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# Synthesis of Cyclolinear Poly(carbosilane)-*g*-poly(methyl methacrylate or styrene) Random Copolymers

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ABSTRACT: The cyclolinear polycarbosilane, (poly(1-hexyl-1,3-ditolyl-1,3-disilacyclobutane) poly(HDTDSCB)), which has tolyl groups attached to the main chain Si atoms, was prepared by ADMET polymerization with the second-generation Grubbs catalyst, and 10%, 5%, and 2% of the tolyl groups were brominated by reactions with *N*-bromosuccinimide. A series of well-controlled poly(methyl methacrylate) (PMMA) anions of 2.5K, 5K, and 10K molecular weight were introduced via the "grafting onto" strategy at low temperature to the randomly 10%, 5%, and 2% brominated poly(HDTDSCB), respectively, without any lithiation or ring opening of the disilacyclobutane in the main chain. Because of side reactions initiated by the PS anion under similar conditions, a "grafting from" strategy by ATRP was employed to yield the corresponding poly(HDTDSCB)-*g*-PS random copolymers. The product poly(HDTDSCB)-*g*-(PMMA or PS) random copolymers were purified by using total adsorption−desorption interaction chromatography, which involves selective adsorption of the polycarbosilane on a C18 HPLC column from a $CH_2Cl_2/CH_3CN$ (50/50) eluent, while the excess PMMA or PS homopolymer eluted. This method was also successfully applied to the separation of larger quantities of the copolymers by using multiple injections onto the C18 column.

## Introduction

Considerable effort has been expended over the past decade to develop a suitable replacement for $SiO_2$ as a low-*k* (dielectric constant $<2.3$) interlayer dielectric (ILD) material for use in future generations of integrated circuits.[1] There have been many reports regarding organic materials such as PTFE (poly(tetrafluoroethylene)),[1−3] poly(arylene ether),[1,4] poly(imides),[1,5] etc., as promising candidates for low-*k* materials. Because most organic dielectric materials have a dielectric constant between 2.5 and 3.5, it is necessary to introduce porosity to reach the very low *k* values ($\leq 2.0$) needed for the ITRS 45 nm node and beyond. However, in general, these organic materials do not have sufficient thermal and mechanical stability for use as dielectric materials in ICs, especially when the introduction of porosity is needed to reach *k* values of $\leq 2.0$. On the other hand, inorganic materials[1,6] typically have appreciably higher dielectric constants, requiring an excessive amount of porosity to reach $k < 2.0$. Therefore, increasing focus has been placed in recent years on inorganic−organic hybrid materials as a source of low-*k* materials with suitable thermomechanical stability to survive IC manufacture.

Our previous work has shown that the polycarbosilane films obtained by spin-coating of the cyclolinear polycarbosilane, $[-(CH_2)_6\text{-}cyclo\text{-}\{(CH_3)Si(CH_2)_2Si(CH_3)\}-]_n$, followed by heating to 300 °C to induce cross-linking by ring opening,[7] exhibit dielectric constants as low as 2.3, without any added porosity, along with excellent thermomechanical and Cu barrier characteristics.[8] However, to reach dielectric constants below 2.0, which is needed for future generations of ILDs, it will be necessary to introduce porosity into these films in controlled amounts as nanopores having diameters of less than ca. 10 nm. This study was undertaken to investigate possible routes to graft copolymers of this cyclolinear polycarbosilane with organic polymers that can be either thermally or photochemically removed to generate pores of controlled sizes. Two such polymers are poly(methyl methacrylate) (PMMA) and poly(styrene) (PS), which are known to undergo thermally[9] and, in the case of PMMA, photochemically[10] induced depolymerization. We describe here the successful preparation of such PCS-*g*-PMMA and -PS graft copolymers, by using both "grafting onto" and "grafting from" approaches to attach the organic copolymer as nearly monodisperse side chains of controlled molecular weight. This is the first step in an ongoing effort to demonstrate the potential utility of such graft copolymers as ultralow-*k* ($k < 2.0$) dielectric materials.

The use of PMMA as a porogen in dielectric materials has been previously reported using a fluoropolymer as the base structure.[3] The PMMA blocks in the PFS-*b*-PMMA block copolymers were selectively decomposed by UV irradiation, and PFS films with pore sizes in the range 30−50 nm were obtained. Although the dielectric constant reached 1.8, the fluoropolymer remains un-cross-linked and thus would not be expected to exhibit suitable thermomechanical properties for ILD processing.

To introduce a homogeneous pore size using PMMA or PS, the "grafting onto" method[11] is more efficient compared to the "grafting from" method[12] because the molecular weight can be predicted, and the corresponding vinyl momomers easily undergo homogeneous anionic polymerization to produce polymer anions having narrow PDI. However, it is necessary to use excess homopolymer anion to efficiently graft it onto the functionalized main chain, and the remaining excess homopolymer should be removed from the graft copolymer after complete reaction, as a homopolymer-free copolymer is essential

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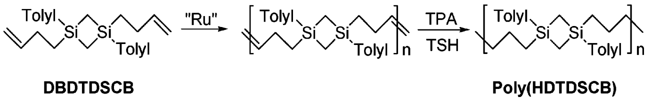
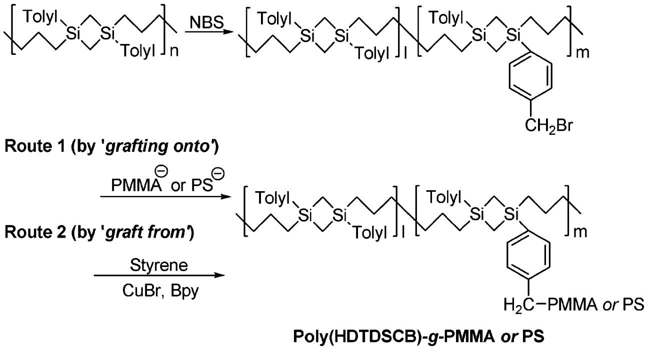
**Scheme 1. Synthesis of Poly(HDTDSCB)**



**Scheme 2. Synthesis of Poly(HDTDSCB)-*g*-PMMA or PS**



to study the block or graft copolymer morphology and its thermal and mechanical properties. The total adsorption−desorption interaction chromatography (TADIC) technique developed by Chang[13] offers a very useful strategy to remove the inevitably remaining homopolymer residue in the synthesis of block or graft copolymers easily and cleanly using selective segment adsorption of the copolymer to a silica or C18 column under controlled eluent composition or temperature. Until now, the study of TADIC has been focused on the adsorption of PS, PMMA, and PEO blocks; for the successful application of the "grafting onto" method to polycarbosilane, the selective adsorption−desorption conditions of the polycarbosilane need to be found.

