# Hyperbranched Polyglycidol on Si/SiO$_2$ Surfaces via Surface-Initiated Polymerization

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ABSTRACT: We demonstrate a new procedure to synthesize covalently linked hyperbranched polyglycidol brushes on Si/SiO$_2$ surfaces via anionic ring-opening multibranching polymerization of glycidol at 110 °C. Optimization of the polymerization experiments by exploiting reinitiation cycles produced polyglycidol brushes with ellipsometric thickness values of up to 70 nm. $^{13}$C NMR spectroscopy analysis of cleaved polymer allowed the elucidation of the structure and degree of branching of the polymer.

## Introduction

In recent years, there has been considerable interest in the synthesis of polymer brushes via controlled or "living" surface-initiated polymerizations.[1−7] These ultrathin polymer films would provide a chemically and mechanically robust layer (in contrast to self-assembled monolayers) to control surface properties such as corrosion inhibition, chemical sensing, and cellular engineering. Typically, the polymer brushes are grown from gold or Si/SiO$_2$ substrates that are functionalized with initiator-terminated self-assembled monolayers.[8−10] Examples of the reactions include controlled radical polymerizations, such as atom transfer radical polymerization (ATRP),[1,8−10] ring-opening metathesis polymerization,[6] and living anionic[11] or cationic[12] polymerizations. Brushes with functional groups can be used to increase the loading capacity for the covalent coupling of biomolecules to surfaces. Dendritic and hyperbranched polymers could provide even higher densities of reactive groups on the surface.[13−16]

Typically, dendrimers and hyperbranched polymers have been *grafted to* surfaces by reacting polymers with reactive groups on the surfaces. Newkome et al.[17] demonstrated the synthesis and characterization of immobilized dendrimers on silica or glass. Bergbreiter et al.[18−21] have shown the formation of poly(acrylic acid) grafts on polyethylene or polypropylene via reaction with $-CO_2H$ groups on the surfaces. Furthermore, Fujiki et al.[22] have postgrafted hyperbranched polyamidoamines from terminal amino groups of polymer chains grafted onto silica surfaces. The postgrafting reaction was achieved by repeated Michael additions of methyl acrylate to amino groups in conjunction with amidation of the resulting ester units. However, very few papers have reported the formation of surface-initiated hyperbranched polymers using *grafting-from* techniques. The advantage of the grafting-from method is the higher degree of control over the placement of polymers and the opportunity to create much thicker films. Mori et al.[23] described the synthesis of hyperbranched polymer-silica hybrid nanoparticles by self-condensing vinyl polymerization (SCVP) via ATRP from silica surfaces. ATRP initiators were covalently linked to the surface of silica particles, followed by SCVP of an initiator-monomer ("inimer"), which has both a polymerizable acrylic group and an initiating group in the same molecule. Brush growth was hard to control, and substantial amounts of polymers were formed in solution.

In this paper we utilize a grafting-from technique to form hyperbranched polyglycidol on Si/SiO$_2$ surfaces via anionic ring-opening polymerization of glycidol. To our knowledge, this is the first example of a study where polymer brushes are grown directly from the surface using surface Si−OH groups as initiators, eliminating the need for initiator functionalized self-assembled monolayers. Sunder et al.[24] have shown successfully that the anionic polymerization of glycidol in conjunction with 1,1,1-tris(hydroxymethyl)propane (TMP) as the initiator yields hyperbranched aliphatic polyethers with controlled molecular weights and narrow molecular weight distribution.[24,25] A recent study described the synthesis and utilization of pH-responsive molecular nanocarriers for the encapsulation of polar guest molecules based on the selective and reversible shell functionalization of dendritic polyglycidol and polyethylenimine.[26] Hyperbranched polyglycidol brushes attached to surfaces could open up new avenues for surface chemistry and encapsulating layers. Here, we have optimized the reaction conditions for the polymerization of glycidol to grow hyperbranched polymer brushes directly on silica surfaces.

## Materials and Methods

Glycidol (97%) and hydrofluoric acid (40%) were obtained from Fluka Chemika, and glycidol was distilled and dried over molecular sieves prior to use. Toluene was distilled from sodium. Anhydrous methanol (99.8%), tetrahydrofuran, and sodium lumps were purchased from Aldrich, Fisher Chemicals, and Riedel-de Haen, respectively; all these chemicals were used as received. Silicon test wafers were obtained from Compart Technology Ltd.: thickness, 525 ± 50 $\mu$m; type/dop, p/B; Res, 1−10 ohm cm. Silica gel (200 m$^2$/g) was obtained from Aldrich. Deionized water was obtained from an Elgastat option 3 water purifier. Prior to the polymerization reactions, the Si wafers were treated with a mixture of hydrogen peroxide (1 part by vol), ammonium hydroxide (1 part by vol), and distilled water (5 parts by vol) for 20 min at 70 °C and then thoroughly washed with distilled water and ethanol and dried under a N$_2$ stream.

