# Heterofunctional Linking Agents for the Synthesis of Well-Defined Block Copolymers of Dimethylsiloxane and *tert*-Butyl Methacrylate or 2-Vinylpyridine

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The synthesis of block copolymers with a high degree of molecular and compositional homogeneity has facilitated researchers in understanding properties such as morphology,[1,2] dynamics,[3] adsorption,[4,5] and rheology.[6] Furthermore, block copolymers have found useful applications[7] and are potential candidates for many others.[8] The most powerful method for the synthesis of block copolymers is the sequential addition of monomers by anionic polymerization. Unfortunately, there are pairs of polymeric blocks, such as poly(dimethylsiloxane) (PDMS) and polymethacrylates (PMA), that cannot be prepared by this procedure, because the nucleophilicity of the living polymeric blocks does not match the electron affinity of the other monomer. To overcome this problem, Hogen-Esch et al.[9] prepared an −OH end-capped poly(methyl methacrylate) (PMMA) using an α-OH protected initiator. In a second step, the −OH group was transformed, after deprotection, to −OLi group and used to initiate the polymerization of hexamethylcyclotrisiloxane ($D_3$). Although the block copolymers prepared are well-defined, the weak point of this methodology is the instability of the −C−O−Si− group that connects the two blocks. Other methods have been reported for the synthesis of PDMS-*b*-PMA by combining anionic with group transfer,[10] atom transfer radical,[11] or free radical polymerization.[12] The above procedures (refs 10−12) lead to materials with high molecular and compositional polydispersity.

An alternative and perhaps more versatile approach for the synthesis of block copolymers would be one that employs a linking agent with two different functional groups (heterofunctional linking agent). The reactivity of the two groups should be different toward dissimilar macroanions. On the basis of the greater reactivity of the $-Si(Me)_2-Cl$ than $-Ph-CH_2-Cl$ group toward silicon−oxygen nucleophiles,[13] we are proposing 2-(chloromethylphenyl)ethyldimethylchlorosilane (CMPDMS) as an efficient heterofunctional linking agent for the synthesis of well-defined block copolymers of PDMS and poly(*tert*-butyl methacrylate) (PTBMA) or poly(2-vinylpyridine) (P2VP).

**Experimental Section. a. Equipment and Materials.** *n*-Butyllithium (1.6 M) in hexanes, hexamethylcyclotrisiloxane ($D_3$) (98%), 2-vinylpyridine (98%), *tert*-butyl methacrylate (99%), $(CH_3)_3SiCl$ (99%), benzene (99%), tetrahydrofuran (THF) (99%), CsI (99.999%), and LiCl (99%) were purchased from Aldrich. CMPDMS (98%), a mixture of para and meta isomers, was purchased from ABCR. Purification of monomers and solvents to the standards required for anionic polymerization has been described in detail elsewhere.[14] *s*-BuLi was prepared in vacuo from *s*-butyl chloride and lithium dispersion. Addition and removal of the reagents were performed using break-seals and constrictions.[14] CMPDMS was purified by fractional distillation under high vacuum ($10^{-6}$ Torr).

Size exclusion chromatography (SEC) experiments were carried out at 25 °C in two different setups. In the first a Waters model 510 pump, a Waters model 410 differential refractometer, and three styragel columns with a porosity range from $10^3$ to $10^6$ Å were used. Chloroform was the carrier solvent at a flow rate of 1.0 mL/min. In the second setup a Waters 610 pump, a Waters model 410 differential refractometer 996 diode-array UV detector ($\lambda = 240$ nm where only P2VP absorbs), and six columns with a porosity range of $10^2$−$10^6$ Å were used. THF was the carrier solvent at a flow rate of 1 mL/min. The differential refractive index increment d*n*/d*c* in mL/g of P2VP, PTBMA, and PDMS in chloroform at 25 °C is 0.075, 0.005, and −0.044 mL/g, respectively. The d*n*/d*c* values in mL/g at 25 °C in THF of P2VP, PTBMA, and PDMS are 0.155, 0.06, and 0.005 (almost zero), respectively. The differential refractive index increments were measured with a Chromatix KMX-16 refractometer, operating at 633 nm and calibrated with aqueous NaCl solutions.

The number-average molecular weight ($M_n$) of the precursors and the final products were determined either with a Jupiter model 231 recording membrane osmometer (MO) at 37 °C or with a Jupiter model 233 vapor pressure osmometer (VPO) at 50 °C. The solvent was toluene distilled over $CaH_2$. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker 300 MHz instrument with $CDCl_3$ as the solvent, at 25 °C.

