 5: M_n vs. time plots for linking reactions with various [PTPB]/[TMPCl] ratios.

Whith [PTPB]/[TMPCl] = 0.35 the M_n maximum was only about 5,000 and according to ^{1}H NMR spectroscopy 36% of the PIB-Cl chain ends remained unreacted. With [PTPB]/[TMPCl] = 0.52 and 0.70, similar maximum M_ns (~10,000) were obtained, indicating an average of four arms.

The kinetics and mechanism of linking was also investigated by lowering [TMPCl] and [$TiCl_4$], in order to take samples at the early stages of the reaction. The samples were quenched and subsequently analyzed by ^{1}H NMR spectroscopy and GPC. The results indicated that linking takes place in two fairly well separated steps. In the first step PIB^+ reacts with the allyltrimethylsilyl functionality as ~90% of the allyltrimethylsilyl functionality has disappeared after 3 minutes. From the GPC chromatogram shown in Figure 6, at this stage linking is negligible. A bimodal molecular weight distribution is clearly visible after 6 minutes and with increasing reaction time the high M_n peak increases at the expense of the low M_n peak. After 120 minutes a star polymer with an average of four arms is formed and only a small amount of unreacted PIB arm remains unreacted.

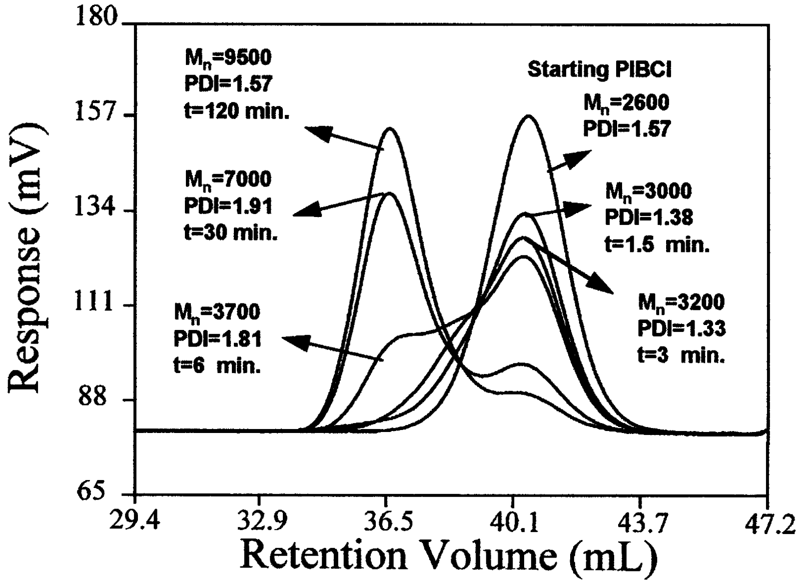


Figure 6: Synthesis of star polymers. Reaction conditions: [TMPCl]=4x10^{-3} M, [DTBP]=3x10^{-3} M, [TiCl$_4$]=3.6x10^{-2} M, [IB]=1.48x10^{-1} M, [PTPB]=2.57x10^{-3} M, solvent system hexane/CH$_3$Cl 60/40 (v/v), T=-80 °C.

Conclusion

By the appropriate selection of a *bis*-allylsilane rapid and quantitative coupling of living PIB$^+$ can be achieved. While macromonomer (I) was found to possess low reactivity in addition reactions with PIB$^+$, an unhindered and reactive macromonomer can be obtained in a reaction of PIB$^+$ with PTPB. A four arm star polymer can readily be prepared with high efficiency at [PTPB]/[PIB$^+$] ~ 0.5.

Acknowledgment

This material is based on research supported by the Dow Corning Corporation.

References

1. Coca S, Faust R (1997) Macromolecules 30: 649
2. Bae YC, Fodor Z, Faust R (1997) Macromolecules 30: 198
3. Bae YC, Faust R (1998) Macromolecules 31: 2480
4. Hadjikyriacou S, Faust R, Suzuki T (1997) US Patent Application #965,443
5. Wilczek L, Kennedy JP (1987) J. Polym. Sci., Polym. Chem. Ed. 25: 3255
6. Iván B, Kennedy JP (1990) J. Polym. Sci., Part A: Chem. Ed. 28: 89
7. Storey FR, Maggio LT (1998) Polymer Preprints 39(1): 327
8. Hadjikyriacou S, Faust R (1996) Macromolecules 29: 5261
9. Wilczek L, Kennedy JP (1987) Polym. Bull. 17: 37
10. Marsalko TM, Majoros I, Kennedy JP (1993) Polym. Bull. 31: 665
11. Marsalko TM, Majoros I, Kennedy JP (1995) Macromol, Symp. 95: 39
12. Storey RF, Shoemake KA, Chisholm BJ (1996) J. Polym. Sci.: Part A: Polym Chem. A34:775