**Ellipsometry** measurements were carried out on a DRE ELX-02C ellipsometer with a 632.8 nm laser at 70° from the normal. A refractive index of 1.46 (equal to poly(ethylene glycol) (PEG)) was used for calculations of polymer thickness.

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A minimum of three different spots was measured on each sample.

**GPC.** Analysis was carried at 70 °C in DMF on a Polymer Laboratories pump (1 cm$^3$/min), using one PLgel MIXED-C column of pore size 5 $\mu$m (linear range of MW: 200−2 000 000) with Knauer differential refractometer detector calibrated against PS standards.

**NMR Spectra.** $^1$H NMR spectra were obtained at 400 MHz on a Bruker DPX-400 MHz machine, and $^{13}$C NMR spectra were obtained at 125 MHz on a Bruker DRX-500 MHz machine.

**IR Spectra.** Spectra were recorded on a Perkin-Elmer 1600 FT-IR spectrometer. Samples were prepared by casting on NaCl plates prior to analysis.

**Synthesis of Hyperbranched Polyglycidol in Bulk.** This procedure has been followed using the example given in the literature.[24] Into a flask under nitrogen was added 0.405 g ($3.02 \times 10^{-4}$ mol) of 1,1,1-tris(hydroxymethyl)propane (TMP) to 6.52 mg ($1.21 \times 10^{-4}$ mol) of sodium methoxide. Then 10 g (0.15 mol) of glycidol was added slowly over 12 h to the stirred melt at a temperature of 95 °C. Then the product was precipitated twice from methanol into acetone and then dried overnight at 80 °C in a vacuum oven. The resultant polymer was a viscous oil (9.602 g, 0.145 mol, 96%). $\upsilon_{max}$ (NaCl plates/cm$^{-1}$ 3302 broad [$\upsilon$(O−H)]; 2904 medium [$\upsilon$(C−H)]; 1645 sharp [$\upsilon$(C−O−C)]; 1460 sharp [$\upsilon$(C−OH)]. $^1$H and $^{13}$C NMR identical to literature.[24] $^1$H NMR: $\delta_H$ (400 MHz, CD$_3$COD) 5.8 (singlet, OH); 3.8 (multiplet, CH); 3.4−3.7 (multiplet, CH$_2$). $^{13}$C NMR: $\delta_C$ (125 MHz, CD$_3$COD) 81 (CH); 80 (CH); 74 (CH$_2$); 73 (CH$_2$); 72.4 (CH$_2$); 71.2 (CH$_2$); 70.9 (CHOH); 64.5 (CH$_2$OH); 63 (CH$_2$-OH). GPC (DMF): $M_n$ = 10 200 g mol$^{-1}$; $M_w$ = 14 300 g mol$^{-1}$; $M_w/M_n$ = 1.4.

**Surface-Initiated Polymerization of Glycidol on Si Wafer.** Polymer film growth was achieved by placing the Si wafer (1.5 cm$^2$) into a 50 mL flask under a N$_2$ atmosphere. The Si wafer was treated with 20 mL of an in situ formed solution of sodium methoxide (0.043 mol/L) for 1 h at 60−70 °C. The sodium methoxide solution was removed via a syringe, and a fresh aliquot of anhydrous methanol (20 mL) was added to the flask to wash the Si wafer. This process of washing with methanol was repeated twice. This washing procedure was repeated three times using toluene (3 × 30 mL). The Si wafer was then dried under vacuum using a temperature of 100 °C for at least 15 min. Under a N$_2$ atmosphere freshly distilled and dried glycidol (2 mL, 0.03 mol) was added to ensure full coverage of the Si wafer in the flask. The polymerization was then allowed to proceed for 15 min at 110 °C, after which removing the substrates from the reaction flask stopped the reaction. The reaction solution was poured into THF (400 mL), and no precipitate or other evidence for the presence of polymer was observed. The Si wafers were washed with water/ethanol and dried under a N$_2$ stream. The ellipsometric thickness measured was 2.9 nm, and the ellipsometer was calibrated with the refractive index of poly(ethylene glycol) (PEG), 1.46. To reinitiate the polymer brushes, the samples were placed in sodium methoxide solution, and the whole procedure described above was repeated.