**b. Synthesis of the *ω*-Functionalized Chloromethylphenyl PDMS.** A detailed description is given for the synthesis of *ω*-functionalized chloromethyl PDMS with molecular weight of $2.5 \times 10^4$ g/mol.

A reactor was attached on a high-vacuum line, evacuated, and flame-dried. Then, under vacuum, 2−3 mL of 1.6 M solution of *n*-BuLi in hexanes was introduced through a septum. Subsequently, the septum was removed by heat-sealing the glass septum holder, and 40 mL of purified benzene was distilled in the reactor under vacuum. The reactor was then removed from the vacuum line by heat-sealing, and the solution of *n*-BuLi was used to wash the apparatus. The solution was transferred to a side flask and was immersed in a water bath thermostated at 50 °C. Thus, benzene was brought to reflux washing traces of *n*-BuLi along with impurities or reaction products to the side flask. After rinsing the reactor 5−6 times, the solvent was distilled in the main flask, and the side flask was removed by heat-sealing. Then, 8.0 g of a 50% (w/w) solution of $D_3$ in benzene was added into the reactor along with 4.0 mL of a $4.0 \times 10^{-2}$ mol/L solution of *s*-BuLi in hexanes. The mixture was left at ambient temperature for 2 h, and then 40 mL of purified THF was added. After 2 h,[15] the reactor was placed at −20 °C for 7 days.[16] One gram of living PDMS (22.5 mL) was removed and neutralized with $(CH_3)_3SiCl$ for characterization. The remaining 3 g of living PDMS ($1.2 \times 10^{-4}$ mol) was neutralized with 1.0 mL of a $1.3 \times 10^{-1}$ mol/L solution in benzene of CMPDMS. A small aliquot was removed for character-

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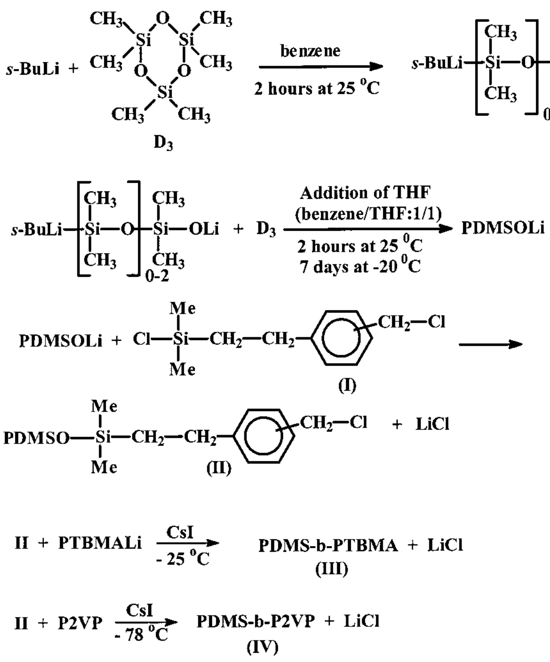
**Scheme 1**



ization, and the reaction product was transferred to a flask with a break-seal and sealed off the main apparatus.

$^1$H NMR (300 MHz, CDCl$_3$) for (I) of Scheme 1: $\delta$ 7.19−6.85 ($C_6\mathit{H}_4$), 4.45 ($-C\mathit{H}_2Cl$), 2.55−2.66 ($Ph-C\mathit{H}_2$-$CH_2-Si$), 0.95−1.05 ($Ph-CH_2-C\mathit{H}_2-Si$), 0.22 ($(C\mathit{H}_3)_2$-Si−). Integration gave the expected ratios of protons.

$^1$H NMR (300 MHz, CDCl$_3$) for (II) of Scheme 1: $\delta$ 7.19−6.85 ($C_6\mathit{H}_4$), 4.45 ($-C\mathit{H}_2Cl$), 2.55−2.66 ($Ph-C\mathit{H}_2$-$CH_2-Si$), 2.45 ($CH_3-C\mathit{H}_2-CH(CH_3)$-Si−O−), 0.95−1.05 ($Ph-CH_2-C\mathit{H}_2-Si$), 0.8−0.9 ($C\mathit{H}_3-CH_2-CH(C\mathit{H}_3)-Si-$ O−), 0.4−0.45 ($-C\mathit{H}(CH_3)-Si-$), 0.22 ($(C\mathit{H}_3)_2Si-$), 0.1 ($-Si(C\mathit{H}_3)_2-O-$). Integration gave a ratio of ($-C\mathit{H}_2Cl$):($Ph-C\mathit{H}_2CH_2-Si$) 1:1.