In comparison to the "grafting onto" approach by anionic coupling, the "grafting from" method by ATRP offers convenient and mild radical reactive sites and generally results in little or no excess of the graft homopolymer,[14] while the prediction of the molecular weight of the growing side chain is problematic in this case. In the case of the cyclolinear polycarbosilane which is the chosen "host" polymer for the grafting reactions, additional complications are encountered due to (1) the reactivity of the imbedded disilacyclobutane rings toward ring-opening (RO) by many transition metal complexes, including certain Cu(II) derivatives that have been used for the RO polymerization (ROP) of phenyl-substituted disilacyclobutanes,[15,16] and (2) the relatively acidic nature of the bridging (Si)−$CH_2$−(Si) groups in these rings, which leads to proton abstraction by various organolithium reagents.[17]

This research employs the tolyl-substituted cyclolinear polycarbosilane, [−{$(CH_2)_6$-*cyclo*-{Si(tolyl)$(CH_2)_2$Si(tolyl)}−] (poly(HDTDSCB)), as the parent polymer for the grafting reactions, where the tolyl methyl group provides a convenient site for bromination using peroxide-initiated *N*-bromosuccinimide as the source of Br[18] (Scheme 2). The resultant randomly distributed Si−$C_6H_4CH_2Br$ groups serve as the initiator sites for growing PS by the ATRP "grafting from" approach and also as the reactive sites for the "grafting onto" approach by anionic coupling reaction with well-controlled PMMA or PS anions. In the latter case, we developed critical total adsorption−desorption interaction chromatography (TADIC) conditions to separate the excess PMMA or PS homopolymer from the poly(carbosilane)-containing polymers by polycarbosilane adsorption onto a C18 column. This paper describes the preparation, separation, and characterization of the graft copolymers by NMR, GC, GPC, HPLC, and DSC methods.

## Results and Discussion

**Synthesis of the Cyclolinear Polycarbosilane Homopolymer, Poly(HDTDSCB).** The synthesis of the disilacyclobutane (DSCB) monomer and its subsequent polymerization by ADMET followed the same general approach described by Wu et al. for the corresponding dimethyldibutenyl-DSCB.[7] The viscous liquid product contains two isomers, trans:cis = 6:4, as confirmed by $^1$H NMR, and the boiling points of the two isomers were different by about 10−15 °C at 0.2 mmHg. This means that it is possible to change the isomer ratio by distillation. In addition, we found that the isomers could also be separated by crystallization of 1,3-dichloro-1,3-ditolyl-1,3-disilacyclobutane in hexane. The *trans*-DCDTDSCB could be crystallized in hexane while *cis*-DCDTDSCB was soluble in hexane. The monomers were characterized by $^1$H NMR and $^{29}$Si NMR, and the purity was checked by GC (>98%).

The unsaturated homopolymer was prepared by acyclic diene methathesis (ADMET) polymerization with second-generation Grubbs catalyst (Scheme 1) as was previously reported[7,19] without isomer separation and showed almost same isomer composition (trans:cis = 6:4) as the starting monomer. Although the conversion was 85%, a substantial amount of low molecular weight polymer remained and the PDI was broad (2.2). Moreover, the obtained polymer had a deep dark brown color, presumably because of the affinity between the vinyl group and Grubbs catalyst. The unsaturated homopolymer was reduced by a diimide-induced hydrogenation reaction using the method developed by Han.[20] After reduction, most of the Grubbs catalyst can be removed by precipitation in methanol, yielding a light brown liquid. The clear, light yellow, viscous, reduced poly(HDTDSCB) was obtained by reprecipitation from toluene with methanol followed by filtration through a silica or alumina column. All of these procedures were followed by using $^1$H NMR and $^{29}$Si NMR spectroscopy. The unsaturated −CH= proton peak appeared at 5−5.2 ppm, and the peak had clearly disappeared after reduction, which means that the unsaturated groups were reduced cleanly and the disilacyclobutane ring was preserved (0.5 ppm) without any ring opening (the ring-opened methylene peak, which appears at 0.1 ppm, was entirely absent). The $M_n$ of the obtained reduced poly(HDTDSCB) was 10K and PDI was 1.9 (Table 1), which means the average number of repeat units is 29 and there are 58 tolyl groups per chain on the average. The $T_g$ value for this polymer (−6 °C) was determined by DSC and found to be ca. 59 deg higher than that of the related poly(1-hexyl-1,3-dimethyl-1,3-disilacyclobutane),[7] presumably due to the greater polymer chain torsional barriers resulting from the larger tolyl groups.

**Syntheses of the Poly(HDTDSCB)-*g*-PMMA and PS Copolymers.** Scheme 2 (route 1) shows the procedures employed for the syntheses of the graft copolymers by random bromination of the tolyl groups and coupling reaction with the PS or PMMA anion. To facilitate observation of the copolymer properties and microstructure (to be reported subsequently), a 30% volume fraction of side chain was targeted. The main chain polymer was randomly brominated with NBS/benzoyl peroxide, and the bromination ratio was assigned by comparing the integration of the brominated methylene $^1$H NMR peak at 4.2 ppm with the integration of the unbrominated tolyl−methylene peak at 2.2−2.4 ppm (Figure 1). Polymer samples with 10%, 5%, and 2% of the tolyl groups brominated were prepared; this corresponds to an average of 5.8, 2.9, and 1.3 brominated sites per polymer chain (Table 1).

An excess of the PMMA homopolymer anion is needed to ensure complete coupling with the brominated sites. A 5 times

**Table 1. Molecular Characterization of the Poly(HDTDSCB)-*g*-PMMA Copolymer Prepared by the Anionic Coupling Method**

| sample | $M_n$ of poly(HDTDSCB)[a] (PDI) | av no. of brominated sites per chain[b] | $M_n$ of grafted PMMA[a] (PDI) | chemical composition of PMMA (wt %)[b] | $M_n$ of poly(HDTDSCB)-*g*-PMMA[a] (PDI) |
|---|---|---|---|---|---|
| CPCSRG-10−2.5 | 10K (1.9) | 5.8 | 2.5K (1.2) | 25 | 17K (2.1) |
| CPCSRG-10−5 | 10K (1.9) | 2.9 | 5K (1.1) | 37 | 17K (2.2) |
| CPCSRG-10−10 | 10K (1.9) | 1.3 | 10K (1.1) | 33 | 19K (5.0) |

[a] Determined by GPC relative to polystyrene. [b] Calculated by $^1$H NMR.