**Surface-Initiated Polymerization of Glycidol on Silica Gel.** Polymer brush growth was achieved by placing 10 g of silica gel and a stirrer bar into a 100 mL flask under a N$_2$ atmosphere. The silica gel was then treated with 40 mL of an in situ formed solution of sodium methoxide (0.17 mol/L) for 1 h at 25 °C. Then the sodium methoxide solution was removed via a syringe, and a fresh aliquot of anhydrous methanol (40 mL) was added to the flask to wash the silica gel. The process of washing with methanol was repeated twice. This procedure was repeated three times using toluene (3 × 30 mL). The silica gel was then dried under vacuum using a temperature of 100 °C for at least 15 min. Under a N$_2$ atmosphere distilled and dried glycidol (10 mL, 0.15 mol) was added to ensure full coverage of the silica gel in the flask. The mixture was stirred for 45 min at 110 °C, after which removal of the silica gel from the reaction flask stopped the reaction. The reaction solution was poured into THF (400 mL), and no precipitate or other evidence for the presence of polymer was observed. The silica gel was washed with water/ethanol and dried under a N$_2$ stream. To reinitiate the polymer brushes, the samples were placed in sodium methoxide solution, and the whole procedure described above was repeated. $\upsilon_{max}$ (NaCl plates/cm$^{-1}$ 3183 medium [$\upsilon$(O−H)]; 2900 medium [$\upsilon$(C−H)]; 1611 sharp [$\upsilon$(C−O−C)]; 1457 sharp [$\upsilon$(C−OH)].

**Cleavage of Polymer Brush.** Polyglycidol brushes were cleaved by stirring the polymer functionalized silica gel (5 g) (reinitiated twice at 110 °C for 45 min) in 40 mL of an aqueous solution of HF (4%) for over 5 h at 50 °C. Neutralizing the aqueous solution with sodium bicarbonate solution dropwise stopped the reaction. Then the excess water was removed under vacuum to give a white powder. No attempts were made at separating the cleaved polymer from the other compounds in the mixture. The white powder mixture was analyzed using $^1$H and $^{13}$C NMR spectroscopy: $^1$H NMR: $\delta_H$ (400 MHz, D$_2$O) 3.9−3.8 (multiplet, CH); 3.4−3.7 (multiplet, CH$_2$). $^{13}$C NMR: $\delta_C$ (125 MHz, D$_2$O) 81.0 (CH); 79.0 (CH); 72.0 (CH$_2$); 70.7 (CH$_2$); 70.1 (CH$_2$); 69 (CH$_2$); 68 (CHOH); 62.5 (CH$_2$OH); 61.1 (CH$_2$-OH); 60.6 (CH$_2$OH). GPC (DMF): $M_n$ = 5800 g mol$^{-1}$; $M_w$ = 10 400 g mol$^{-1}$; $M_w/M_n$ = 1.8.