**c. Synthesis of PTBMA and Linking Reaction with the *ω*-Functionalized Chloromethylphenyl PDMS.** The preparation of living PTBMA, having a molecular weight of 2.5 × 10$^4$ g/mol, was performed in a reactor similar to the one used above. A solution of 1,1-diphenylhexyllithium (DPHL) in THF was used for washing and rinsing the apparatus. The solvent was distilled in the main flask, and DPHL along with impurities was removed by heat-sealing the side flask. Four milliliters of a 1.0 × 10$^{-1}$ mol/L solution of DPHL and 1 mL of a 1.6 × 10$^{-1}$ mol/L solution of LiCl[17] in THF were added, the solution was placed in a dry ice/2-propanol cooling bath (−78 °C), and 10 g of *tert*-butyl methacrylate was distilled while stirring to the solution. After 30 min, depending on the molecular weight, an appropriate amount of (II) (Scheme 1) that contains 1.2 × 10$^{-3}$ mol of $-Ph-CH_2-Cl$ groups was added along with a catalytic amount of CsI (molar ratio of CsI/CLi = 0.3/1) in THF. The reaction mixture was placed for 3 days at −25 °C. The excess of living PTBMA was neutralized with MeOH. The diblock copolymer was separated from the excess of PTBMA by adding a 10% THF solution of the mixture of polymers in a 5/1 (v/v) mixture of MeOH/H$_2$O. The precipitant was dissolved in THF, and the procedure was repeated three times.

$^1$H NMR (300 MHz, CDCl$_3$) for (III) of Scheme 1: $\delta$ 6.85−7.19 ($C_6\mathit{H}_4$), 2.55−2.66 ($Ph-C\mathit{H}_2CH_2-Si$), 1.8−2.2 ($-C\mathit{H}_2-C(CH_3)$(COO-*tert*-butyl)−), 1.2−1.6 (*tert*-butyl), 0.8−1.1 ($(C\mathit{H}_3)-C(CH_2)-$), 0.22 ($(C\mathit{H}_3)_2Si-$), 0.1 ($-Si$-$(C\mathit{H}_3)_2-O-$).

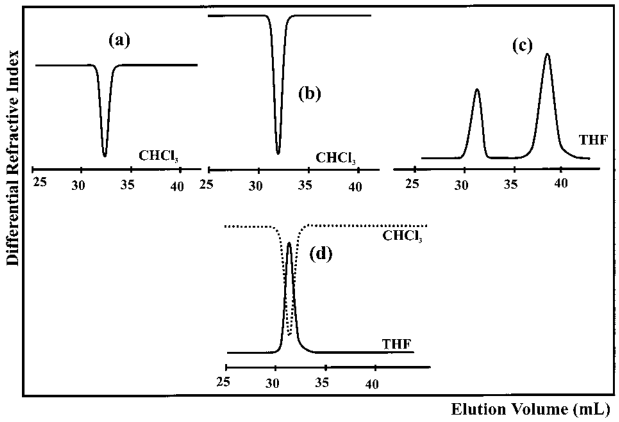


**Figure 1.** Monitoring the synthesis of PDMS-*b*-PTBMA (80) by SEC: (a) PDMS living chain terminated by (CH$_3$)$_3$SiCl, (b) PDMS living chain terminated by the heterofunctional linking agent, (c) reaction product of (b) with living PTBMA, (d) fractionated PDMS-*b*-PTBMA.

**d. Synthesis of P2VP and Linking Reaction with the *ω*-Functionalized Chloromethylphenyl PDMS.** The preparation of living P2VP, having a molecular weight of 1.5 × 10$^4$ g/mol, was performed in a reactor similar to the one used above. A solution of DPHL in THF was used for washing and rinsing the apparatus. The solvent was distilled in the main flask, and DPHL along with impurities was removed by heat-sealing the side flask. Four milliliters of a 1.0 × 10$^{-1}$ mol/L solution of *s*-BuLi in THF was added, solution was placed in a dry ice/2-propanol cooling bath (−78 °C), and 6 g of 2-vinylpyridine was distilled while stirring into the solution. After 30 min, an appropriate amount of (II) (Scheme 1) containing 1.2 × 10$^{-3}$ mol of $-Ph-CH_2-Cl$ groups was added, along with a catalytic amount of CsI (molar ratio of CsI/CLi = 0.3/1) in THF. The reaction mixture was placed for 3 days at −78 °C. The excess of living P2VP was neutralized by adding a small aliquot of MeOH. The diblock copolymer was separated from the excess of P2VP by precipitation in a mixture of H$_2$O:MeOH 1:2 (v/v).