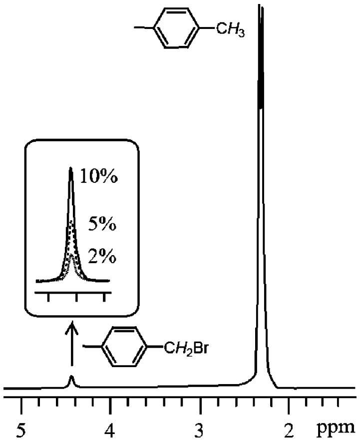


**Figure 1.** $^1$H NMR spectra of 10%, 5%, and 2% partially brominated poly(HDTDSCB).

molar excess of PMMA anion with respect to the amount of brominated sites was used. Two methods were used to remove the excess PMMA homopolymer homopolymer from the graft copolymer. In the case of the low molecular weight, 2.5K and 5K, PMMA, the difference in solubility for the PMMA homopolymer, relative to the poly(HDTDSCB)-*g*-PMMA copolymer in methanol, was sufficient to allow separation by reprecipitation from THF/methanol, whereas the TADIC technique was used for the 10K PMMA due to the lower solubility of the higher molecular weight PMMA homopolymer in methanol. Figure 2a,b shows the GPC curves before and after anionic coupling reactions of 2.5K and 5K PMMA anions to partially brominated poly(HDTDSCB), and Table 1 lists the molecular characterization data for the separated graft copolymers (CPCSRG-10−2.5, CPCSRG-10−5). The PMMA homopolymer (2.5K, 5K) peak was clearly absent **(**see Supporting Information, Figure S3**)**, indicating that the excess PMMA homopolymer in these cases was selectively removed by the reprecipitation, followed by cold (for 2.5K PMMA) or hot (for 5K PMMA) methanol treatment, because of the difference of the solubility between poly(HDTDSCB) and PMMA in methanol. Compared with the poly(HDTDSCB) homopolymer, the molecular weight of the separated graft copolymers was higher after the coupling reaction (Table 1). The chemical composition of PMMA in the separated graft copolymer was calculated by comparing the integration of the methylene (*H*) $^1$H NMR peak at 3.6 ppm with the integration of the tolyl−methylene peak (a) at 2.2−2.4 ppm (Figure 3). The highly grafted sample with low molecular weight PMMA (CPCSRG-10−2.5) showed a difference in solubility relative to the sample with a low grafting density having a high molecular weight PMMA side chain but with the same poly(HDTDSCB)/PMMA overall composition. In particular, in contrast to (CPCSRG-10−5), (CPCSRG-10−2.5) was found to be soluble in hot methanol, as was confirmed by GPC and $^1$H NMR spectroscopy. This could be due to the formation of a micelle in the case of the CPCSRG-10−2.5 copolymer under these conditions.

Although the PMMA homopolymer (10K) can be removed with hot methanol, it was difficult to verify clean separation by GPC because of the similarity of molecular weight of the PMMA homopolymer to that of the copolymer. Therefore, the total adsorption and desorption interaction chromatography (TADIC) technique was applied to separate excess of PMMA homopolymer from the graft copolymer. A C-18-bonded HPLC silica column was employed with 50/50 $CH_2Cl_2/CH_3CN$ (v/v) as an initial eluent for 4 min. As is shown in Figure 4, under these conditions, the poly(HDTDSCB) segment undergoes selective absorption to the C-18 column, while the PMMA homopolymer was eluted from the column before the solvent (s) was eluted (Figure 4a). The adsorbed graft copolymer was later obtained by applying a solvent gradient of increasing $CH_2Cl_2$ composition to 100%. This makes it possible to accumulate the poly(HDTDSCB) segment in the C-18 column, and a larger scale separation, by multiple injection to the C-18 column, can be achieved (Figure 4b). The remaining PMMA homopolymer can be eluted during the successive injections because of little enthalpic affinity to the C18 column, and the accumulated polymer having poly(HDTDSCB) segment can be obtained cleanly and quickly compared to fractional precipitation and preparative GPC.

There are reports of the lithiation of the methylene position adjacent to the silicon atom and/or ring opening of disilacyclobutane under strongly basic conditions because of its high acidity and high ring strain.[17] The lithiation and/or nuclophilic ring opening depends on the base species, solvent, and ligand employed, such as TMEDA or HMPA. Boileau reported[17] that the lithiated disilacyclobutane ring in the presence of toluene transfers its Li to the toluene, forming phenylmethyllithium, which is followed by polymerization of the disilacyclobutane species. Thus, in the coupling reaction between brominated poly(HDTDSCB) and the PMMA anion, it is expected that this lithiation will result in ring opening and, consequently, inter- or intrachain cross-linking. The coupling reaction of brominated poly(HDTDSCB) with 5 times molar excess of PMMA anion at 0 °C undergoes the ring-opening cross-linking reaction to the extent of about ≤10%, based on the results obtained by $^1$H NMR and the TADIC HPLC technique. Thus, the ring-opened methylene proton peak appeared at 0.1 ppm in the $^1$H NMR spectrum (Figure 5), and many peaks at retention times between 1.5 and 4 min were observed in the HPLC. On the contrary, the coupling reaction at −78 °C did not produce any proton peaks at around 0.1 ppm in the $^1$H NMR spectrum of the product copolymer, and there were no peaks between 1.5 and 4 min in the HPLC (Figure S3). As shown in Figure 3, the brominated tolyl−methylene $^1$H NMR peak (4.2 ppm) had clearly disappeared after the coupling reaction, and grafted PMMA proton peaks were clearly evident at 0.83 (g), 1.8 (h), and 3.62 ppm (i). The GPC traces of the three copolymer samples indicate clean conversion of the brominated poly(HDTDSCB) into the corresponding graft copolymer (Figure 2), with an increase in the $M_n$ of 7−9K, consistent with the expected enhancement in molecular weight due to the grafting of ca. 30 wt % PMMA. In the case of the CPCSRG-10−2.5 sample, the GPC curve appears to shift fairly uniformly to higher molecular weight with slight broadening toward the high molecular weight side. Because of the high degree of bromination (10%) of the PCS

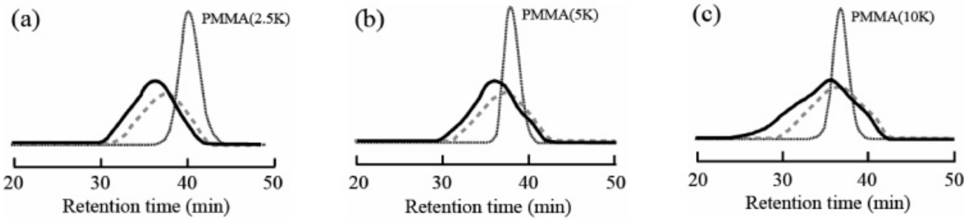


**Figure 2.** GPC (UV = 240 nm) curves before (- - -) and after (—) the coupling reaction of the partially brominated poly(HDTDSCB) and PMMA anion ((a) CPCSRG-10−2.5, (b) CPCSRG-10−5, and (c) CPCSRG-10−10)) compared to the GPC trace for the corresponding isolated PMMA homopolymer.