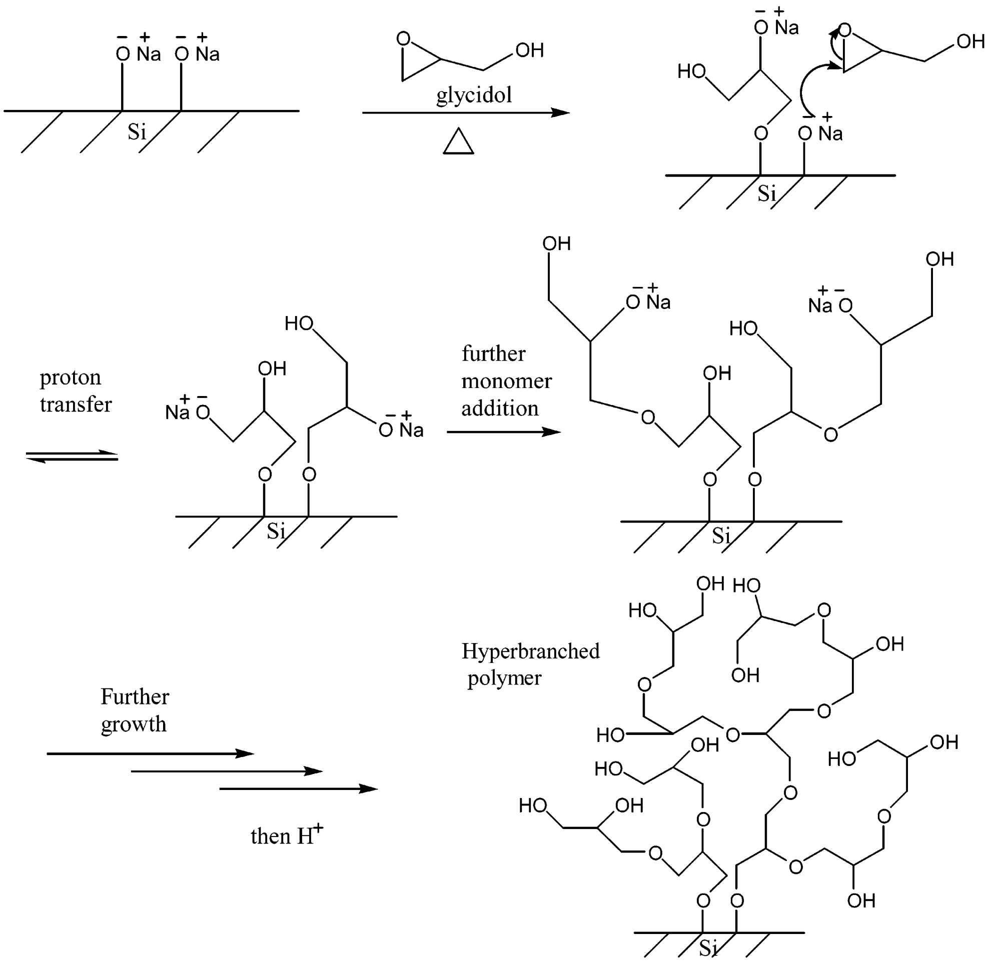
**Synthesis of Esterified Polyglycidol on Si Wafer.** Under N$_2$, into a 50 mL flask containing the polyglycidol brush covered Si wafer (ellipsometric thickness of 2.9 nm) was added pyridine (50 mL), 4-(dimethylamino)pyridine (50 mg, $4.1 \times 10^{-4}$ mol), and palmitoyl chloride (2 mL, $6.6 \times 10^{-3}$ mol). The mixture was refluxed at 140 °C for 24 h. Then the substrate was removed from the flask and washed with CH$_2$Cl$_2$ and dried using a N$_2$ stream. The ellipsometric thickness measured was 4.8 nm, and the ellipsometer was calibrated with refractive index of PEG, 1.46. Esterified polyglycidol brushes on silica gel were obtained in a similar procedure as for Si wafer.

## Results and Discussion

**Formation of Hyperbranched Polyglycidol on Si/SiO$_2$ Surfaces.** Scheme 1 describes the proposed mechanism for the anionic ring-opening multibranching polymerization of glycidol.[24] To initiate hyperbranched brush growth of polyglycidol on Si/SiO$_2$ surfaces, the Si−OH bonds were deprotonated using sodium methoxide solution. After washing the Si/SiO$_2$ surfaces extensively with anhydrous methanol and toluene, distilled glycidol was added to the surfaces under nitrogen, and the polymerization was carried out at a temperature between 90 and 125 °C. The initiator (deprotonated silanol groups) attacks the glycidol monomer on the unsubstituted side and hence produces a secondary alkoxide. This alkoxide can now attack another glycidol monomer or exchange a proton with a neighboring primary alcohol group. The amount of initiator compared to the amount of monomer present is very small, since the initiator sites are only present on the surface of Si/SiO$_2$. For every monomer reacting with the initiator, two potential active sites are attached to the surface; therefore, the concentration of active sites relative to hydroxyl groups decreases, but the actual number of active sites should remain constant. After a set time (15−90 min) the Si/SiO$_2$ substrate was removed from the reaction flask and rinsed with water and methanol.

The low concentration of active sites on the polymer brush is the key to the controlled growth of the brushes. This mechanism leads to controlled brush growth as long as the majority of proton transfer occurs inside the brush film and does not involve unattached glycidol monomers, since this could lead to brush termination and bulk polymerization. We will discuss this issue in more detail below. After polymerizing at various temperatures (from 90 to 125 °C) the optimal reaction temperature was found to be 110 °C. The results from the brush growth at 110 °C are shown in Figure 1a. The

**Scheme 1. Proposed Mechanism for the Formation of Hyperbranched Polyglycidol on a Si Wafer Surface via Anionic Ring-Opening Multibranching Polymerization**



thickness of the polymer layer increases linearly with time, indicating that the polymerization has controlled character.