$^1$H NMR (300 MHz, CDCl$_3$) for (IV) of Scheme 1: $\delta$ 6.85−8.2 ($C_6\mathit{H}_4 + C_6\mathit{H}_4N$), 2.55−2.66 ($Ph-C\mathit{H}_2CH_2-Si$), 1.0−2.0 ($C\mathit{H}_2-C\mathit{H}$).

**Results and Discussion.** A series of different PDMS-*b*-PTBMA copolymers and one PDMS-*b*-P2VP copolymer have been prepared using the heterofunctional linking agent CMPDMS and anionic polymerization techniques. The reaction sequence for both block copolymers is given in Scheme 1. In Figures 1 and 2 the SEC chromatograms for the synthesis of PDMS-*b*-PTBMA (80) and PDMS-*b*-P2VP, as examples, are presented.

To ensure complete reaction of the living PDMS with the chlorosilane group of CMPDMS, a slight excess (~10%) of the linking agent was used. The complete lack of formation of any homocoupling product (reaction with the chloromethyl group, too) (Figures 1 and 2) indicates that this reaction is selective as suggested in ref 18. This is also supported by the fact that the ratio between the $^1$H NMR peaks of ($-C\mathit{H}_2Cl$) ($\delta$ 4.45) and ($Ph-C\mathit{H}_2CH_2-$Si) ($\delta$ 2.55−2.65) before and after the linking reaction of CMPDMS with living PDMS stays constant, proving that the $Ph-CH_2Cl$ group did not participate in the linking reaction.

**Table 1. Molecular Characteristics of the Diblock Copolymers and Their Precursors**

| sample | $M_n$(PDMS) $\times 10^{-3\ a}$ | $M_n$(PTBMA or P2VP) $\times 10^{-3\ a}$ | $M_n$(diblock) $\times 10^{-3\ a}$ | $M_w/M_n$[b] | % PDMS[c] (w/w) | % PDMS[d] (w/w) |
|---|---|---|---|---|---|---|
| PDMS-*b*-PTBMA (80)[f] | 55.0 | 11.1 | 65.2 | 1.03 | 83 | 81 |
| PDMS-*b*-PTBMA (70)[f] | 42.1 | 13.4 | 57.1 | 1.03 | 76 | 74 |
| PDMS-*b*-PTBMA (50)[f] | 27.2 | 27.0 | 55.3 | 1.02 | 50 | 51 |
| PDMS-*b*-P2VP | 4.3[e] | 15.1 | 20.2 | 1.07 | 22 | 20 |

[a] Membrane osmometry (MO) in toluene at 37 °C. [b] Size exclusion chromatography (SEC) in THF at 25 °C. [c] Calculated from $M_n$ values of both blocks. [d] $^1$H NMR at 25 °C. [e] Vapor pressure osmometry (VPO) in toluene at 50 °C. [f] Approximately the PDMS content (w/w).

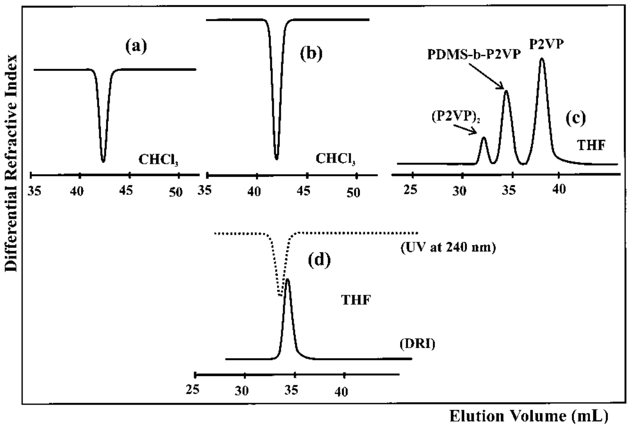


**Figure 2.** Monitoring the synthesis of PDMS-*b*-P2VP by SEC: (a) PDMS living chain terminated by $(CH_3)_3SiCl$, (b) PDMS living chain terminated by the heterofunctional linking agent, (c) the reaction product after the linking reaction of (b) with living P2VP, (d) the fractionated PDMS-*b*-P2VP with RI detector (—) and UV detector (· · ·).

To increase the efficiency of the linking reaction of the $\omega$-functionalized chloromethylphenyl PDMS with the living PTBMA, a catalytic amount of CsI was added. The chloride is transformed in situ to the more reactive iodide. When the linking reaction was performed without CsI, only 30% conversion was obtained. A 2-fold excess of the living PTBMA was used in order to accelerate the linking reaction with the chloromethylphenyl group of the macromolecular linking agent PDMS−PhCH$_2$Cl. The complete lack of any traces of PDMS in the reaction products (Figure 1) indicates that the coupling of the living PDMS with the linking agent as well as the linking reaction of the macromolecular linking agent PDMS−Ph−CH$_2$−Cl and living PTBMA are quantitative. The diblock copolymer was separated from excess PTBMA by precipitating the reaction product in a mixture of MeOH/H$_2$O (5/1 v/v), which is a nonsolvent for PDMS. The yield of diblock copolymer was between 70 and 80%.