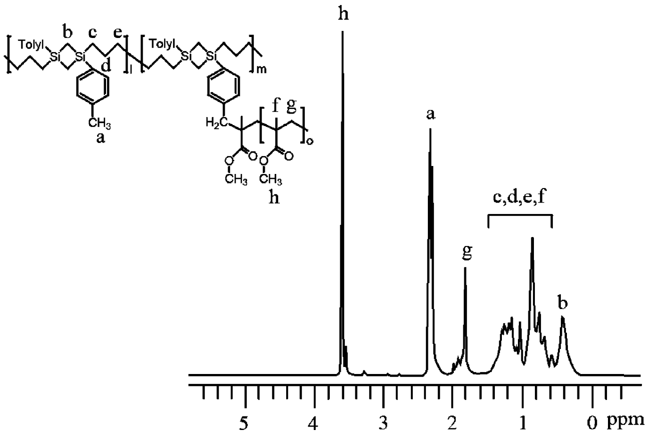


**Figure 3.** Representative $^1$H NMR spectrum of the poly(HDTDSCB)-*g*-PMMA copolymer (CPCSRG-10−2.5).

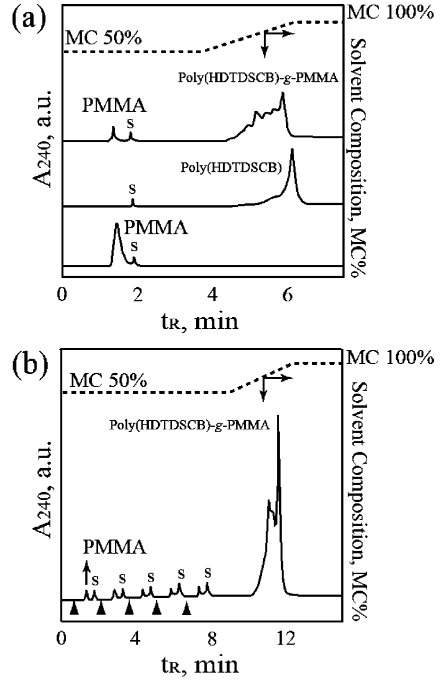


**Figure 4.** TADIC separation conditions (a) and multiple injections (b) showing the separation of excess PMMA homopolymer from the poly(HDTDSCB)-*g*-PMMA (CPCSRG-10−10) copolymer (s: solvent; ▲: injections).

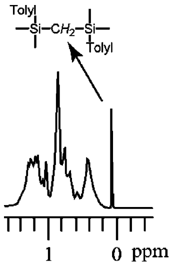


**Figure 5.** $^1$H NMR characterization of the partially ring-opened poly(HDTDSCB)-*g*-PMMA obtained from the coupling method between partially brominated poly(HDTDSCB) and PMMA anion at 0 °C.

used for grafting the 2.5K PMMA, the significant shift in the GPC profile clearly supports the conclusion that CPCSRG-10−2.5 should contain more than one grafted PMMA chain. In contrast, in the case of the CPCSRG-10−5 and CPCSRG-10−10 samples, the GPC peak terminates at about the same retention time as the PCS homopolymer. We attribute this to the likely presence of residual PCS homopolymer due to the relatively low degree of bromination in these cases (5 and 2%). Because of the high polydispersity of the starting PCS homopolymer and the random nature of the bromination process, many PCS chains would be statistically unbrominated at the low bromination degree leading to the formation of ungrafted PCS homopolymer upon reaction with PMMA, particularly at the low end of the molecular weight range. The molecular weight of the grafted PMMA also strongly affects the polydispersity of the graft copolymers. In particular, the polydispersity of CPCSRG-10−10 has increased to 5.0 after the coupling reaction, while the polydispersities of the CPCSRG-10−2.5 and CPCSRG-10−5 samples remain relatively close to that of the PCS homopolymer (Table 1). This large increase in polydispersity is attributed to the fact that the $M_n$ of the PMMA side chains in this case is essentially the same as that of the PCS homopolymer, which, along with the high initial polydispersity of the PCS and the resultant higher number of bromination sites for the higher molecular weight species, leads to a substantial extension of the high end of the molecular weight distribution for the homopolymer. Thus, judging from the $^1$H NMR spectra and the GPC traces, the coupling reaction was carried out successfully at low temperature without any lithiation or ring opening of the disilacyclobutane ring in the backbone.

The anionic coupling reaction of the PS anion to the partially brominated poly(HDTDSCB) was also investigated because the graft copolymer is expected to provide a nonpolar, nanoporous, polycarbosilane-based material after thermal degradation of the PS. In the case of the coupling reaction carried out at room temperature, about 40−60% of insoluble material was obtained because of the cross-linking of the disilacyclobutane ring in the main chain. The remaining soluble polymer was characterized by $^1$H NMR, and the proton peak corresponding to the ring-opened Si−C$H_2$−Si linkage was observed at 0.1 ppm, as was seen for the product of the PMMA anionic coupling reaction at 0 °C. To decrease the effective nuclophilicity of the PS anion, the coupling reaction temperature was decreased to −78 °C in THF. Although the amount of ring-opened and cross-linked polymer was decreased in this case to 20−25%, it was impossible to avoid the ring-opening reaction. Generally, the reactivity of anionic species can be affected by solvent, counterion, ligand, and other factors. In particular, the apparent propagation rate constant of PS is decreased by 2 and 3 orders

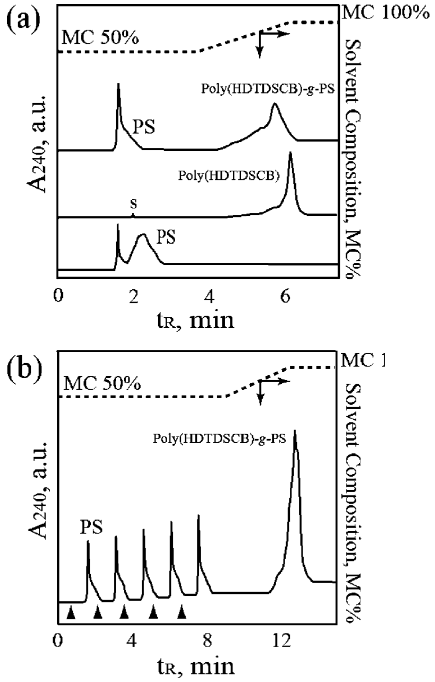


**Figure 6.** TADIC separation conditions (a) and multiple injections (b) showing the separation of excess PS homopolymer from poly(HDTDSCB)-*g*-PS copolymer (s: solvent; ▲: injections).