Experiments carried out at 125 °C gave a steeper graph compared to the graph obtained for the 110 °C series, but significant bulk polymerization occurred after approximately 75 min. At 110 °C the polymerization proceeded without apparent polymerization (gelling up of the liquid phase) in reactions run for 90 min. $^{13}$C and $^{1}$H NMR spectra of the bulk glycidol after 45 min were identical to glycidol as received from Fluka, indicating the presence of only very small amounts of polymer in the reaction medium, if any at all. Overall, the polymerization reaction is mostly confined to the surface. However, a GPC trace of the bulk glycidol did show small amounts of low molecular weight oligomers ($M_n$ = 700 g mol$^{-1}$) in the glycidol after approximately 45 min. These polymers could result from autopolymerization of the glycidol, but this is quite unlikely as shown by Sandler et al.[27] They found only 0.9% of the pure glycidol autopolymerized with heat. The other process that could be responsible for the presence of bulk polyglycidol is by active site transfer from the growing polymer brushes to glycidol in solution via proton transfer.

**Increase in Polyglycidol Brush Thickness via Reinitiation.** The optimum reaction conditions for brush formation yielded a maximum thickness of approximately 15 nm only. To increase the thickness ofthe polyglycidol brush further, reinitiation of the poly-

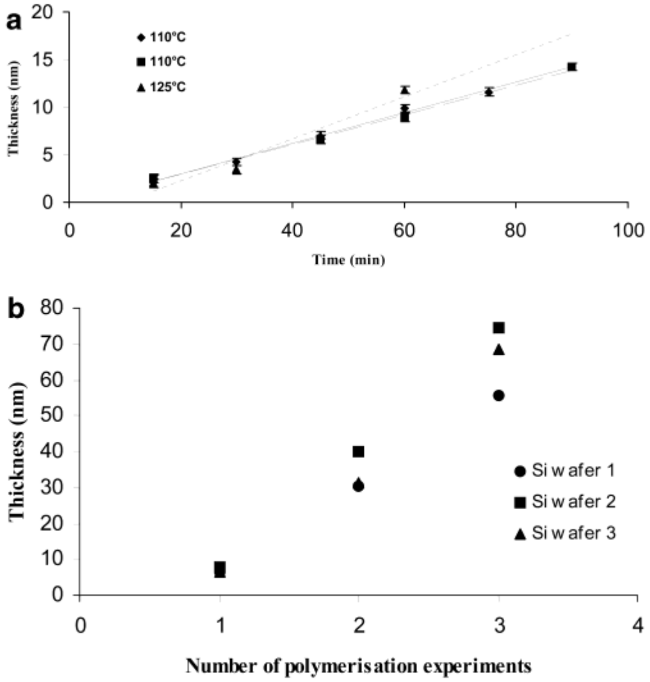
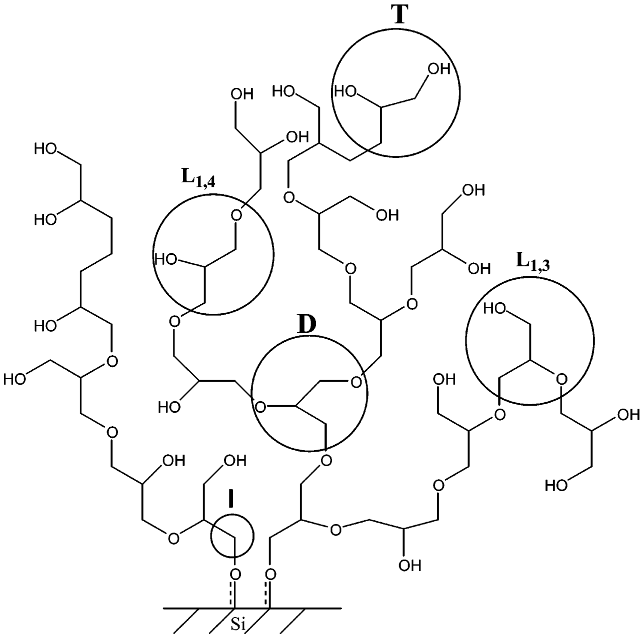


**Figure 1.** (a) Increase in polyglycidol brush thickness (measured by ellipsometry) vs polymerization time on Si wafer using various temperatures. (b**)** Increase in polyglycidol brush thickness on Si wafer (measured by ellipsometry) as a result of reinitiation experiments carried out at 110−115 °C for 45 min.



**Structual units**

**$L_{1,4}$ - linear unit**
**$L_{1,3}$ - linear unit**
**T - terminal unit**
**D - dendritic unit**
**I - secondary initiator site**

$$DB = \frac{2D}{2D + L_{1,3} + L_{1,4} + I}$$

**Figure 2.** Schematic structure of hyperbranched polyglycidol displaying assigned structural units used in the degree of branching equation.

glycidol brush was carried out by exposing the brush films to sodium methoxide and carrying out the same polymerization method as for the initial polyglycidol brush. Every subsequent polymerization was allowed to proceed for 45 min. The results from this series of experiments are shown in Figure 1b. The reinitiation procedure is very successful and reproducible, giving rise to thick brushes (around 70 nm after two reinitiation cycles) of polyglycidol as measured by ellipsometry (Figure 1b). We hypothesize that this rapid increase in brush growth is due to the larger number of reactive groups (that actually initiate a polymer chain) on the surface of hyperbranched polyglycidol as compared to the silicon surface.