A similar yield was obtained for the PDMS-*b*-P2VP block copolymer. In this case the living P2VP can react with both electrophilic groups, −Si(Me)$_2$−Cl and −Ph−CH$_2$−Cl, of the linking agent. As a consequence, the slight excess of the linking agent used resulted in formation of a small amount of the dimer (P2VP)$_2$. This dimer along with excess P2VP can be removed by precipitating the reaction product in a mixture of MeOH/H$_2$O (2/1 v/v). The composition of MeOH/H$_2$O differs from that of PDMS-*b*-PTBMA for solubility reasons. The final yield of both copolymers depends on (a) the solubility difference between the two blocks in the fractionation environment, (b) the composition of final products, and (c) the capability of the experimentalist.

The molecular characteristics of the fractionated copolymers are given in Table 1. The low polydispersity index of the final copolymers along with the good agreement of the compositions calculated from $M_n$ and those found by $^1$H NMR analysis indicates that the molecular and compositional homogeneity is high. This is also supported by the narrow molecular and compositional peaks obtained by SEC (Figures 1 and 2).

In conclusion, by using a heterofunctional linking agent, we have prepared for the first time well-defined and stable block copolymer of dimethylsiloxane and *tert*-butyl methacrylate or 2-vinylpyridine. Using the same approach, tri-, tetra-, and pentablock ter-, quarter-, and quinterpolymers have been prepared. The synthesis and morphology will be given in a forthcoming paper.[19]

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## References and Notes

(1) Bates, F. S.; Fredrickson, G. H. *Annu. Rev. Phys. Chem.* **1990**, *41*, 525.
(2) Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.
(3) Anastasiadis, S.; Vogt, S.; Fytas, G. *Phys. Rev. Lett.* **1993**, *70*, 2415.
(4) Massey, J. A.; Temple, K.; Cao, L.; Rharbi, Y.; Raez, J.; Winnik, M. A.; Manners, I. *J. Am. Chem. Soc.* **2000**, *122*, 11577.
(5) Won, Y. Y.; Davis, H. D.; Bates, F. S. *Science* **1999**, *283*, 960.
(6) Floudas, G.; Vlassopoulos, D.; Stamm, M. *J. Chem. Phys.* **1996**, *104*, 2083.
(7) Aggarwal, S.; Hargis, I.; Livigni, R.; Fabris, H.; Marker, L. In *Advances in Elastomers and Rubber Elasticity;* Mark, J. E., Ed.; Plenum Press: New York, 1986; p 17.
(8) Chan, V.; Hoffman, J.; Lee, V. Y.; Iatrou, H.; Avgeropoulos, A.; Hadjichristidis, N.; Miller, R. D.; Thomas, E. L. *Science* **1999**, *286*, 1716.
(9) Hogen-Esch, T. E.; Mason, J. R.; Ladd, B. J.; Helary, G.; Belorgey, G. In *Contemporary Topics in Polymer Science; Advances in New Materials*; Riffle, J., Salamone, J. C., Eds.; Plenum Press: New York, 1992; Vol. 7, p 339.
(10) Lim, K.; Webber, S.; Johnston, K. *Macromolecules* **1999**, *32*, 2811.
(11) Miller, P.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 8760.
(12) Miyata, T.; Obata, S.; Uragami, T. *Macromolecules* **1999**, *32*, 3712.
(13) Thomas, S. *Organic Synthesis, "The Role of Boron and Silicon"*; Oxford University Press: New York, 1991; p 47.
(14) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.
(15) Zilliox, J. G.; Roovers, J. E. L.; Bywater, S. *Macromolecules* **1975**, *8*, 573.
(16) Bellas, V.; Iatrou, H.; Hadjichristidis, N. *Macromolecules* **2000**, *33*, 6993.
(17) Varshney, S. K.; Hautekeer, J. P.; Fayt, R.; Jerome, R.; Teyssie, P. *Macromolecules* **1990**, *23*, 2618.
(18) Liu, Q.; Wilson, G.; Davis, R.; Riffle, J. *Polymer* **1993**, *34*, 3030.
(19) Hashimoto, T.; Hasegawa, H.; Iatrou, H.; Bellas, V.; Hadjichristidis, N., to be published.

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