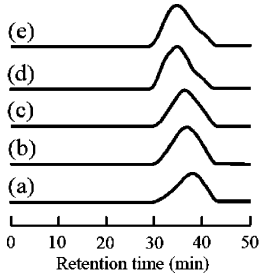


**Figure 7.** GPC (UV = 240 nm) curves before (a) and after (b) 2, (c) 4, (d) 7, and (e) 11 h in the synthesis of poly(HDTDSCB)-*g*-PS by using ATRP.

**Table 2. Molecular Characterization of the Poly(HDTDSCB)-*g*-PS Copolymers Prepared by the ATRP Method**

| reaction time (h) | $M_n$[a] (PDI) | chemical composition of PS (%)[b] |
|---|---|---|
| 0 | 10K (1.9) | 0 |
| 2 | 13K (2.2) | 34 |
| 4 | 15K (2.3) | 46 |
| 7 | 19K (2.5) | 66 |
| 11 | 20K (2.6) | 70 |

[a] Determined by GPC relative to polystyrene. [b] Weight chemical composition calculated by comparing the integration of the ortho-position proton peak of PS with the integration of tolyl−methylene peak of poly(HDTDSCB) in $^1$H NMR.

of magnitude in a nonpolar solvent (cyclohexane) compared to the rate constants in a polar solvent (THF).[21] The decrease in propagation rate with decreased solvating power of the reaction medium is due mainly to the decreased fraction of free ions present relative to ion pairs. Therefore, we used cyclohexane to suppress the ring-opening reaction of the disilacyclobutane in the PS anionic coupling reaction. The obtained polymer was entirely soluble in both hexane and THF. To remove the excess PS homopolymer and confirm the selective adsorption of the poly(HDTDSCB) segment to the C18 column, we applied the TADIC HPLC technique with this sample as was described previously in the case of the CPCSRG(PMMA)-10−10 separation. As shown in Figure 6a, a 10 times molar excess of PS homopolymer was eluted at 2−3 min elution time under the same TADIC conditions, and the poly(HDTDSCB) segment was fully adsorbed to the C-18 column. Moreover, multiple injections showed results that were consistent with that of poly(HDTDSCB)-*g*-PMMA (Figure 6b). The $^1$H NMR spectrum of the separated copolymer showed <10% of the ring-opened proton peak at 0.1 ppm.

As an alternative strategy to suppress the ring opening of the disilacyclobutane rings in the main chain, we used the ATRP method to prepare the poly(HDTDSCB)-*g*-PS copolymer because it employs relatively mild reaction conditions compared to the anionic coupling reaction (Scheme 2 (route 2)). In addition, in this “grafting from” method, we do not need to separate the homopolymer from the graft copolymer after the reaction. In this case, we used CuBr and 2,2′-bipyridyl to graft PS from 6% brominated poly(HDTDSCB). After 2, 4, 7, and 11 h, the GPC peaks showed a clean shift to the increasingly higher molecular weight of the graft copolymer (Figure 7, Table 2), and a shoulder attributed to a small amount of unbrominated, low molecular weight poly(HDTDSCB) appeared after 7 h (Figure 7d,e). The presence of some unbrominated poly(HDTDSCB) is expected statistically due to the random nature of the bromination process and the relatively low molecular weight and polydispersity of the poly(HDTDSCB). In the $^1$H NMR spectra of the four graft copolymer samples (Figure 8), the integration of the proton peaks (f, g) of PS relative to that of the $C_6H_4{-}CH_3$ proton peak (a) of poly(HDTDSCB) showed an increase with increasing reaction time and indicated a PS composition of 34, 46, 66, and 70% after 2, 4, 7, and 11 h, respectively (Table 2). It is notable that no proton peaks attributable to the $Si{-}CH_2{-}Si$ linkage were seen for these four samples in the $^1$H NMR spectra; however, another type of $Si{-}CH_x$ proton peak appeared at −0.3 ppm after 7 h, which was assigned to a $Si{-}CH_3$ environment. Thus, it appears that some ring opening does occur in this case, at least after 7 h, but that the ring-opened proton peak species was different from that produced by the anionic coupling reaction of PMMA or PS to brominated poly(HDTDSCB).

The metal-catalyzed ring-opening polymerization of disilacyclobutanes is well-known, although the metal catalysts employed are usually from the Pt group metals.[22−24] Nonetheless, Nametkin[15] and Ogawa et al.[16] have reported the polymerization of disilacyclobutanes by metal halides such as $AuCl_3$, $CuCl_2$, and CuCl. Ogawa used CuCl for catalytic ring-opening polymerization with several disilacyclobutane derivatives; the exothermic peak resulting from the ring opening of disilacyclobutane was in the range 145−155 °C in his DSC study. Generally, disilacyclobutanes undergo thermally induced ring opening above 200 °C, and the temperature can be decreased to 140 °C in the presence of copper species or even to room temperature by transition metal complexes such as platinum[23] or $Pt(acac)_2$.[24] To test for the catalytic effect of the ATRP catalyst on the disilacyclobutane ring opening, we mixed an excess of CuBr−Bipy complex with the poly(HDTDSCB) homopolymer (mole ratio of CuBr−Bipy:poly(HDTDSCB) = 1:3) and investigated the effect on the exothermic peak produced by ring opening in the DSC. As is shown in Figure 9, without CuBr−Bipy the thermal cross-linking started at ca. 270 °C, and the peak shape was somewhat broad (two exothermic peaks occur due to the presence of two DSCB isomers in the cyclolinear polymer; this will be discussed further in a subsequent paper). However, the temperature was decreased to 220 °C by the CuBr−Bipy addition, and the exothermic peak shape became sharper, indicating a catalytic effect. The catalytic ring opening of the disilacyclobutane rings with CuBr showed similar

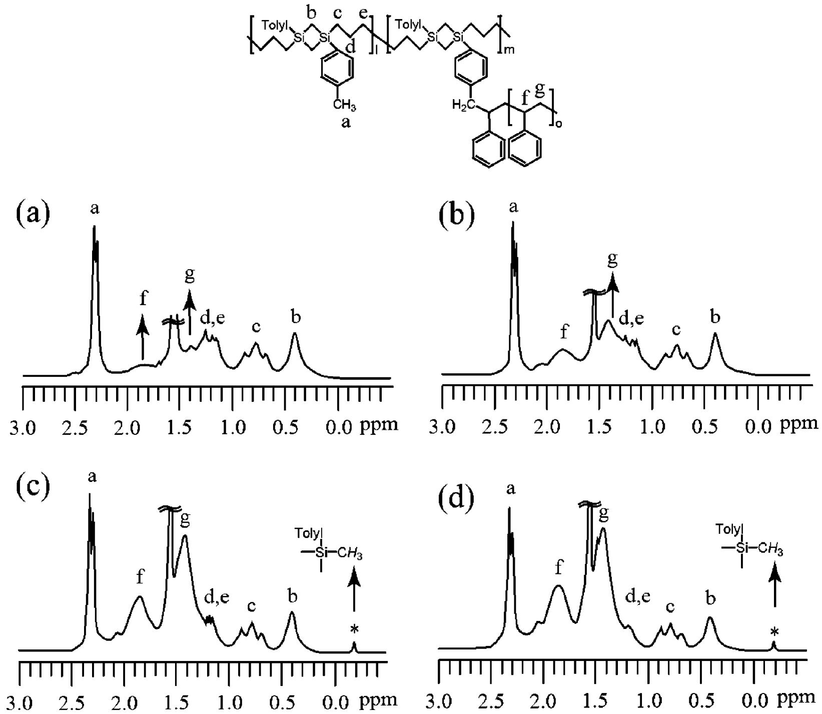


**Figure 8.** $^1$H NMR spectra after (a) 2, (b) 4, (c) 7, and (d) 11 h in the synthesis of poly(HDTDSCB)-*g*-PS by using ATRP.