**Estimation of the Degree of Branching of Polyglycidol Brushes.** With polymers covalently attached to planar Si wafers it is not possible to employ $^{13}$C NMR spectroscopy to elucidate the structure of the hyperbranched polymers. A larger surface area to cleave the brushes from is required, so we grew and detached the polymer brushes from silica gel. Brushes were grown in a similar procedure as in the case of Si wafers. To ensure sufficient amounts of polymers, the brushes were reinitiated at least two times. The polyglycidol brushes were cleaved by stirring the silica gel in an aqueous solution of HF (4%). After neutralizing the solution with sodium bicarbonate, the cleaved brushes were dried and redissolved in D$_2$O for NMR analysis, shown in Figures 3 and 4. GPC analysis of the cleaved polyglycidol gave a molecular weight of $M_n$ = 5800 g mol$^{-1}$ and a polydispersity ($M_w/M_n$) of 1.8.

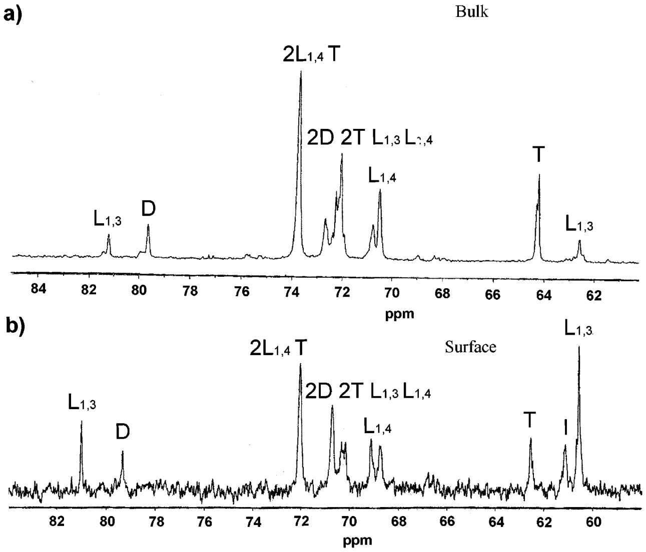


**Figure 3.** $^{13}$C NMR spectra of polyglycidol (a) formed in bulk via anionic polymerization at 95 °C initiated with TMP (solvent: CD$_3$OD) and (b) cleaved brushes from silica gel, prepared via surface-initated polymerization at 110 °C (solvent: D$_2$O). Carbons belonging to the terminal, dendritic, linear 1,3, linear 1,4, and initiator units are indicated by T, D, $L_{1,3}$, $L_{1,4}$, and I, respectively.

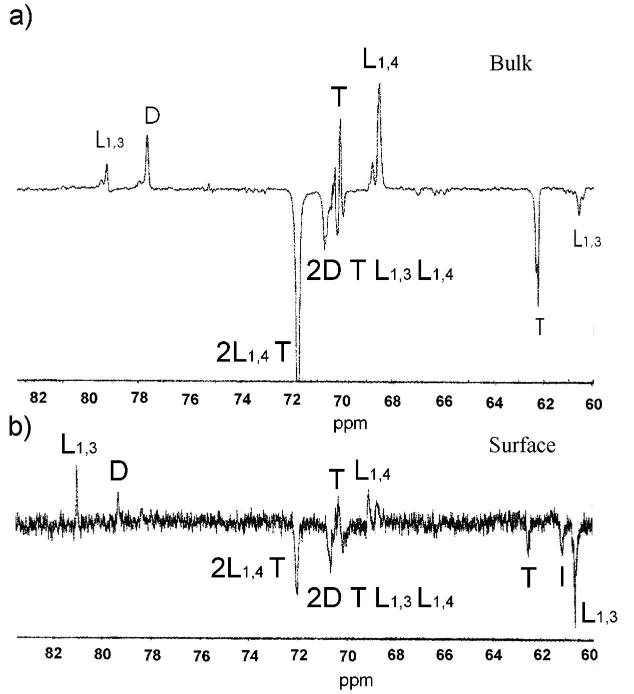


**Figure 4.** $^{13}$C NMR spectra of polyglycidol (a) formed in bulk via the anionic polymerization at 95 °C initiated with TMP (solvent: CD$_3$OD) and (b) cleaved brushes (D$_2$O) from silica gel, prepared via surface-initiated polymerization at 110 °C (solvent: D$_2$O). Carbons belonging to the terminal, dendritic, linear 1,3, linear 1,4, and initiator units are indicated by T, D, $L_{1,3}$, $L_{1,4}$, and I, respectively.

