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Room-temperature one-step immobilization of rod-like helical polymer onto hydrophilic substrates†

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A facile, one-pot immobilization method for a rigid rod-like helical polysilane, poly(*n*-decyl-*i*-butylsilane), was developed onto hydrophilic surfaces at room temperature in the presence of triethylamine as a catalyst.

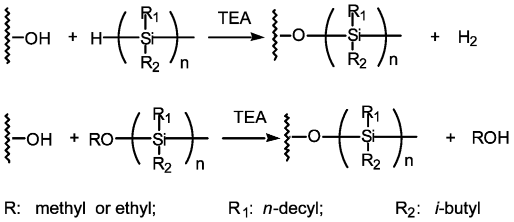
Surface-grafted functional polymers have attracted increasing attention in recent years in both fundamental study and practical applications.[1] Rod-like helical polysilanes, a class of Si-catenated semiconducting polymers, have many excellent optical and electronic properties due to highly delocalized σ-electrons along the silicon backbone.[2,3] The end-grafted rod-like helical polysilanes on solid surfaces may have potential applications such as molecular electronic and photonic devices.[4] Previous studies demonstrated that a few polysilanes could be grafted onto hydrophobic surfaces (Silicon wafer and quartz) by a "cut and graft" technique.[4,5] This technique, however, is very tedious, multi-step procedure, because all these immobilization treatments require an expensive ultra high-vacuum line apparatus, highly dry chemicals, highly flammable and toxic reagents, and skilful technique. Therefore, the development of an innovative, short-step, safer, facile immobilization process of polysilanes onto solid surfaces is of an immediate concern, since polysilanes are sensitive to the graft reaction conditions.

Herein we demonstrate a very simple, mild method to immobilize a highly soluble, rigid rod-like helical polysilane, poly(*n*-decyl-*i*-butylsilane) (PDBS) to hydrophilic surface (quartz and mica) at *room temperature* in the presence of small amount of triethylamine (TEA). PDBS[2,3] used in this experiment was prepared *via* the conventional Wurtz-type condensation of *n*-decyl-*i*-butyldichlorosilane in hot toluene.† According to the Wurtz coupling mechanism proposed previously,[6] the growing chains of polysilanes have three possible termini: silyl radical (polysilane-Si·), silyl anion (polysilane-Si) and silyl chloride (polysilane-Si–Cl). The polysilane-Si· and polysilane-Si groups may then abstract hydrogen atoms from toluene and/or crownether molecules during the polymerization or from alcohol molecules in the subsequent precipitating process, leading to Si–H termini.[6] While polysilane-Si–Cl reacted with ethanol or methanol in the precipitating process, leading to Si–OR end groups. The final isolated PDBS thus should have Si–H and/or Si–OR termini. These end groups were characterized by our FT-IR measurement.†

It is well known that both Si–H and Si–OR groups are directly able to react with Si–OH groups under very mild reaction conditions.[7–15] Therefore, by chemically coupling the Si–H and/or Si–OR end groups of PDBS with OH groups on the hydrophilic surface of quartz and mica, PDBS-grafted solid surface may be possible (Scheme 1). The procedure is very simple. Several freshly pretreated quartz substrates[16] and newly cleaved mica substrates were immersed in a solution of PDBS in isooctane. The concentration of this solution was 0.01 M (based on the Si repeat units). A small amount of TEA was added as a catalyst. After different reaction time, the samples were taken out and repeatedly rinsed with dry *n*-hexane which is a very good solvent for PDBS. The samples were then immersed in fresh *n*-hexane for 2 h. The process was repeated once more to completely remove physically adsorbed polymer chains on solid surface. Finally, the samples were sufficiently washed with *n*-hexane, and dried over in a stream of nitrogen gas.

Because the rod-like PDBS affords an intense UV absorption band at 319 nm due to 7_3 helical main-chain conformation,[2,3] PDBS grafted onto solid substrate thus could be easily detected by normal UV absorption and AFM techniques.

Fig. 1 compares UV absorption spectra of PDBS onto both hydrophilic and hydrophobic quartz substrates under the completely identical reaction conditions. When hydrophilic quartz was used, a sharp, intense absorbance band at 319 nm due to the rod-like helical PDBS can clearly be seen (Fig. 1a). This absorbance, however, did not significantly decrease after leaving the sample in *n*-hexane in the dark overnight.† Contrarily, when hydrophobic quartz was used, only a very weak absorbance band at 319 nm , probably resulted from physical adsorption, was observed (Fig. 1b). If PDBS was spin-coated onto a quartz substrate surface, the absorbance band at 319 nm completely disappeared after the sample was washed with *n*-hexane in the same way as that used in the end-grafted samples (Fig. 1c),† which indicates that physically adsorbed PDBS chains could be completely removed by this



Scheme 1 Graft of PDBS onto hydrophilic surface of quartz and mica: (top) graft reaction between Si–H end groups of PDBS and Si–OH groups at surface; (bottom) graft reaction between Si–OR end groups of PDBS and Si–OH at surface.