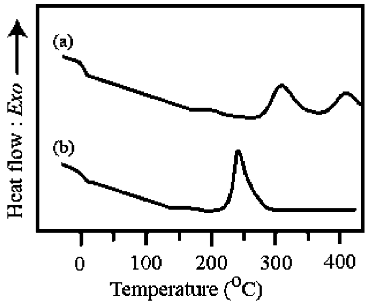


**Figure 9.** DSC scan of the poly(HDTDSCB) homopolymer (a) without and (b) with CuBr.

results with that of the CuBr−bipyridyl complex in a separate DSC study. Therefore, since the ATRP reaction temperature was 95 °C, which is much lower than the 240 °C initiation temperature for the CuBr-catalyzed ring opening, it is reasonable to suppose that the rate of the ring-opening reaction is relatively slow under these conditions. Another reason for the suppression of the ring-opening reaction may be the stabilized nature of the radical site in ATRP along with the low concentration of radical species.[14]

In addition, the course of the ring-opening reaction is clearly different in the case of the ATRP method as compared with that which occurs during the anionic coupling reaction. The formation of the Si−CH$_2$−Si linkage in the anionic coupling reaction presumably involves nucleophilic attack of the anion species at the silicon atoms of the disilacyclobutane ring in the main chain, followed by a cross-linking reaction. In contrast, in the case of the ATRP process, we speculate that when ring opening does become evident after about 7 h, the radical formed at the methylene positions of the disilacyclobutane rings in the main chain may be have a lower reactivity than that of the free radical, finally undergoing ring opening without cross-linking to produce Si−CH$_3$ units only after adding methanol. Moreover, we suspect that this presumed Si−CH$_2^{\bullet}$ radical serves as an initiation site for styrene polymerization based on the $^1$H NMR spectrum. Thus, if we compare the integration values of the Si−C$H_3$ proton after 7 and 11 h, it was slightly decreased after 11 h; this could mean that the formed radical initiates the styrene monomer, followed by polymerization. However, we can see that the ring was relatively well preserved, judging from the fact that the integration ratio between proton (b) and proton (c) (Figure 8) in the graft copolymer was almost the same in the $^1$H NMR spectrum. The amount of Si−CH$_3$ formed was less than 2% after both 7 and 11 h in the ATRP grafting reaction, indicating that the poly(HDTDSCB)-*g*-PS graft copolymer with intact DSCB cyclic rings incorporated in the main chain can be obtained by using the ATRP strategy.

## Experimental Section

**Materials.** All solvents were purified by distillation and transferred by the cannula method or a gastight syringe under a N$_2$ or Ar atmosphere. Chloromethyltrichlorosilane was kindly donated by Starfire Systems, Inc. 4-Bromo-1-butene was purchased from Alfa Aesar Co. THF was purified by distillation from purple sodium/benzophenone solution and transferred using the trap-to-trap distillation method on a high-vacuum line for anionic polymerization. Styrene (St) (Aldrich, 99%) was dried with CaH$_2$ for 1 day followed by distillation and then distilled again from a solution of dibutylmagnesium and stored at −10 °C. Methyl methacrylate (MMA) (Aldrich, 99%) was distilled from excess of triethylaluminum solution (1.0 M in hexanes) and distilled again just before use. 1,1-Diphenylethylene (DPE) was purified with oligo(St) anion solution and distilled by the trap-to-trap distillation method. Copper(I) bromide (CuBr) (99.999%) was stirred in glacial acetic acid overnight, filtered, washed with absolute ethanol, and dried under vacuum at 60 °C overnight. Magnesium, 4-bromotoluene, the second-generation Grubbs catalyst, tripropylamine, *p*-toluenesulfonylhydrazide, *N*-bromosuccinimide (NBS), benzoyl peroxide, 1,1-diphenylethylene (DPE), *sec*-BuLi, and 2,2′-dipyridyl (>99%) were purchased from Aldrich Chemical Co. and used as received without further purification.

**Instrumentation.** $^1$H NMR (500 MHz) and $^{29}$Si NMR (99.3 MHz) spectra were obtained in CDCl$_3$ on a Varian 500 MHz Unity INOVA spectrometer. Gel permeation chromatography (GPC) with a refractive index and UV detector was carried out on four Shodex and Styragel columns (KF-8025, KF-804, HR4, KF-805) using THF as an eluent at a flow rate of 1 mL/min. Molecular weights were determined relative to polystyrene standards to obtain $M_n$ and the molecular weight distribution. HPLC was carried out using a dual piston pump (Lab Alliance, Series 1500), a six-port sample injector (Rheodyne, 7125), and a Shimadzu dual UV detector (SPD-10Avp) operated at wavelengths of 240 and 260 nm. A C18 analytical column (Zorbax SB-C18, 100 Å pore, 5 $\mu$m particle size, 150 × 4.6 mm i.d.) was used. DSC measurements were carried out with a TA 2920 instrument from −20 to 430 °C (heating rate 10 °C/min).

**Synthesis of 1,3-Di(but-3-enyl)-1,3-ditolyl-1,3-disilacyclobutane (DBDTDSCB).** The synthesis procedures employed for DBDTDSCB were similar to those described in our previous report.[7]

**1. Preparation of Chloromethyldichlorotolylsilane.** The product from the reaction of chloromethyltrichlorosilane and tolylmagnesium bromide was collected at 80 °C/0.6 mmHg. Yield: 56%. $^1$H NMR (CDCl$_3$): $\delta$ 2.42 (s, 3H, $C_6H_4CH_3$), 3.30 (s, 2H, $SiCH_2Cl$), 7.31−7.70 (q, 4H, $C_6H_4$), $^{29}$Si NMR (CDCl$_3$): $\delta$ 7.68.