Sunder et al.[24,25] have described the assignment of the signals of the $^{13}$C NMR spectrum of hyperbranched polyglycidol, and a schematic structure is shown in Figure 2. Propagation can occur in a number of different ways. A single addition at the secondary alkoxide (resulting from the ring-opening of the epoxide) yields a linear 1,3 ($L_{1,3}$) unit. Monomer addition at the primary alkoxide (formed after intramolecular proton transfer) results in a linear 1,4 ($L_{1,4}$) unit being incorporated into the polymer brush. When both alcohols are substituted with an additional monomer, a branching point (D) is

**Table 1. Structural Assignment of Polyglycidol Samples Using $^{13}C$ NMR Spectroscopy**

| | shift (ppm) | |
|---|---|---|
| structural unit | hyperbranched polyglycidol formed in bulk | cleaved hyperbranched polyglycidol |
| $L_{1,3}$ | 62.8 | 60.6 |
| I | | 61.1 |
| T | 64.3 | 62.5 |
| $L_{1,4}$ | 70.5−70.8 | 68.8−69.1 |
| 2D, 2T, $L_{1,3}$, and $L_{1,4}$ | 71.9−72.7 | 70.1−70.7 |
| 2 $L_{1,4}$ and T | 73.8 | 72.1 |
| D | 79.8 | 79.3 |
| $L_{1,3}$ | 81.4 | 81.2 |

introduced. However, if no monomers are added, the unit is terminal (T). The cleavage of the polymer brushes from the surface can lead to three different units resulting from the initiator sites. If the first glycidol monomer has reacted fully, the cleaved site will give a signal for the pendant $CH_2OH$ that is identical to a $L_{1,3}$ unit. If the first monomer underwent proton transfer and subsequently only the primary alkoxide reacted, a structural unit identical to a T unit would be formed. Only if reaction took place at the secondary alkoxide (formed directly in the initial ring-opening) a unique structure ($PG{-}O{-}CH(CH_2OH)_2$) will be formed, and in this case the $CH_2OH$ signal is different from the signals observed for the polymerization in bulk; the $CH_2OH$ pendants in this case have been designated as an I unit. Figures 3 and 4 show $^{13}C$ NMR spectra of hyperbranched polyglycidol synthesized in bulk[28] using slow monomer addition (Figures 3a and 4a) via the technique described by Sunder et al.[24] and on a Si surface (Figures 3b and 4b).

Figure 3 clearly shows the similarity between our surface-initiated brushes and the hyperbranched polyglycidol synthesized in bulk. All structural elements ($L_{1,3}$, $L_{1,4}$, D, and T) are present in our brushes, and the values are listed in Table 1. Furthermore, Figures 3b and 4b show a signal at 61.1 ppm that is due to the presence of an I unit in the polyglycidol brush. For comparison, we estimated the degree of branching (DB) using eq 1[29] (Figure 3) and the intensities for the different units obtained from $^{13}C$ APT measurements (Figure 4). The DB of the polyglycidol formed in bulk is 0.46 (literature values[24] up to 0.59), while the DB for the brushes is 0.31.

Interestingly, the $L_{1,3}/L_{1,4}$ ratio is quite different on the brushes compared to the bulk polymers (1:1 instead of ∼1:3). The signals for $L_{1,3}$ at 62.8 and 81.4 ppm in the bulk polymers are very small compared to both $L_{1,4}$ at 73.8 ppm and D at 79.8 ppm. The spectrum in Figure 3b shows that the brushes contain a rather large proportion of $L_{1,3}$ (peaks at 60.6 and 81.2 ppm). In bulk, the $L_{1,4}$ dominates because the primary alkoxide experiences less steric hindrance compared to the secondary.[24,31] A theoretical study of glycidol hyperbranching polymerization by Vazquez et al.[32] shows that the activation energy for primary alkoxide attack on a glycidol monomer in the gas phase is less than that for secondary; this relationship is reversed in solution where the activation energy for reaction at the secondary alkoxide is lower, so secondary attack ($L_{1,3}$) is preferred kinetically. However, the products arising from primary alkoxide ($L_{1,4}$) attack are less sterically hindered and therefore preferred thermodynamically. Vazquez et al.[32] have also shown that the activation energy for proton transfer is less than for propagation, causing branching to dominate in bulk polymerization. Our results on the surface-initiated polymerization of glycidol show that branching still occurs, with a preference for forming the kinetic product. We hypothesize that the increase in monomer-to-initiator ratio on the surfaces increases the rate of propagation that favors polymerization at the secondary alkoxide; the decrease in the degree of branching can be attributed to an increase in the steric demand on the surface.