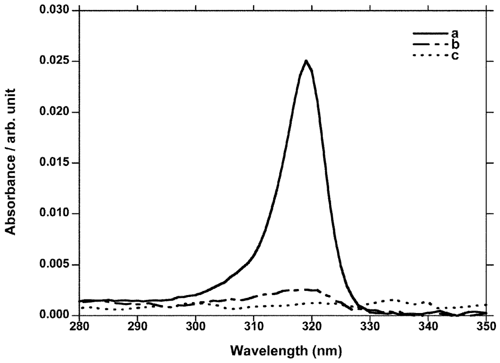


Fig. 1 UV spectra of PDBS (M_w = 7.86 × 10^5, M_w/M_n = 2.12) (a) grafted on hydrophilic quartz, (b) grafted on hydrophobic quartzs and (c) spin-coated on hydrophilic quartz after being completely washed with *n*-hexane. Reaction conditions for graft: [PDBS] = 0.01M and triethylamine (0.5 mL) in isooctane (10 mL) at room temperature for 48 h.

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† Electronic Supplementary Information (ESI) available: Preparation of PDBS and monomer, a mechanism for the formation of Si–H and/or Si–OR end groups in PDBS synthesis, FT-IR chart of PDBS (M_w = 6500, M_w/M_n = 1.16), comparision of UV spectra of spin-coated sample before and after washing and comparison of UV spectra of end-gratfted sample before and after it was immersed in *n*-hexane overnight. See http://www.rsc.org/suppdata/cc/b3/b310985b/

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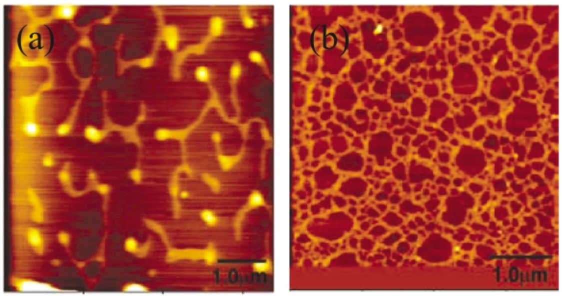

Fig. 2 AFM image of surface-grafted PDBS (M_w = 7.86 × 10^5, M_w/M_n = 2.12) onto mica. Reaction condition: room temperature, TEA (0.5 mL) in isooctane (10 mL), [PDBS] = 0.01 M (based on Si repeat units), reaction time: for Fig. 2a, 0.5 h; for Fig. 2b, 2 h.

washing method. These results clearly suggest that PDBS was chemically grafted onto the hydrophilic surface, not physically adsorbed onto the surface.

The immobilization of PDBS at hydrophilic surface was further confirmed by AFM observation of the PDBS grafted onto mica. Fig. 2a shows a tapping mode AFM image of the surface-grafted PDBS onto mica in air at room temperature. This AFM image proves a certain rope-like conformation of PDBS expected from the long persistent length (~60 nm).[3] The chain length of an ideal rod-like PDBS with this M_w was estimated to be 660 nm which is much longer than the persistent length, an greatly entangled molecular image (Fig. 2b) of PDBS in a high-grafting density sample on the mica was thus observed due to supramolecular interaction among the polymer chains.

Fig. 3 shows the results of time-course UV measurements of PDBS with two different molecular weights grafted onto the respective hydrophilic and hydrophobic surfaces. When hydrophobic substrates were used, the UV intensity at 319 nm (I_{319}) of all the samples with different reaction time is very weak and does not increase with the reaction time. This means that PDBS cannot be grafted onto the hydrophobic surface due to the lack of reactive Si–OH groups of the surface.

On the other hand, when hydrophilic substrates were used, the I_{319} increases with the reaction time for both lower-M_w (M_w = 7.86 × 10^5, M_w/M_n = 2.12) and ultrahigh-M_w (M_w = 2.37 × 10^6, M_w/M_n = 1.76) fractions. For the lower-M_w fraction, the I_{319} steeply increases at the first 6 h, then increases gradually and tends to reach a constant value. For the ultrahigh-M_w, the I_{319} increases quickly at the first 10 h, then increases very slowly with the reaction time. Moreover, the I_{319} for the lower M_w fraction increases more steeply than that for the ultrahigh-M_w fraction. The initial graft reaction rate of the former is greater than that of the latter. This is because the effective density of the reactive end groups of the ultrahigh-M_w fraction is much lower than that of the lower-M_w fraction and the encapsulation of the end groups by the same polymer chain itself in the ultrahigh-M_w fraction is likely to be more serious than that in the lower-M_w fraction. The end groups of the lower-M_w fraction thus have more opportunities to react with Si–OH groups on the quartz surface.