**2. Preparation of 1,3-Diisopropoxy-1,3-ditolyl-1,3-disilacyclobutane (DIPTDSCB).** This compound was obtained from the Grignard coupling of chloromethylchloroisopropoxytolylsilane with magnesium and was collected by distillation at 140 °C/0.6 mmHg. Yield: 40%. $^1$H NMR (CDCl$_3$): $\delta$ 0.88 (s, 4H, $SiCH_2Si$), 1.02−1.23 (d, 12H, $OCHCH_6$), 2.3−2.4 (d, 6H, $C_6H_4CH_3$), 3.93−4.25 (m, 2H, $OCHCH_6$), 7.0−7.7 (m, 8H, $C_6H_4$), $^{29}$Si NMR (CDCl$_3$): $\delta$ −3.57 (trans), −4.5 (cis).

**3. Preparation of 1,3-Dichloro-1,3-ditolyl-1,3-disilacyclobutane (DCDTDSCB).** After reaction of the DIPTDSCB with acetyl chloride and ferric chloride, the DCDTDSCB was collected by vacuum distillation at 160 °C/0.4 mmHg. Yield: 70%. $^1$H NMR (CDCl$_3$): $\delta$ 1.41 (s, 4H, $SiCH_2Si$), 2.41 (s, 6H, $C_6H_4CH_3$), 7.28−7.72 (q, 8H, $C_6H_4$). $^{29}$Si NMR (CDCl$_3$): $\delta$ 12.36.

**4. Preparation of 1,3-Di(but-3-enyl)-1,3-ditolyl-1,3-disilacyclobutane (DBDTDSCB).** The final product was collected, after reaction of the DCDTDSCB with the Grignard reagent formed from 4-bromo-1-butene, by vacuum distillation at 180 °C/0.2 mmHg. Yield: 70%, $^1$H NMR (CDCl$_3$): $\delta$ 0.55 (m, 4H, $SiCH_2Si$), 0.93−1.07 (t, 4H, $SiCH_2CH_2$), 2.02−2.08 (q, 4H, $CH_2CH_2CH$), 2.19 (s, 6H, $C_6H_4CH_3$), 4.8−5.03 (m, 4H, $CH_2CHCH_2$), 5.7−6.0 (m, 2H, $CH_2CHCH_2$), 7.01−7.5 (m, 8H, $C_6H_4$). $^{29}$Si NMR (CDCl$_3$): $\delta$ 0.61 (trans), 0.4 (cis).

**ADMET Polymerization.** The DBDTDSCB (>98%) was placed in a round-bottom flask equipped with a glass stopcock and dried under vacuum for 1 day. After the flask was introduced into an inert atmosphere glovebox, the second-generation Grubbs catalyst (100:1/monomer:catalyst) was added, and the mixture was stirred under vacuum at 50 °C. After 1 day, an additional aliquot of catalyst was added and stirring at 65 °C was continued for 6 days. A minimal amount of dried THF, sufficient to allow continued stirring, and catalyst were added periodically while monitoring the $M_w$ change of the polymer until it did not increase. The resultant unsaturated poly(1-(hex-3-enyl)-1,3-ditolyl-1,3-disilacyclobutane) polymer was precipitated by pouring into methanol and then vacuum-dried. Yield: 85%. $^1$H NMR (CDCl$_3$): $\delta$ 0.3−0.57 (br, 4H, $SiCH_2Si$), 0.65−0.95 (br, 4H, $SiCH_2CH_2$), 1.72−2.01 (br, 4H, $CH_2CH_2CH$), 2.21−2.39 (br, 6H, $C_6H_4CH_3$), 5.01−5.21 (br, 2H, $CH_2CHCH_2$), 7.01−7.53 (br, 8H, $C_6H_4$).

**Hydrogenation of Unsaturated Poly(1-(hex-3-enyl)-1,3-ditolyl-1,3-disilacyclobutane).** 5 g of unsaturated poly(1-(hex-3-enyl)-1,3-ditolyl-1,3-disilacyclobutane) dissolved in 300 mL of xylene was added to a 500 mL of round-bottom flask equipped with a condenser under nitrogen at room temperature. Tripropylamine (TPA) (4.3 g, 0.03 mol) and *p*-toluenesulfonhydrazide (TSH) (5.6 g, 0.03 mol) were added to this flask, and the mixture was heated at 110 °C for 5 h. Additional equivalents of TPA and TSH were added to the mixture, and it was stirred for 10 h. After cooling, the solution was filtered and precipitated twice into an excess of methanol. A hexane solution of the poly(1-hexyl-1.3-ditolyl-1,3-disilacyclobutane) (poly(HDTDSCB)) was passed through a silica-packed column to remove the Grubbs catalyst. The product viscous liquid polymer was dried under vacuum for 2 days. Yield: 90%. $^1$H NMR (CDCl$_3$): $\delta$ 0.3−0.57 (br, 4H, $SiCH_2Si$), 0.65−0.95 (br, 4H, $SiCH_2CH_2$), 1.02−1.5 (br, 8H, $CH_2CH_2CH_2$), 2.21−2.39 (br, 6H, $C_6H_4CH_3$), 7.01−7.53 (br, 8H, $C_6H_4$). $T_g$ (by DSC) = −6 °C.

**Graft Copolymer Syntheses. 1. Synthesis of Partially Brominated Poly(HDTDSCB).** Partially brominated poly(HDTDSCB) was prepared by using *N*-bromosuccinimide (NBS)/benzoyl peroxide in carbon tetrachloride solution. To obtain 10%, 5%, and 2% brominated poly(HDTDSCB), each of 8.9 mg (0.5 mmol), 4.5 mg (0.25 mmol), and 1.8 mg (0.1 mg) of NBS and a half molar ratio of benzoyl peroxide to NBS were added to 2.5 g (0.25 mmol) of poly(HDTDSCB) in 80 mL of carbon tetrachloride. The solution was shielded from light and refluxed for 9 h at 60 °C. After filtering with a 0.2 $\mu$m syringe filter, the solution was poured in methanol and filtered, and the resultant solid polymer was then filtered and vacuum-dried overnight at 60 °C. $^1$H NMR (CDCl$_3$): $\delta$ 0.3−0.57 (br, 4H, $SiCH_2Si$), 0.65−0.95 (br, 4H, $SiCH_2CH_2$), 1.02−1.5 (br, 8H, $CH_2CH_2CH_2$), 2.21−2.39 (br, 6H, $C_6H_4CH_3$), 7.01−7.53 (br, 8H, $C_6H_4$).

**2. Preparation of Poly(HDTDSCB)-*g*-PMMA.** The anionic polymerization of methyl methacrylate (MMA) was carried out in THF −78 °C with 1,1-diphenyl-3-methylpentyllithium as an anionic initiator. In a 250 mL round-bottom flask equipped with a high-vacuum stopcock, 80 mL of dried THF and a distilled 1.2 times molar excess of 1,1-diphenyl ethylene with respect to the target initiator concentration were introduced. *sec*-BuLi was slowly added dropwise until the light red color of 1,1-diphenyl-3-methylpentyllithium appeared to remove impurities, and the calculated amount of *sec*-BuLi was added.