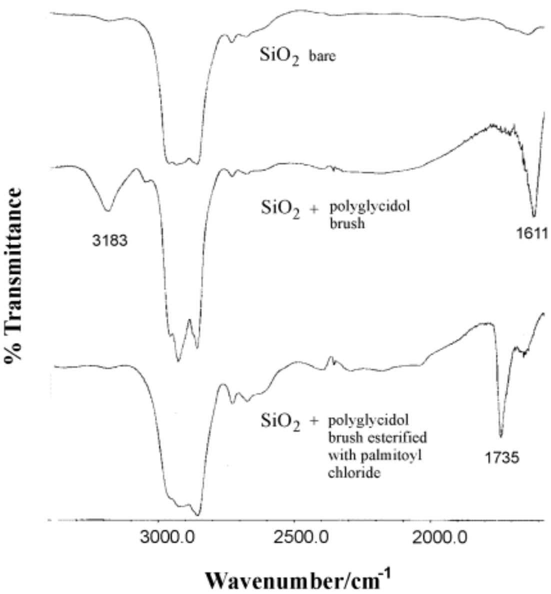


**Figure 5.** IR spectrum (Nujol) of $SiO_2$ bare (top trace), polyglycidol brushes initiated from the surface and doubly reinitiated on $SiO_2$ at 110 °C (middle trace), and polyglycidol brushes on $SiO_2$ esterified with palmitoyl chloride in pyridine at 140 °C (bottom trace).

**Esterification of Hyperbranched Polyglycidol on Si/Silica Gel Surfaces.** The hydroxyl groups present in polyether polymers have the ability to undergo a multitude of postfunctionalization reactions. Both polyglycidol brushes on Si wafers and silica gel were reacted with palmitoyl chloride in the presence of pyridine and 4-(dimethylamino)pyridine following a procedure described by Sunder et al.[33] Figure 5 shows the IR spectra for polyglycidol and esterified polyglycidol on silica gel. The spectroscopic evidence supports the formation of the polyglycidol on the surface of $SiO_2$ particles. The peak at 1611 $cm^{-1}$ is attributed to the ether group (C−O−C) in the polyglycidol brush. The peak attributed to the OH stretch can be seen at 3183 $cm.^{-1}$ The bottom trace for the esterified polyglycidol on silica gel indicates that the esterification reaction was successful in converting essentially all OH groups, as evidenced by the absence of OH stretch signals and the presence of the expected ester carbonyl peak at 1735 $cm.^{-1}$ The success of esterification of the polyglycidol brushes can be further evidenced by the change in polarity of the polyglycidol brush surfaces on Si wafers before and after esterification. Six polyglycidol films of ellipsometric thicknesses ranging from 3 to 40 nm (formed at 110 °C) measured an average advancing contact angle of $\theta_{adv} = 35°$; this value increased to an average $\theta_{adv} = 110°$ after esterification. The receding contact angles increased from $\theta_{rec} = 0°$ (pinned) to $\theta_{rec} = 82°$, clearly showing the hydrophobic nature of the surface.

## Conclusion

A new surface-initiated polymerization was used to synthesize covalently linked hyperbranched polyglycidol brushes on Si/SiO$_2$ surfaces via anionic polymerization of glycidol at 110 °C. Furthermore, reinitiation cycles of the polymerization experiments allowed the formation of up to 70 nm thick polyglycidol brushes. The hydroxyl end groups on the brushes can be easily esterified in postpolymerization reactions. The $^{13}$C NMR spectra of the cleaved polyglycidol in conjunction with the $^{13}$C NMR spectra of the sample of polyglycidol formed in bulk were used to elucidate the structure and degree of branching of the polyglycidol on Si/SiO$_2$ surfaces. The degree of branching was lower than that of hyperbranched polyglycidol formed in bulk, which is mainly due to a combination of high monomer-to-initiator ratios leading to a higher rate of propagation and an increase in steric hindrance on the surfaces. This study demonstrates that hyperbranched polymers of controlled thickness can be formed on Si/SiO$_2$ surfaces, which opens up new opportunities for altering surface chemistry of materials via surface-initiated polymerizations.

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