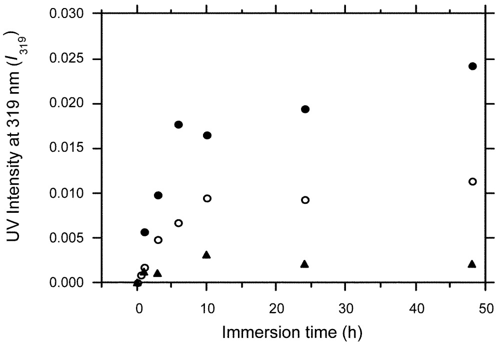

Fig. 3 Time-course change in intensity of Siσ-Siσ* transition at 319 nm of two PDBS samples onto hydrophilic and hydrophobic surfaces. (filled circles) lower-M_w fraction (M_w = 7.86 × 10^5, M_w/M_n = 2.12) onto hydrophilic surface; (open circles) ultrahigh-M_w fraction (M_w = 2.37 × 10^6, M_w/M_n = 1.76) onto hydrophilic surface; (filled triangles) the lower-M_w fraction onto hydrophobic surface. Reaction conditions: [PDBS] = 0.01 M and triethylamine (0.5 mL) in isooctane (10 mL) at room temperature.

In addition, the value of I_{319} (~0.024) of the lower-M_w fraction after 48 h is about twice, compared to that of the I_{319} (~0.011) of the ultrahigh-M_w fraction after the same reaction time. This suggests that fewer PDBS chains of the ultrahigh-M_w fraction were grafted onto the surface than those of the lower-M_w fraction. Presumably, a great molecular entanglement of the ultrahigh-M_w PBDS onto quartz happened, leading to a dramatic decrease in immobilization reaction rate of PDBS onto hydrophilic Si–OH sites at the surface.

In conclusion, a facile, one-pot immobilization method for a rigid rod-like helical polysilane onto hydrophilic surface at room temperature in the presence of triethylamine was successfully developed. This new approach can be applied for immobilization of other polysilanes. A more quantitative study using quartz crystal microbalance (QCM) and variable temperature UV and fluorescence measurements is currently in progress.

Notes and references

1 (*a*) B. Zhao and W. J. Brittain, *Prog. Polym. Sci.*, 2000, **25**, 677; (*b*) J. M. Buriak, *Chem. Rev.*, 2002, **102**, 1271.
2 M. Fujiki, *Macromol. Rapid Commun.*, 2001, **22**, 539.
3 M. Fujiki, J. R. Koe, K. Terao, T. Sato, A. Teramoto and J. Watanabe, *Polym. J.*, 2003, **35**, 297.
4 (*a*) K. Furukawa, K. Ebata and M. Fujiki, *Adv. Mater.*, 2000, **12**, 1033; (*b*) K. Furukawa, *Acc. Chem. Res.*, 2003, **36**, 102.
5 K. Ebata, K. Furukawa and N. Matsumoto, *J. Am. Chem. Soc.*, 1998, **120**, 7367.
6 H. K. Kim and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1988, **110**, 3321.
7 K. Sakamoto, K. Obata, H. Hirata, M. Nakajima and H. Sakurai, *J. Am. Chem. Soc.*, 1989, **111**, 7641.
8 W. Yoshida, R. P. Castro, J.-D. Jou and Y. Cohen, *Langmuir*, 2001, **17**, 5882.
9 J. Hu, M. Wang, H.-U. G. Weier, P. Frantz, W. Kolbe, D. F. Ogletree and M. Salmerson, *Langmuir*, 1996, **12**, 1697.
10 C. R. Kessel and S. Granick, *Langmuir*, 1991, **7**, 532.
11 S. Minko, S. Patil, V. Datsyuk, F. Simon, K.-J. Eichhorn, M. Motornov, D. Usov, I. Tokarev and M. Stamm, *Langmuir*, 2002, **18**, 289.
12 R. Zhang, J. E. Mark and A. R. Pinhas, *Macromolecules*, 2000, **33**, 3508.
13 Y. Li and Y. Kawakami, *Macromolecules*, 1999, **32**, 8768.
14 J. Chrusciel, *Pol. J. Chem.*, 1997, **71**, 977.
15 R. J. Klingler, T. R. Krause and J. W. Rathke, *J. Organomet. Chem.*, 1988, **352**, 81.
16 The hydrophilic surface substrate was prepared as follows: quartz substrates were placed in a freshly prepared "piranha" solution (3 : 1 (v/v) of conc. sulfuric acid and hydrogen peroxide) at 70 °C for 1 h. The substrates were sufficiently rinsed with distilled water and THF, dried in a stream of nitrogen gas, and used immediately. Hydrophobic surface substrate was prepared as follows:A piece of hydrophilic quartz was immersed in a solution of *n*-dodecyltriethoxylsilane in hexane (1 : 100 (v/v) of *n*-dodecyltriethoxylsilane and hexane) overnight. It was then rinsed with a large amount of distilled water and THF, and dried in a stream of nitrogen gas.