After adding *sec*-BuLi at −78 °C, the purified MMA monomer was immediately added to the solution, and it was stirred for 3 h. A 5 times molar excess of the PMMA anion solution was added to the brominated poly(HDTDSCB) in THF at 0 or −78 °C and stirred for 3 h. After the coupling reaction, an excess of dried 1-butanol was introduced, followed by pouring into 10 times the volume of methanol. The obtained graft copolymer was dried using a vacuum oven for 2 days. $^1$H NMR (CDCl$_3$): $\delta$ 0.3−0.57 (br, 4H, $SiCH_2Si$), 0.65−0.95 (br, 7H, $SiCH_2CH_2$ and $C{-}CH_3$ overlapped), 1.02−1.5 (br, 8H, $CH_2CH_2CH_2$), 2.21−2.39 (br, 6H, $C_6H_4CH_3$), 3.6 (s, 3H, $OCH_3$), 7.01−7.53 (br, 8H, $C_6H_4$).

**3. Preparation of Poly(HDTDSCB)-*g*-PS.** Poly(HDTDSCB)-*g*-PS was prepared by both an anionic coupling reaction and the ATRP method.

*By the Anionic Coupling Method.* All polymerizations were carried out under dry argon in a flask equipped with two-way high-vacuum stopcocks, and all glassware was flamed under vacuum before use. The anionic polymerization of styrene was carried out in THF at −78 °C or cyclohexane at 50 °C. In a 250 mL round flask, dried THF and distilled styrene monomer were added under an argon atmosphere. After degassing three times, 1.4 M *sec*-BuLi in hexane was added at −78 °C in THF or 50 °C in cyclohexane and stirred vigorously for 30 min or 3 h, respectively. A 5 times molar excess of PS anion solution with respect to the bromination sites of poly(HDTDSCB) was introduced to 6% brominated poly(HDTDSCB) dissolved in dried THF at −78 °C or cyclohexane at room temperature and stirred for 60 min. After completion of the coupling reaction, an excess of dried 1-butanol was introduced, followed by pouring into 10 times the volume of methanol. The obtained graft copolymer was dried in a vacuum oven for 2 days.

*By the ATRP Method.* 14.3 mg (0.1 mmol) of purified CuBr, 31 mg (0.2 mmol) of 2,2-bypyridyl, and 1 mL (9.6 mmol) of styrene were placed in a Schlenk flask. 0.1 g (0.02 mmol) of 6% partially brominated poly(HDTDSCB) dissolved in 3 mL (28.8 mmol) of styrene was transferred to the Schlenk flask at room temperature. After three cycles of freeze−pump−thaw were performed to remove oxygen, the flask was immersed in a 95 °C oil bath. Samples were taken out from the flask via syringe after 2, 4, 7, and 11 h and precipitated into methanol. $^1$H NMR (CDCl$_3$): $\delta$ 0.3−0.57 (br, 4H, $SiCH_2Si$), 0.65−0.95 (br, 7H, $SiCH_2CH_2$ and $C{-}CH_3$ overlapped), 1.02−1.7 (br, 10H, $CH_2CH_2CH_2$ and $CHPhCH_2$), 1.7−2.1 (br, 1H, $CHPh$), 2.21−2.39 (br, 6H, $C_6H_4CH_3$), 6.25−7.53 (br, 13H, $C_6H_4$ and $CHPh$).

**Total Adsorption−Desorption Interaction Chromatography (TADIC) To Remove Excess PMMA or PS Homopolymer.** The obtained polymer mixture of PMMA or PS (10K) homopolymer with the graft copolymer from the anionic coupling procedure was dissolved in 50/50 $CH_2Cl_2$/$CH_3CN$(v/v) to make a 5 mg/mL solution. 20 $\mu$L of the solution was injected, and 50/50 $CH_2Cl_2$/$CH_3CN$ (v/v) was employed as an initial eluent for 4 min. The eluent composition was slowly increased to 100% $CH_2Cl_2$ at a rate of 20%/min and maintained for 1 min. For larger scale separations, multiple injections were applied in the TADIC strategy. The polymer solution was injected five times every 90 s under 50/50 $CH_2Cl_2$/$CH_3CN$ (v/v) isocratic conditions, and the eluent composition was increased to 100% $CH_2Cl_2$ at a rate of 15%/min and maintained for 2 min.

## Conclusions

A cyclolinear polycarbosilane, poly[−$(CH_2)_6$-*cyclo*-{SiTolyl-$(CH_2)_2$SiTolyl}−] poly(HDTDSCB), was synthesized by ADMET polymerization, and a series of PMMA (2.5K, 5K, and 10K) side chains were successfully grafted onto the polycarbosilane chain via a "grafting onto" anionic coupling reaction with partially brominated poly(HDTDSCB), without lithiation or ring opening of disilacyclobutane in the main chain at low temperature (−78 °C). Because of the acidity of the proton in the disilacyclobutane ring, lithiation and/or ring opening occurred by treatment with the PMMA anion at 0 °C, as was confirmed by $^1$H NMR spectroscopy, resulting in eventual cross-linking of the copolymer. On the other hand, because of the more basic character of the corresponding PS anion, some ring opening of the disilacyclobutane moieties in the main chain of poly(HDTDSCB) was evidenced in efforts to apply this "graft onto" strategy with 6% brominated poly(HDTDSCB) even at −78 °C in THF or in cyclohexane. However, the "grafting from" method by ATRP showed relatively good conversion to poly(HDTDSCB)-*g*-PS without cross-linking or appreciable ring opening up to at least 7 h under the ATRP reaction conditions. In addition, we found that the excess of PMMA or PS homopolymer in the as-synthesized samples can be removed from the poly(HDTDSCB) containing homo or graft copolymer through the TADIC strategy, in which the poly(carbosilane)-based polymer was selectively adsorbed onto a C18 column at a 50/50 $CH_2Cl_2$/$CH_3CN$ (v/v) eluent condition and the graft copolymer was eluted by changing the eluent composition to 100% $CH_2Cl_2$. A multiple injection technique was applied in which the PS or PMMA homopolymer was eluted during successive sample injections and the accumulated poly(carbosilane)-based polymer on the C18 column at 50/50 $CH_2Cl_2$/$CH_3CN$ (v/v) was obtained by increasing the $CH_2Cl_2$ eluent composition.

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**Supporting Information Available:** TADIC figures showing free of PMMA homopolymer from purified CPCSRG-10−2.5 and CPCSRG-10−5; TADIC figure of poly(HDTDSCB)-*g*-PMMA copolymer after coupling reaction at 0 °C. This material is available free of charge via the Internet at http://pubs.acs.org.

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